CHAPTER 3

RESULT & DISCUSSION
3.1 Crystalline hydration of smectite at different relative humidities

3.1.1 Introduction

Swelling of smectite clays is an interesting and important phenomena because of its great influence on natural soil conditioning, water retention, petroleum engineering, particularly bore-hole instability etc. It is one of the most studied properties of smectite clays (31,135-137).

Smectite comprises negatively charged mica like sheets (chapter 1). These sheets are negatively charged because of isomorphous substitution. The clay sheets are held together by charge balancing counter ions like Na\(^+\) or Ca\(^{2+}\) which mainly occupy the interlayer space (Fig.3.1). The solvation of interlayer cations give rise to swelling (Fig. 1.3). Swelling may be of two types – (i) Crystalline swelling - where the interlayer hydration is due to solvation of cations only and limited amount of water is adsorbed in the interlayer spacing. The basal spacing increases from 9.6Å to 20Å (135); (ii) Osmotic swelling which arises from sorption of water on external surface and pores of clay. Unlimited adsorption of water may occur due to difference between ion concentration close to the clay surface and in the pore water (6).

Crystalline swelling is dominantly influenced by nature of counter ions (128,138-140), net silicate layer charge and charge location. Spatial arrangement of the water molecules is largely determined by the position of exchangeable cations which depends on the location of the net negative charge. At increasing relative humidity smectites adsorb water vapour to form one or more layer
Exchangeable Na$^+$ .x H$_2$O (External Site)

Exchangeable Na$^+$ .x H$_2$O (Internal Site)

- Al$^{3+}$, Mg$^{2+}$, Fe$^{3+}$
- O - Oxygen
- Si$^{4+}$; Occasionally Al$^{3+}$
- @ - Hydroxyls

Fig. 3.1. Layered structure of Na-Mnt clay with outer and inner ion-exchange sites.
hydrates (128). In spite of large number of experiments, microscopic structure of water and distribution of counter ions near the clay-water interface is still a controversial subject in clay colloid science. It is (31) claimed that counter ion solvation has a dominant role in the swelling of clays and equally (141) hydration of clay surface is considered to be important. In this work, the role of counter ions in interlayer hydration of clay is evaluated under different relative humidity (RH) over a long period. The following forms of Mnt are considered for the present study, such as- Na-montmorillonite (Na-Mnt), Ca-montmorillonite (Ca-Mnt) and \( \frac{1}{2} \text{Na-} \frac{1}{2} \text{Ca-montmorillonite (Na-} \frac{1}{2} \text{Ca-Mnt)} \). 

3.1.2 Result and Discussion

The basal spacing values \((d_{001} \text{ in Å})\) are plotted (Fig.3.2) against the different periods of hydration of the clay films at different RH. The basal spacings for Ca-Mnt (Fig. 3.2.a) at 11% RH are almost constant at around 12.5 Å over the whole period of exposure, indicating a single layer of water (142). At 32% RH the basal spacing increased to about 15.0 Å from 12.5 Å within 24 hrs and thereafter, it increases slightly to 15.6 Å during 240 hrs of exposure, which corresponds to a two-layer hydration of the clay. At 42% and 68% RH the basal spacing remains almost constant at about 15 Å. The \(d_{001}\) value at 84% RH increases from 12.5 Å to 15.6 Å during 24 hrs of hydration and thereafter gradually increases to 16.8 Å to 240 hrs. This value corresponds to 2-3 layers of water in the clay interlayer. At 100% RH the basal spacing increases to about 16.8 Å up to 24 hrs and then increases to 18.8 Å during 240 hrs indicating three complete water layers.
Fig. 3.2. Variation in basal spacings (d₀₀₁) of Mnt with various period of hydration at different relative humidity - (a) ½Na-½Ca Mnt, (b) Na- Mnt and (c) Ca-Mnt.
Fig. 3.2.b shows the hydration pattern for Na-Mnt. The $d_{001}$ value of 11.8 Å (dried over $P_2O_5$) changes to 12.4 Å on 24 hrs hydration in 11% RH, which is constant over whole period indicating a monolayer of water in the interlayer space. At 32% and 42% RH also the hydration is not beyond single water layer. At 68% and 84% RH the clay adsorbs two layers of interlayer water ($d_{001}$ values are at about 14.2 to 15.0 Å). At 100% RH the basal spacing increases from 11.4 to 14.2 Å within 24 hrs and thereafter it increases to 19.8 Å during 72 hrs of hydration which correspond to adsorption of four layers of water. During 240 hrs of hydration, the $d_{001}$ value attained is about 20 Å.

Fig. 3.2.c depicts the hydration pattern for $\frac{1}{2}$Na-$\frac{1}{2}$Ca Mnt. During the hydration period, the $d_{001}$ value at 11% RH is maintained around 12.4 Å. At 32, 42, 68 and 84% RH, the $d_{001}$ value increases from 12.4 to 14.2 Å corresponding to two layers of water which slightly increases up to 240 hrs of hydration. At 100% RH the $d_{001}$ value increases from 12.4 to 15.0 Å within 24 hrs of hydration. On increasing the hydration period to 240 hrs the $d_{001}$ value increases gradually to 18.8 Å which corresponds to three layers of water.

The c-spacing for a completely dry Mnt is 9.6 Å and for a monolayer hydrate it is about 12.5 Å. Beyond the solvation of the exchangeable cations, the water adsorbed by smectites can condense in micropores and external surfaces. Again, the fraction of interlamellar surface covered by water molecules at a given water content depends strongly on the nature of the exchangeable cation (31). The
greater is the solvation energy of the cation the greater is the amount of internal surface hydrated.

It has been suggested (31) that the first stage of water adsorption by smectite clays is the solvation of exchangeable cations by either three (monovalent cation) or more (bivalent cation) water molecules which corresponds to interlamellar c-axis spacings large enough to accommodate either one or two layers of water molecules. The second stage of hydration is the formation of either an octahedral solvation complex for the monovalent exchangeable cation or a second solvation sheath for the bivalent exchangeable cations. This stage is more dependent on the solvation of interlayer cations and may not result in formation of complete monolayers of water molecules in the interlamellar space. For Na-Mnt the macroscopic swelling may be controlled by the competition between the formation of hydrogen bonds between water protons and oxygen in the tetrahedral sheets of the clay and the adsorption of water in the clay hexagonal cavities (142).

If the \( \frac{1}{2}\text{Na} - \frac{1}{2}\text{Ca} \) Mnt is intrastratified i.e. some interlayer contain only \( \text{Na}^+ \) and others only \( \text{Ca}^{2+} \) (140), then the hydration patterns will show characteristics of both Na- and Ca-Mnt. It is seen that Na-Mnt adsorbs a monolayer of water from 11 to 42% RH even after 240 hrs of exposure whereas Ca-Mnt adsorbs two layers of water for the same period of hydration within the same range of RH (131,143,144). Thus, \( \frac{1}{2}\text{Na} - \frac{1}{2}\text{Ca} \)-Mnt can be expected to show two \( d_{001} \) values corresponding to single and double layers of water molecules. But
it is quite evident from the results given in Fig. 3.2 (c & a) that hydration pattern of $\frac{1}{2}$Na - $\frac{1}{2}$Ca-Mnt almost conforms with that of Ca-Mnt. This may be attributed to segregation of the cations (145), i.e Na$^+$ ions reside on the external surface of the clay platelets and Ca$^{2+}$ ions occupy the interlayer space (Fig.3.3). It has been found that the amount of adsorbed water decreases with the decrease of the amount of exchangeable cations in the interlayer sites, suggesting the important role of the latter in hydration of Mnt clays (33).

On displacement of monovalent cations (Na$^+$) from the interlayer, the restricted spacing of about 10Å provides a favorable site for divalent cation (Ca$^{2+}$). This may be one cause of segregation or demixing. While another reason may be that the number of Na$^+$ ions required to satisfy the CEC of the clay is double that of Ca$^{2+}$ ions and thus there may be greater repulsion between interlayer Na$^+$ ions. Hence, interlayer sites are preferably occupied by Ca$^{2+}$ ions in a $\frac{1}{2}$Na-$\frac{1}{2}$Ca-Mnt. Thus on prolonged hydration such bi-ionic smectite behaves like a Ca-Mnt clay.

3.1.3 Conclusion

Crystalline swelling of smectite type clays is largely influenced by the nature of interlayer cations. Ca-Mnt does not hydrate beyond 19Å even in very dilute suspension while Na-Mnt may swell beyond 20Å. For a bi-ionic clay the interlayer cations preferably 'demix' other than occupying the same layer.
Fig. 3.3. Schematic presentation of segregation of Na\(^+\) and Ca\(^{2+}\) ions on clay platelets
3.2 Intercalation reactions of metal complexes with Na-Mnt

3.2.1 Intercalation reactions of trisdiimine metal complexes with Na-Mnt

3.2.1.1 Introduction

Intercalation chemistry of swelling clays like smectite is a developing science of materials which include a vast range of heterogenous catalyst, eco-friendly adsorbents, chemical sensors, bioactive agents, slow release pesticides and drugs and so on (1-3, 6, 22-25, 68). Especially, Mnt is found to be more versatile for designing different heterogeneous products (25). Intercalation i.e., insertion of an inorganic or organic moiety into the clay interlayers takes place through (i) ion exchange- where the interlayer cations like Na\(^+\) or Ca\(^{2+}\) are substituted by the inorganic or organic cation, often increasing the basal spacing (d\(_{001}\) spacing) according to the dimension of the intercalated cation (1,4,17) and (ii) ion dipole interaction- where the polar organic or inorganic molecules enter the interlayer through interaction with the interlayer cations (6,28), increasing the basal spacing according to the degree of polarisation. Intercalation of the ion pair in many cases of metal salts or metal complex salts is known as intersalation (66, 68). So far, both intercalation and intersalation reactions are carried out by different methods by several workers and require from a few hours to few days (3,68,121,128,161-163). Any industrial application of such metal complex intercalated / intersalated products (162) will require precise and viable methods for preparation of the same. Moreover, in the adsorption study of optically active metal complexes (20,118,120,148,149,161,165-167), long intercalation
reaction time may be detrimental to investigate the reaction mechanism and also the products because of short racemisation period of most of the enantiomeric species (133,168). Again, from the environmental and industrial point of view for separation of toxic metal complexes, intersalation reaction may play a significant role. Systematic study on the preparation of metal complex intercalated / intersalated montmorillonite composites has not been carried out. In view of above, an attempt has been made to curtail the total intercalation / intersalation reaction period and also to simplify the reaction procedure by applying different dynamic conditions like ultrasonication, refluxing, autoclaving and vigorous stirring (169). The present study describes the results of interaction between Na-Mnt and the metal complexes \([\text{Ni(L-L)}_3]\text{SO}_4\) and \([\text{Ni(L-L)}_3]\text{Cl}_2\), particularly the effect of intersalation reaction on interlamellar metal complex layers formation.

3.2.1.2 Results and Discussion

The details of intersalation reaction i.e. adsorption of metal complex salts in excess (>CEC) by the clay (slurry) are shown in Fig. 3.4. It reveals that the highest amount of metal complex adsorption occurs under ultrasonic condition while under stirring condition lowest adsorption is found. Adsorption under refluxing condition is higher, in general, than that of autoclaving one except in some cases. Therefore, the sequence of adsorption at higher loading (>CEC) is ultrasonication > refluxing > autoclaving > stirring. Under ultrasonic condition,
<table>
<thead>
<tr>
<th>CEC-Eqv. metal complex added</th>
<th>Meq metal complex adsorbed/100 g clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Stirring</td>
</tr>
<tr>
<td>2</td>
<td>[Ni(phen)$_3$]SO$_4$</td>
</tr>
<tr>
<td>3</td>
<td>[Ni(phen)$_3$]Cl$_2$</td>
</tr>
<tr>
<td>4</td>
<td>[Ni(bpy)$_3$]SO$_4$</td>
</tr>
<tr>
<td></td>
<td>[Ni(bpy)$_3$]Cl$_2$</td>
</tr>
</tbody>
</table>

Fig. 3.4. Adsorption isotherm of [Ni(phen)$_3$]SO$_4$, [Ni(phen)$_3$]Cl$_2$, [Ni(bpy)$_3$]SO$_4$ and [Ni(bpy)$_3$]Cl$_2$ on Na-Mnt (heated at 100°C for 1 hr).
adsorption of $[\text{Ni(phen)}_3\text{SO}_4]$ and $[\text{Ni(phen)}_3\text{Cl}_2]$ are 2.9 and 2.5 CEC-Eqv. respectively when treated the dispersed clay with 4 CEC-Eqv. of the metal complexes. On the other hand, under the same conditions of treatment, the complexes $[\text{Ni(bpy)}_3\text{SO}_4]$ and $[\text{Ni(bpy)}_3\text{Cl}_2]$ show adsorption of 2.1 and 1.9 CEC-Eqv. respectively. Similar observations are noticed in case of 2 CEC-Eqv. treatment. Thus, the phen containing complex irrespective of its anions shows higher adsorption by the clay than that of bpy containing one. This difference of adsorption can be attributed to more rigid structure of phen containing metal complex compared to that of bpy, which leads to more efficient packing (148,161,170) in interlamellar spacing of the clay.

In intersalation reaction the excess (>CEC) adsorption is considered to be due to intermolecular interaction and a van der Waals type of attraction between the metal complex salts caused by closeness of the adsorbates in the clay interlayer space(20,118,148,165,171).

The anion has a profound influence on the amount of adsorption and in the present study, $\text{SO}_4^{2-}$ ion containing complex show higher adsorption than $\text{Cl}^-$ containing ones (3). This may be due to greater ability of $\text{SO}_4^{2-}$ ions to order the intersalated phases and to compensate simultaneously the excess positive charge caused by adsorption beyond CEC (172). In addition, the greater tendency of ion pairing of $\text{SO}_4^{2-}$ ion compared to $\text{Cl}^-$ ion increases its ability to intersalate (148, 172). In conformity to this observation it is also seen from XRD patterns that the
intercalation reaction of [Ni(phen)$_3$]SO$_4$ with Na-Mnt in presence of (NH$_4$)$_2$SO$_4$ has shown an increase in adsorption of the metal complex while adsorption of the [Ni(phen)$_3$]Cl$_2$ complex is not influenced by addition of NH$_4$Cl (Fig.3.5). Dispersed Na-Mnt on treatment with 4 CEC-Eqv. of [Ni(phen)$_3$]Cl$_2$ for 24 hrs under stirring, yields an intercalated clay product which showed d$_{001}$ spacing of 28.5 Å, but for the [Ni(phen)$_3$]SO$_4$ metal complex the d$_{001}$ spacing is about 28.9 Å (Fig.3.5 b & d). On addition of 4 CEC-Eqv. of NH$_4$Cl, the chloride complex exhibited the same basal spacing value i.e., 28.5 Å for the same period of interaction (Fig.3.5a) while, on addition of (NH$_4$)$_2$SO$_4$ to the sulphate complex, the intercalated clays showed an increase in the d$_{001}$ spacing to about 30.5 Å (Fig.3.5c).

It is known that ultrasonication increases the rate of intercalation and other type of reactions (163, 173, 174). In case of intercalation reaction of [Ni(phen)$_3$]SO$_4$ and [Ni(bpy)$_3$]SO$_4$ it is found that ultrasonication leads to maximum adsorption during 25 – 35 min but beyond it, desorption occurs (Fig. 3.6). The amount of adsorption of [Ni(phen)$_3$]SO$_4$ for 1 and 60 min are almost same and are slightly higher than that of CEC but in case of [Ni(bpy)$_3$]SO$_4$, the adsorption is below the CEC. Therefore, the intercalation reaction is dependant on ultrasonication period and a critical time period is there for maximum adsorption, beyond that region on either side, adsorbed
Fig. 3.5. XRD patterns for [Ni(phen)$_3$]Cl$_2$-Mnt in presence (a) and in absence (b) of NH$_4$Cl; [Ni(phen)$_3$]SO$_4$-Mnt in presence (c) and in absence (d) of (NH$_4$)$_2$SO$_4$. 
Fig. 3.6. Adsorption isotherm of [Ni(phen)$_3$]SO$_4$ and [Ni(bpy)$_3$]SO$_4$ on Na-Mnt carried out under ultrasonic irradiation for different periods.
amount is less. Thus, adsorption under ultrasonication condition is reversible type.

The results of adsorption by the aggregated (solid) and dispersed clays carried out under vigorous stirring condition are shown in Table 3.1. Results indicate that dispersed clay, in general, adsorbs higher quantity of metal complexes than that of the undispersed one. In order to simplify the reaction conditions, room temperature dried clay (basal spacing $d_{001}$ 12.5Å i.e. interlayer space of about 2.9Å corresponding to the presence of monolayer of water between the layers and as per the equation [1], the attractive energy is 6.7 mJ/m$^2$) was directly added to the metal complex salt solution and adsorption reaction was carried out. The clay adsorbs very quickly up to the

<table>
<thead>
<tr>
<th>Metal complexes</th>
<th>Metal complexes added (CEC-Eqv.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>Solid</td>
</tr>
<tr>
<td>[Ni(phen)$_3$]SO$_4$</td>
<td>114</td>
</tr>
<tr>
<td>[Ni(phen)$_3$]Cl$_2$</td>
<td>114</td>
</tr>
<tr>
<td>[Ni(bpy)$_3$]SO$_4$</td>
<td>114</td>
</tr>
<tr>
<td>[Ni(bpy)$_3$]Cl$_2$</td>
<td>114</td>
</tr>
</tbody>
</table>

Values are in meq/100 g of clay
CEC and within a few minutes the reaction is over irrespective of the concentration (<CEC) of the metal complex. The basal spacing (d₀₀₁) of such products derived either from solid or slurry of clay, is enhanced from 12.5 Å to about 17.6 Å indicating that cation of the metal complex having diameter about 8 Å exist in the interlamellar spacing with its three fold axis perpendicular to the silicate layer surface. When the clay (solid) is treated with metal complex in excess (>CEC), the amount adsorbed is higher than the CEC. This excess adsorbed amount depends upon the reaction conditions as well as the treatment dose. The intercalated products irrespective of amount adsorbed, show basal spacing of about 17.6 Å confirming a monolayer product (3,68). Therefore, the excess (>CEC) metal complex salt is assumed to exist laterally in the interlamellar spacing as cation-anion pair between the exchanged metal-complex cations since the distance between the exchanged charge sites on the same silicate layer is about 10 - 15 Å (27).

Na-Mnt shows interlayer swelling on treatment with water and ultimately results in delamination of the platelets. Therefore, the ratio of internal and external sites (Fig. 3.1) depends upon the aggregation number which in turn depends upon the dispersion of the clay (161,162,166). The layers of such clay are held together by van der Waals forces as a face-to-face aggregate and may be expressed by the following equation [1] as -
where, $V_A$ is van der Waals energy (erg cm\(^{-1}\)), $d$ is the half-distance between the plates, $\Delta$ is the unit layer thickness (9.6Å) and $A$ is a constant having value $\sim 10^{-12}$. Due to swelling, $V_A$ decreases and the clay ultimately delaminates. Since, $V_A$ is weak, comparatively low energy is required to intercalate into the layers by some suitable species. As the layers move apart from each other, attractive energy decreases and therefore energy required for expansion will be less (150). And at layer separation of about 6.5Å, the value of $V_A$ is only 0.6 mJ/m\(^2\). Therefore, intercalation reaction of air dried (at room temperature) clay having interlayer separation of about 2.5 Å with cationic species like [Ni(phen)]\(^{2+}\) or [Ni (bpy)]\(^{2+}\) does not involve much energy (27). Recently, solid-solid intercalation reaction between Na-Mnt (dried at 120°C and showing interlayer separation by 2.9Å) and [Co(phen)]\(^{2+}\) complex has been reported to occur (127). For such exchange reaction at least a minimum quantity of liquid state i.e. interlamellar hydrated phase is required for ionic transport and this may indicate that why Na-Mnt dried at 300°C does not intercalate with the metal complex (127) because of absence of interlamellar liquid phase. The intercalation reaction exhibited by predispersed clay is more prominent than that of undispersed one (Table 3.1). The basal spacing ($d_{001}$) of such intercalated product is about 29±1 Å which is almost equivalent to the summation of the single layer thickness (9.6 Å) of the clay.
platelet, diameter (~16 Å) of the two cations of the metal complex and the diameter of SO$_4^{2-}$ (~4 Å) and thus, indicates the formation of bilayer cationic metal complex within the interlamellar spacings (20, 118, 165, 167). Moreover, if the intercalated compounds are not washed thoroughly, basal spacing ($d_{001}$) above 30 Å is obtained and in case of [Ni(phen)$_3$]SO$_4$-Mnt, the value is above 32 Å (Fig. 3.8) indicating the formation of pseudo-trilayer metal complex in the interlamellar spacing and this is perhaps the first report of such intercalated compound. Therefore, bilayer or pseudo-trilayer formation of the complexes in the interlamellar spacings does not only depend upon the amount of metal complex adsorbed by intercalation reaction but also depends upon the mode of pretreatment of the clay.

The exchange reaction of Na-Mnt clay with divalent metal ions, from the thermodynamic principle, leads to increase in entropy and is an endothermic process (27). The van't Hoff equation [2] indicates that in an endothermic reaction (where $H_o$ is positive) the equilibrium shifts towards adsorption as the temperature is raised. Therefore, increase of temperature favours the adsorption reaction. Our study also shows that stirring at room temperature shows the lowest

\[ \frac{d \ln K}{dT} = \frac{H_o}{RT^2} \]  

[2]

(\text{where, } K = \text{equilibrium constant of exchange, } H_o = \text{enthalpy, } R = \text{constant, } T = \text{absolute temperature})
adsorption compared to conditions at higher temperature such as refluxing, autoclaving, and ultrasonication (in ultrasonic system, although the overall temperature of the reaction mass rises slightly, it develops tremendous high temperature momentarily in the internal mass). This is also evident from the adsorption reaction of \([\text{Ni(phen)}_3]\text{SO}_4\) on Na-Mnt at different temperatures under autoclaving condition. The amount of adsorption was found to increase with increasing reaction temperature (Table 3.2).

Table 3.2 Amount of \([\text{Ni(phen)}_3]\text{SO}_4\) adsorbed on Na-Mnt under different autoclaving conditions

<table>
<thead>
<tr>
<th>Temperature(°C)</th>
<th>Pressure (atm.)</th>
<th>([\text{Ni(phen)}_3]\text{SO}_4) adsorbed (Meq/100 g clay)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>0.5</td>
<td>147</td>
</tr>
<tr>
<td>90</td>
<td>0.7</td>
<td>157</td>
</tr>
<tr>
<td>100</td>
<td>1.0</td>
<td>160</td>
</tr>
<tr>
<td>110</td>
<td>1.4</td>
<td>165</td>
</tr>
<tr>
<td>120</td>
<td>2.0</td>
<td>176</td>
</tr>
</tbody>
</table>

Again, ultrasonic condition not only favours the adsorption reaction by raising local temperature, but may also enhance the reaction by delamination and
cracking down the particles into smaller size and thereby increasing reactive surface area and improving mass transport. It is revealed by the enhancement of surface area from 93.8 m²/gm for Na-Mnt before sonication to 119.3 m²/gm for Na-Mnt after sonication.

In dehydrated system, the silicate layers of the clay are in fully collapsed state (Fig. 3.7A) and therefore, adsorption takes place predominantly on external surface of the layers (6). But in partly dehydrated system where the layers of the clays are already slightly separated, intercalation reaction with appropriate species occurs. It has been reported (171) that hydrated metal ions in the interlamellar spacing do possess the similar ionic mobility as that found in bulk of solution. This ionic mobility may prompt the cation exchange reaction and help to expand the layers. Therefore, intercalation or intersalation reactions of the metal complexes with the clay surface take place in the opposite fashion when the clays are in highly aggregated (room temperature dried) and dispersed forms. Fig. 3.8 depicts the state of the reactions, i.e. in aggregated form, work requires to be done to prop open the layers for accommodation of the bulky metal complexes into the interlamellar space while in case of predispersed clay, the platelets which are already adsorbed with metal complex laminate to form layered structure. Therefore, the formation of monolayer, bilayer or pseudo-trilayer metal complex in the interlamellar space could be easily explained from the Fig. 3.8.
Fig. 3.7. X-ray diffraction patterns and schematic representation of: (A) collapsed NaNt, (B) dried (room temperature) NaNt, (C) intercalated [Ni(phen)$_3$]-Mnt, and (D and E) intersalated products of [Ni(phen)$_3$]SO$_4$ with NaNt.
Fig. 3.8. Monolayer and bilayer formation of metal complexes in the interlamellar spacing (A) from aggregated clay and (B) from dispersed clay.
The $d_{001}$ reflection near 17.8 Å of the monolayered intercalated product obtained from $[\text{Ni(phen)}_3]SO_4$ and clay (dried) are stable up to 350°C but at 450°C, it shifts to 12.8 Å indicating decomposition of the interlamellar metal complexes (Fig. 3.9). On further heating up to 550°C, the $d_{001}$ reflection shows a value at 9.7 Å confirming a complete collapsed structure of Mnt (Fig. 3.9 E). The $d_{001}$ reflection of the bilayered compound at 28.5 Å (Fig. 3.10) is stable up to 250°C and thereafter changes to monolayer showing $d_{001}$ reflection at 17.6 Å which is stable up to 450°C. On heating to 550°C, the basal spacing ($d_{001}$) is found to be 12.9 Å which comes down to 10.0 Å on further heating at 650°C. This clearly reflects that stability of monolayer derived from bilayer is higher than that obtained directly from the metal complex and dried clay. This extra thermal stability is assumed to be due to the presence of higher amount of metal complex salt in the interlayer space. Again, the $d_{001}$ reflection of the bilayer metal complex at 650°C (Fig. 3.10) shows slightly higher value than that of monolayer compound at 550°C (Fig. 3.9) indicating that in the former, residue of decomposed products still persists in the interlayer space. It may be mentioned here that the thermal stability of low loaded metal complexes ($< 0.5$ CEC) is only up to 250°C, beyond that basal spacing ($d_{001}$) comes down to 12.5 Å from that of 17.5 Å. This clearly indicates that the amount of metal complexes loaded into the interlayer space has a direct contribution to the thermal stability.
Fig. 3.9. X-ray diffraction patterns of [Ni(phen)$_3$]-Mnt monolayered compound treated at: (A) room temperature, (B) 250°C, (C) 350°C, (D) 450°C and (E) 550°C (each sample heated for 1 hr).
Fig. 3.10. X-ray diffraction patterns of [Ni(phen)$_3$]SO$_4$-Mnt bilayer compounds at (A) room temperature, (B) 100°C, (C) 250°C, (D) 350°C, (E) 450°C, (F) 550°C and (G) 650°C (each sample heated for 1 hr).
Thermal (DTA and TGA) analyses of the intercalated and intersalated [Ni(phen)$_3$]SO$_4$-Mnt products are shown in Fig 3.11. The TGA curve (Fig. 3.11A) of the 1 CEC-Eqv. intercalated product obtained from the dry clay shows a mass loss of about 7.3% up to a temperature of about 100°C which is attributed to moisture loss. There is a gradual mass loss of about 19% in the temperature range 350 to 550°C, which corresponds to the decomposition and partial oxidation of the interlamellar metal complex. The corresponding exothermic DTA peak is observed at 530°C. This observation is corroborated by the static thermal characteristics (Fig. 3.9). In the temperature range 550 to 650°C, the mass loss of about 5.3% is attributed to oxidation of the left out carbonaceous materials from the organic moiety. The corresponding exothermic DTA peak occurs at 625°C. The bilayered 2.9 CEC-Eqv. adsorbed product obtained from the dispersed clay shows (Fig. 3.11B) mass loss of about 9% up to 120°C, which is attributable to moisture loss. There is a gradual mass loss of about 29.2% over the temperature range 300 to 650°C, which is due to decomposition and oxidation of the organic moiety of the metal complex. And the corresponding DTA peak appears at 540°C, which indicates higher thermal stability than the monolayered intersalated product. This observation is also corroborated by the static thermal characteristics (Fig. 3.10).

As a typical example, the characteristic IR bands of [Ni(phen)$_3$]SO$_4$ at 1518, 1425, 1340, 848, 725 and 618 cm$^{-1}$ are found to shift slightly towards higher
Fig. 3.11 (A). Thermal analyses curves (DTA, TGA and DTG) of the intercalated [Ni(phen)$_3$]SO$_4$-Mnt composite.
analyses curves (DTA, TGA, and DTG) of the intersalated \([\text{Ni(phen)}_3]\text{SO}_4\)-Mnt composite.

Fig. 3.11 (B). Thermal analyses curves (DTA, TGA, and DTG) of the intersalated \([\text{Ni(phen)}_3]\text{SO}_4\)-Mnt composite.
range in intercalated or intersalated products (Fig. 3.12). Monolayered intersalated product ($d_{001} \approx 17.5 \, \text{Å}$), prepared from interaction of metal complexes with solid Na-Mnt, shows the characteristics IR bands up to about 350°C. The intensity of the bands at 450°C is considerably reduced and thereafter completely vanishes at 550°C indicating the decomposition of the metal complex. This observation has been corroborated by the XRD reflections (Fig. 3.9E) of the same compound heated at 550°C. The metal complex $[\text{Ni(phen)}_3]\text{Cl}_2$ shows similar result. Fig. 3.13 shows the IR bands for phen and bpy free ligands and their corresponding metal complexes and clay intersalated products. The ring stretching vibrations of the aromatic rings in phen is observed at 1499, 1415 and 1337 cm$^{-1}$, while C=\text=N stretching vibration occurred near 1600 cm$^{-1}$. Bands in the range 1214 to 800 cm$^{-1}$ are due to medium ring vibrations while bands at 733 and 688 cm$^{-1}$ arise from nitrogen substitution in the ring (175). In the metal complexes the bands show shift to slightly higher values in the metal complex, which again shift to higher values on intercalation by the clay as shown in Fig. 3.12. The sulphate and chloride complexes show a small difference in the region of medium ring vibration. The sulphate complex show a large band at 1115 cm$^{-1}$ while chloride complex exhibits similar spectra as the ligand in that region (176). Intersalated clay composites for both sulphate and chloride complexes show same type of IR bands. For bpy ligands, bands at 1574, 1448, 1243 and 650 cm$^{-1}$ also show a small shift to higher values in the metal complex. The characteristic IR bands of
Fig. 3.12. Infrared spectra of (A) Na-Mnt and (B) [Ni\text{phen}_3]SO_4; [Ni\text{phen}_3]-SO_4-Mnt bilayered compounds treated at (C) room temperature dried, (D) 100°C, (E) 250°C, (F) 350°, (G) 450° and (H) 550°C (each sample heated for 1 hr).
Fig. 3.13. IR spectra of free ligands (phen and bpy), their metal complexes and the clay intercalated products.
[Ni(bpy)$_3$]SO$_4$ at 1595, 1465, 1314 and 728 cm$^{-1}$ are found to shift to higher values 1610, 1490, 1360 and 750 cm$^{-1}$ respectively in the intercalated or intersalated products. Thermal stability of the products are similar to those [Ni(phen)$_3$]SO$_4$-Mnt products. When the loading of metal complex is in the range 0.1-0.5 of CEC, the thermal stability is less compared to higher loading and this may be attributed to higher pillaring action in case of the latter.

Surface area of metal-complex-Mnt composites, as determined by N$_2$ adsorption at 77K after degassing at 120°C for 2 hrs and calculated using BET equation, are shown in Table 3.3.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Sample</th>
<th>Surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Na-Mnt</td>
<td>93.8</td>
</tr>
<tr>
<td>2.</td>
<td>0.1 CEC-[Ni(phen)$_3$]-Mnt</td>
<td>65.8</td>
</tr>
<tr>
<td>3.</td>
<td>0.5 CEC-[Ni(phen)$_3$]-Mnt</td>
<td>26.9</td>
</tr>
<tr>
<td>4.</td>
<td>1.0 CEC-[Ni(phen)$_3$]-Mnt</td>
<td>14.9</td>
</tr>
<tr>
<td>5.</td>
<td>2.3 CEC-[Ni(phen)$_3$]-Mnt</td>
<td>1.7</td>
</tr>
<tr>
<td>6.</td>
<td>0.1 CEC-[Ni(bpy)$_3$]-Mnt</td>
<td>44.2</td>
</tr>
<tr>
<td>7.</td>
<td>0.5 CEC-[Ni(bpy)$_3$]-Mnt</td>
<td>40.0</td>
</tr>
<tr>
<td>8.</td>
<td>1.0 CEC-[Ni(bpy)$_3$]-Mnt</td>
<td>32.7</td>
</tr>
<tr>
<td>9.</td>
<td>1.6 CEC-[Ni(bpy)$_3$]-Mnt</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Na-Mnt shows the highest surface area i.e. 93.8 m$^2$/gm. Up to the CEC, as the loading of the metal complexes in the intercalated products increases, the surface...
areas decrease accordingly. But, in intersalated products, the magnitude of surface area is extremely low, which may be attributed to filling up of the empty space in the interlamellar region by the intersalated salt or may be due to formation of impermeable layer for diffusion of N₂ into the interlayer region (3).

3.2.1.3 Conclusion

Intersalation reactions between [Ni(phen)₃]SO₄ or [Ni(phen)₃]Cl₂ or [Ni(bpy)₃]SO₄ or [Ni(bpy)₃]Cl₂ and Na-Mnt carried out under (i) Ultrasound irradiation; (ii) refluxing; (iii) autoclaving and (iv) vigorous stirring are found to complete within about 30 min. Under ultrasonic condition, highest amount of adsorption of metal complexes occurs. Phen containing metal complex gives higher adsorption than those containing bpy. Highly aggregated and dispersed clay give mono- (d₀₀₁~17.5Å) and bilayered (d₀₀₁~28.5Å) or pseudo-trilayered (d₀₀₁~32Å) intersalated products respectively. Adsorption of metal complexes up to about three times of cation exchange capacity of the clay is observed. Dispersed clay always adsorbs higher quantity than the undispersed one. Presence of (NH₄)₂SO₄ enhances the adsorption of [Ni(phen)₃]SO₄ by the clay while no significant effect is observed for NH₄Cl on [Ni(phen)₃]Cl₂ adsorption. Surface areas of the intersalated products are extremely low. Bilayered intersalated products are thermally stable up to about 250°C and beyond it, converts to monolayered one which is stable up to about 450°C. Intersalated products show higher thermal stability than unintersalated one.

**********
3.2.2 Intersalation reactions of trisdiimine metal complexes with different particle size fractions of Na-Montmorillonite

3.2.2.1 Introduction

The lower fraction (-2 μm) of bentonites is rich in Mnt (29,30). In general, the lower size fractions exhibit large surface area and more active exchangeable sites (2,26,30). Smaller sized particles disperse and delaminate more easily and hence may provide more surface for adsorption. This is an important aspect in evaluating catalytic activity of a clay. In this study, intersalation reactions of the different particle size fractions of Na-Mnt i.e., (-0.5), (0.5-1.0), (1.0-1.5) and (1.5-2.0) μm with [Ni(L-L)₃]²⁺ X₂/X', (where L-L = phen, bpy and X = Cl⁻, CH₃COO⁻, X' = SO₄²⁻), complexes are observed under different reaction conditions.

3.2.2.2 Result and Discussion

The adsorption patterns of the metal complexes [Ni(phen)₃]²⁺ and [Ni(bpy)₃]²⁺ by different size fractions of Na-Mnt i.e., (-0.5), (0.5-1.0), (1.0-1.5) and (1.5-2.0) μm under stirring, microwave irradiation and sonication conditions are shown in Fig. 3.14. Under stirring conditions, irrespective of the metal complex, all the particle size fractions, in general, adsorbed above the CEC of the clay i.e., 114 Meq/100 gm within 2 min reaction time. However, on increasing the reaction period, the amount of intersalated metal complex [Ni(phen)₃]SO₄ remains almost same. Thus, the particle size fractions do not show significant variance in
Fig. 3.1: Adsorption of $\text{A-}[\text{Ni(phen)}_3\text{SO}_4$ and $\text{B-}[\text{Ni(bpy)}_3\text{SO}_4$ by different size fractions of Na-Mnt under stirring, microwave irradiation (low) and sonication (horn).
much variation of adsorption with time of treatment is observed. Up to 6 min
treatment, maximum adsorption occurs with 1.0-1.5 µm fraction and thereafter,
desorption starts. In general, adsorption of [Ni(bpy)$_3$]$^{2+}$ by the different fractions
is less compared to [Ni(phen)$_3$]$^{2+}$.

The different size fractions saturate the metal complex [Ni(phen)$_3$]SO$_4$
above the CEC(about 1.5-1.7 CEC-Eqv) within 2 min reaction time under
microwave irradiation, which enhances to about 2.0-2.6 CEC-Eqv. up to 6 min
treatment time. On further increasing the reaction time to 10 min, the adsorption
decreases slightly to about 1.5 to 1.9 CEC-Eqv. Interestingly, the different size
fractions do not vary considerably in the amount of adsorbed metal complex
during any of the reaction periods. In case of [Ni(bpy)$_3$]$^{2+}$ complex, maximum
adsorption up to 2 min time by different size fractions lie in the range 120-125
meq/100 gm.

For intercalation reaction of [Ni(phen)$_3$]SO$_4$ with Na-Mnt, it is observed
that different particle size fractions of clay adsorb different amounts of metal
complex for varying periods of interaction under sonication. The size fraction
(-0.5)µm shows adsorption of about 0.5 CEC-Eqv and 1.7 CEC-Eqv during 2 and
6 min reaction time respectively, but beyond that desorption starts. The other size
fractions adsorb maximum amount in the range 1.9-2.6 CEC-Eqv. during the
sonication period up to 6 min. All the size fractions exhibit a decrease in amount
of intercalated metal complex on increasing the reaction time to 10 min. Similar observation is made in case of [Ni(bpy)$_3$]$^{2+}$ complex, but amount of adsorption is less compared to [Ni(phen)$_3$]$^{2+}$ complex.

XRD patterns of the composites obtained by reacting the metal complex [Ni(phen)$_3$]SO$_4$ with the different particle size fractions of Na-Mnt is shown in Fig. 3.15. The higher fractions, i.e., (1.5-2.0), (1.0-1.5) and (0.5-1.0) μm formed pseudo-trilayer metal complex (basal spacing 30-32.1 Å) in the interlamellar space within 6 min under microwave irradiation. While the lower fraction (<0.5 μm) formed a bilayer-metal complex under the same condition. It is interesting to note that the basal spacing values for intercalated products showed a gradual decrease for higher size fractions with increasing time of treatment beyond 6 min, while for <0.5 μm size fraction the basal spacing showed an increasing trend.

In microwave irradiation, dielectric heating provides an efficient and effective way of super heating. As the intercalation reaction is carried out in an aqueous suspension, the polar water media couples well with the microwave radiation. Thus, when the reaction was done in the ‘simmer’ region (~100°C), the metal complex was adsorbed almost immediately (within 2 min) up to 3.4 times of the CEC of the clay (Table. 3.4). Intersalation in the ‘low’ region (~80°C) is observed to be comparable to that of sonication after 6 min reaction time. The maximum adsorption in this region however, takes place very fast and seems to be
Fig. 3.15. XRD patterns for intersalated [Ni(phen)$_3$]SO$_4$-Mnt composites formed under microwave irradiation (low); A=-0.5, B=0.5-1.0, C=1.0-1.5 & D=1.5-2.0 µm
less time dependent than the sonication. On the other hand, under stirring condition adsorption is fast but the adsorbed amount of metal complex is less compared to other condition beyond 6 min reaction time. Thus, it has been evidenced by experiments that adsorption reaction in clay mineral is endothermic and favoured by high temperature reaction conditions (27). Microwave irradiation superheats the reaction medium, i.e. water, which accelerates the exchange reaction. Moreover, both the support i.e., the clay and the metal complex are polar in nature and therefore, microwave active. However, under microwave irradiation, the particle sizes are observed to be unaffected because it is seen that all the size fractions adsorbed the metal complexes almost in a similar way at different time periods.

Table: 3.4 Adsorption of [Ni(phen)$_3$]SO$_4$ by Na-Mnt under microwave irradiation, sonication (horn) and stirring conditions (1.0-1.5 μm particle size)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Metal complex added (meq/100gm)</th>
<th>Metal complex adsorbed (meq/100gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Microwave</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Simmer (~100°C)</td>
</tr>
<tr>
<td>2</td>
<td>456</td>
<td>376</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>416</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>384</td>
</tr>
</tbody>
</table>
As already indicated in Section 3.2.1, sonication not only favours the adsorption reaction by raising local temperature, but may also enhance the reaction by delamination and cracking down the particles into smaller size and thereby increasing the reactive surface area and improving mass transport (163). Intersalation under sonication is found to be time dependent. In case of larger particle size fractions, sonication leads to further breaking the particles into smaller sizes and more delamination hence facilitate intersalation reaction. As inferred earlier (Section 3.2.1), the intersalation reaction is dependant on ultrasonication period and a critical time period is there for maximum adsorption, beyond that region on either side, adsorbed amount is less. Thus, adsorption under ultrasonic condition is reversible type. This trend was observed in case of treatment with both ultrasonic bath and ultrasonic horn (in case of ultrasonic horn the sonication affects the reaction mixture directly while in case of ultrasonic bath the sonication influences the reaction mixture through the walls of the container and hence the former is more intense). XRD patterns for [Ni(phen)$_3$]SO$_4$ adsorbed by dispersed (1.0-1.5) μm size fraction of Na-Mnt under sonication (horn) for 1 min to 30 min is shown in Fig. 3.16. The intersalation is observed at 1 min reaction time and the basal spacing is about 29.5 Å. On increasing the reaction time, the intensity of the peak increases and after 2 min, the basal spacing becomes almost 30 Å corresponding to the pseudo-trilayer
Fig. 3.16. XRD patterns for intersalated [Ni(phen)$_3$]SO$_4$-Mt composite of 1.0-1.5 μm sized clay fraction under sonication.
composite. The basal spacing enhances to about 32 Å within 6 min, and thereafter gradually reduces to about 29.5 Å up to 30 min treatment time.

Ultrasonic vibration of liquids produces acoustic cavitation, which is rapid formation, growth and implosive collapse of gas vacuoles. This generates short lived (~nano second lifetime), localised ‘hot spots’ whose peak temperatures and pressures have been measured at about 3000 K and about 300 atm (163). The localised nature of sonication makes it more time dependent. On the other hand, in microwave irradiation the whole reaction mixture is excited by dielectric heating at a time, hence it is less time dependent, i.e. adsorption at 2 min reaction time does not differ much to that occurred at 6 min (Fig.3.14). It is interesting to note that, maximum adsorption occurs within 2 min for the dispersed clay under stirring conditions.

The effect of anions on the intercalation reaction of metal complexes with different size fractions of clay under sonication is shown in Table.3.5. It reveals that the order of adsorption by dispersed Na-Mnt is sulphate>chloride>acetate. It is also observed that the sulphate complex forms the pseudo-trilayer more easily than the chloride and acetate complex. For acetate anion, however, the pseudo-trilayer formation under normal condition requires a few days time. The maximum d₀₀₁ values for sulphate, chloride and acetate containing metal complex-clay composites are about 32, 29 and 31 Å respectively.
Table 3.5: Metal complex adsorbed by different fractions of Na-Mnt under sonication (horn) for 6 min

<table>
<thead>
<tr>
<th>Particle size (in μm)</th>
<th>Metal complex adsorbed in meq/100gm of clay</th>
<th>[Ni(phen)$_3$]SO$_4$</th>
<th>[Ni(phen)$_3$]Cl$_2$</th>
<th><a href="CH$_3$COO">Ni(phen)$_3$</a>$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5-2.0</td>
<td></td>
<td>216</td>
<td>199</td>
<td>173</td>
</tr>
<tr>
<td>1.0-1.5</td>
<td></td>
<td>296</td>
<td>206</td>
<td>156</td>
</tr>
<tr>
<td>0.5-1.0</td>
<td></td>
<td>228</td>
<td>206</td>
<td>156</td>
</tr>
<tr>
<td>-0.5</td>
<td></td>
<td>196</td>
<td>206</td>
<td>168</td>
</tr>
</tbody>
</table>

3.2.2.3 Conclusion

Intersalation of trisdiimine complexes like [Ni(L-L)$_3$]X$_2$/X' where, L-L=phen, bpy; X$_2$= Cl', CH$_3$COO' and X'= SO$_4^{2-}$ with different particle size fractions of Na-Mnt, i.e., (-0.5), (0.5-1.0), (1.0-1.5) and (1.5-2.0) μm, has been carried out under stirring, sonication and microwave irradiation. Sonication is found to affect differently on the adsorption of metal complexes. Microwave superheating increases the adsorption of the metal complex but does not influence the size fractions much as that found in case of sonication. The adsorption of the [Ni(phen)$_3$]$_2^{2+}$ complex by different particle size fraction, in general, is higher than those of the [Ni(bpy)$_3$]$_2^{2+}$ complex. The influence of the different anions of the
metal complex [Ni(phen)_3]^{2+} on the intercalation reaction with Na-Mnt follows the order SO_4^{2-} > Cl^- > CH_3COO^-.
3.3 Adsorption of \([\text{Fe(phen)}_3]\text{SO}_4\) by different states of Na-Montmorillonite

3.3.1 Introduction

Swelling clays like Mnt have considerable influence on industry and technology of modern science. Extensive swelling of Na-Mnt in soil result in borehole instability in oil exploration in petroleum industry and cause damage in road structures (137, 142, 177). Intercalation and intersalation of various species into phyllosilicates like Mnt have been studied from a long time (1-22, 178). However, the different swelling states of Mnt has not been considered seriously in such reactions. As it is discussed in section 3.1, hydration of Mnt clays is a complicated mechanism controlled by various factors like nature of interlayer cations, layer charge of the clay etc (6, 29, 177). In this section, the intersalation reaction with some well known species like \([\text{Fe(phen)}_3]\text{SO}_4\) with Na-Mnt clay in different states such as highly aggregated, dispersed and delaminated (completely dispersed) Mnt is studied.

3.3.2 Results and Discussion

The highly aggregated clay particles on sonication disperse to smaller aggregates with individual layers of clay flakes slightly moved apart upon contact with water. On delamination the dispersed clay particles are hydrated indefinitely in water (29). Aggregated clay (RT dried) when treated with 1CEC-Eqv. of metal complex solution, adsorbs the whole amount i.e. 114 meq of the metal complex very fast. The basal spacing changes from about 12.5 Å to 17.0 Å indicating
intercalation (adsorption equals CEC) of a monolayer of $[\text{Fe(phen)}_3]^{2+}$. The complex cations exist with their three fold axis perpendicular to the silicate layers (the layer thickness of the clay platelet is 9.6 Å and diameter of $[\text{Fe(phen)}_3]^{2+}$ is 8 Å, both equaling a value of 17.6 Å). The same clay when treated with excess of metal complex (> 1 CEC-Eqv.) an intersalated (adsorption > CEC) product is formed (Fig.3.17). The intersalated amount depends upon the total amount of metal complex added as well as the pretreatment of the clay. When aggregated clay is treated with 4 CEC-Eqv. of metal complex, monolayer formation in the interlayer space is observed with a $d_{001}$ value of about 18 Å. It is found that irrespective of the amount adsorbed, intersalated clay composites in such cases exhibit basal spacings corresponding to a monolayer product only. It is found that about 10-15 Å distance exist between point charges on the same silicate layer. Therefore, the internal surface is large enough to accommodate the metal complex cations laterally without any appreciable increase in c-axis spacing (Fig.3.18). XRD patterns of the intersalated products obtained from interaction of 4 CEC-Eqv. of metal complex with different states of Na-Mnt carried out for different periods are shown in Fig.3.19. It shows that intersalation reaction between aggregated clay and metal complexes takes place within 2 min and exhibits a basal spacing ($d_{001}$) of 17.5 Å and almost the same interlayer spacing is maintained up to about 15 days of continuous interactions under stirring condition. The product obtained after 21 days of reaction shows two peaks, one at
4 Eqv. of [Fe(Phen)_3]SO_4 added

Fig. 3.17. Adsorption of [Fe(phen)_3]SO_4 by aggregated, dispersed and delaminated states of Na-Mnt (4 CEC-Eqv. metal complex added).
Fig. 3.18. Schematic representation of aggregated, dispersed and delaminated states of Na-Mnt and the intersalated products with mono- and bilayer metal complexes.
Fig. 3.19. XRD patterns of intersalated products from [Fe(phen)$_3$]SO$_4$ and aggregated, dispersed and delaminated states of Na-Mnt under continuous reaction up to 24 days.
17Å and the less intense one at 22 Å implying depletion of the monolayer along with formation of a new layer. After 24 days of stirring the clay composite exhibits a weak peak at 16.6Å showing further depletion. Thus it is evident that in highly aggregated state Mnt clay, even on prolonged treatment with excess metal complex, yields intersalated monolayered metal complex–Mnt composites only.

Similar to the aggregated Mnt, dispersed clay also adsorbs the stoichiometric amount of [Fe(phen)_3]^{2+} very fast, when treated with 1 CEC-Eqv. of the metal complex and the basal spacing (d_{001}) corresponds to monolayered metal complex in the interlamellar space. But when excess metal complex is added (>CEC) to dispersed Mnt, adsorption occurs within 2 min and the intersalated clay composites show d_{001} value of about 27.6 Å and 15.7 Å indicating presence of a bilayer and a simultaneous monolayer formation respectively (3, 68, 167). From the Fig. 3.18 it is seen that the sulphate ion (dimension about 4 Å) is in between the two [Fe(phen)_3]^{2+} cations in the interlayer space. For 30 min of interaction, the intersalated product (Fig. 3.19) shows no peak for basal spacings indicating monolayer species but exhibits a d_{001} value of 27.9 Å corresponding to double layered Mnt (Fig. 3.18). It is also found that when anhydrous clay (heated at 250°C for 1 hr) is dispersed by sonication and treated with 4 CEC-Eqv. of metal complex, an intersalated product with basal spacing of about 29.9 Å is obtained. Up to about 15 days of continuous interaction between metal complex (>CEC) and Mnt, only bilayered Mnt composite is
obtained (Fig.3.19). After that, depletion of the composite starts and after 24 days only a weak peak for monolayered product is observed as evidenced from the XRD pattern (Fig.3.19).

Similar to aggregated and dispersed clay, the delaminated clay shows complete adsorption very fast on treatment with 1CEC equivalent amount of \([\text{Fe(phen)}_3]^{2+}\) leading to formation of only monolayer of metal complex in the interlamellar space. On treatment with excess (>CEC) metal complex also the adsorption occurs very fast and within 2 min intersalated Mnt composite is formed showing basal spacings of 28.1 and 17.3 Å (Fig.3.19) indicating formation of bilayered and monolayered intersalated products respectively. This composite is observed up to 24 hrs of continuous reaction between the metal complex and Mnt. Up to 7 days of interaction, only bilayered species with a basal spacing of about 28.7 Å is present and after 15 days the XRD pattern of the species exhibit basal spacings of 29.4, 21.0 and 17.5 Å indicating transformation of bilayer to monolayer. It completely transforms to monolayered metal complex-Mnt product after 21 days showing a basal spacing of 17.5 Å (Fig. 3.19). Thereafter, on 24 day of reaction, the monolayered species is depleted.

Thus, it is observed that all the three states of Mnt, i.e. aggregated, dispersed and delaminated, adsorb excess of metal complex (Fig. 3.17) but formation of bilayered \([\text{Fe(phen)}_3]^{2+}\)-Mnt composite is found in the latter two states only. Thus, intersalation is not the only requirement of bilayer formation in
Mnt, but also the mode of pretreatment of the clay. The different values of basal spacing \((d_{001})\) corresponding to bilayer formation in the Mnt interlayer space ranges from 29.6-27.0 Å which may be depicted as in the Fig.3.20. Basal spacing of 29.6 Å may be shown as compact alignment of the two complex cations sandwiching an anion with their \(c\)-axis perpendicular to the silicate plane. While, basal spacing of 28.9 to 27.0 Å may be result of other types of alignment between the ions as shown in the Fig.3.20. The clay mineral controls the orientation and relative positions of the complex cations in the interlamellar space based on the match between host and guest shape (20, 118, 167). As clay surfaces have triangular lattice of hollows into which interlamellar guests may protrude. This keying into the silicate surfaces may cause a fraction of such differences in basal spacing values. It has been also suggested by simulation studies (167) that these hexagonal hollows, which are 5.3 Å apart are fairly well matched with the shape of the complexes where the hydrogen in the ligands are 6.2 Å apart. Also, the shortest separation between two similar complex cations on clay silicate layer is about 10.6 Å. Therefore, different i.e., slightly tilting or completely perpendicular or parallel alignments may be possible for the metal complex salts in the clay interlamellar space.

Results of adsorption of \([\text{Fe(phen)}_3]\text{SO}_4\) by Na-Mnt equilibrated in presence of different concentration of NaCl are shown in Fig. 3.21. It shows that as the concentration of NaCl increases, the amount of metal complex adsorbed
Fig. 3.20. Schematic presentation of intersalated $[\text{Fe}(\text{phen})_3]\text{SO}_4$ with different arrangement of cationic and anionic species in the interlamellar region.
Fig. 3.21. Adsorption of $[\text{Fe(phen)}_3]\text{SO}_4$ by Na-Mnt in presence of different concentration of NaCl.
decreases. Basal spacing for such intercalated products is found to be about 29 Å indicating formation of double layered cationic species in the interlamellar space. The decreasing trend may be due to flocculation and reduction of inter-particle distance in clay. In general, flocculation of clay by inert electrolytes is governed by the compression of the double layer. In clays where the particles are charged due to isomorphous substitution within the crystal lattice, the surface charge of particles in an aqueous suspension donot change on the addition of electrolytes. Still the double layers are compressed and surface potential is found to decrease with increasing electrolyte concentration. When two particles approach each other in suspension owing to their Brownian motion, their diffused counter ion atmospheres begin to interfere. It can be shown that this interference leads to repulsion between the particles. At increasing electrolyte concentration the repulsion decreases (29). Also, inter particle attraction and repulsion in clay minerals operated simultaneously in aqueous environment (both fresh and saline). The attraction is independent of salt concentration but repulsion decreases with increasing salt. Thus, on increasing the concentration of NaCl in the clay suspension the clay particles get nearer due to decreasing repulsive force which is due to compression of diffused counter ion atmosphere. At certain concentration, the repulsion decreases to such a limit that the interlayer space allows monolayer hydration only (142). This is evident from the XRD patterns for [Fe(phen)$_3$]-Mnt composite obtained at different extents of flocculation by NaCl (Fig.3.22). The
Fig. 3.22. XRD patterns of [Fe(phen)$_3$]SO$_4$-Mnt composites intersalated in presence of NaCl.
basal spacing attained by the clay composite in absence of the salt is around 29.5 Å, while it gradually decreases to 28.5 Å on addition of increasing amount of NaCl and finally, it is around 17.3 Å only when the salt added is about 5M in concentration.

It is well known that the adsorption of metal complex cations by Mnt clay occurs primarily by ion exchange reaction with the accessible cations in the interlamellar spacing (166). Na-Mnt undergoes extensive interlayer swelling on treatment with water which may ultimately result in delamination of the clay platelets. The ratio of internal and external sites (Fig.3.1) depends upon the aggregation number which is determined by the extent of dispersion of the clay (161, 162, 166). One of the attractive forces responsible for holding the layers of such clay as face-to-face aggregates is van der Waals force (Section 3.2.1).

In dehydrated system, the silicate layers of the clay are in fully collapsed state and therefore, adsorption takes place predominantly on external surface of the layers (6). But, in partly dehydrated system where the layers of the clay are already slightly separated, intercalation reaction with appropriate species occurs easily. It has been reported (171) that hydrated metal ion in the interlamellar spacing posses the similar ionic mobility as that found in bulk of solution. This ionic mobility may prompt the cation exchange reaction and helped to prop open the layers. Therefore, intercalation/intersalation reactions of the metal complexes with the clay surface takes place in the opposite fashion when the clays are in
highly aggregated and delaminated forms. Fig. 3.7 depicts the state of the reaction i.e., in aggregated form work is required to prop open the layers for accommodation of the bulky metal complexes into the interlamellar space, while in case of delaminated clay, the platelets which are already adsorbed with metal complex laminate to form layered structure. Therefore, the formation of monolayered and bilayered metal complex in the interlamellar space could be easily explained from the Fig.3.7. In intersalation reaction the excess (>CEC) adsorption is considered to be due to intermolecular interaction and a van der Waals type of attraction between the metal complex salts caused by closeness of the adsorbate in the clay interlayer (20). Moreover, the shielding of the negative charge of the silicate layers by the first layer of intercalated metal complex cation may allow incorporation of the excess metal complex salt into the interlayer space (3).

3.3.3 Conclusion

Intersalation reaction of [Fe(phen)3]2+ with Na-Mnt is influenced by the hydration states of the clay. Aggregated clay adsorbed metal complexes as a monolayer, while dispersed and delaminated clay form a bilayer of metal complex in interlamellar space. The intersalated amount of the metal complex was found to be highest in case of dispersed clay. The flocculation of the clay by different concentration of NaCl effected the intersalation reaction where increase of salt concentration leads to decrease in adsorption of metal complex by Na-Mnt.

**********

93
3.4 Intercalation reactions of bulky three dimensional cationic metal complexes with Na-Montmorillonite

3.4.1 Introduction

Different micro-porous, shape selective sorbents having definite gallery height can be designed from clay minerals by modifying the size and shape of the interlayer cations. Both organic and inorganic cationic compounds can be incorporated into layered structures like montmorillonite (hereafter Mnt)(2, 6, 17, 37, 79, 179-182). Organic cations like large and long chained alkylamines and tetraalkylammonium ions are intercalated into smectites giving rise to a unique class of organo-inorgano solids. These are found to be useful as chromatographic materials for separation of mixtures of gases (1, 183-186). But, the organo-Mnt clay composites, in general, exhibit limited thermal stability due to decomposition of the organic moiety at comparatively low temperature and hence these composites may not be much useful in systems where comparatively higher temperature is involved. On the other hand, metal-complexes containing suitable organic ligands exhibit comparatively higher thermal stability which further enhances upon intercalation into Mnt (37, 68, 169). Therefore, suitable metal-complexes may be superior to cationic organic molecules as intercalating species in developing microporous Mnt clay composites having higher thermal stability. The aim of the present work is to investigate the intercalation reaction of two bulky three dimension cationic metal-complexes i.e. [Ni(den)$_2$]Cl$_2$ and
[Ni(tpy)_2](ClO_4)_2 (where den = di(2-aminoethyl)amine and tpy = 2,2':6',2"-terpyridine) with Na-Mnt and to evaluate the thermal stability of the products by thermal (TG, DTG and DTA) analyses supplemented by X-ray diffraction (XRD) and infrared (IR) spectroscopy.

3.4.2 Results and discussion

The intercalation reaction between the metal-complexes and Na-Mnt may be presented as:

\[
\text{Na-Mnt} + [\text{Ni(L}_2]\text{]}^{2+} \rightarrow [\text{Ni(L}_2]\text{-Mnt} + \text{Na}^+ \tag{1}
\]

(where L = den, tpy)

The diagrammatic representation of the above reaction may be shown as (Fig.3.23).

3.4.2.1 DTA, TG and DTG Studies

The DTA-TG-DTG curves of Na- and Ni-Mnt are shown in Fig.3.24. Na- and Ni-Mnt each shows the first and second endothermic peaks in the DTA curve in the temperature ranges 50-150°C and 480-520°C. This corresponds to dehydration from the interlayer water and dehydroxylation of the clay, respectively. The TG and DTG curves showed two mass loss stages. In the first stage up to about 150°C, Na- and Ni-Mnt show mass loss of about 14 and 17%, respectively, and correspond to loss of water from the interlayer spacing (26, 129). In the second stage Na- and Ni-Mnt exhibit mass loss of about 3.8 and 4.5%, respectively, in the temperature range 480-520°C, and is attributed to loss
Fig. 3.23. Schematic presentation of intercalation reaction of $[\text{Ni(den)}_2\text{Cl}_2$ or $[\text{Ni(tpy)}_2\text{ClO}_4$ with Na-Mnt.
Fig. 3.24. TG-DTG-DTA curves of (a) solid lines-Na-Mnt and (b) dashed lines-Ni-Mnt.
of OH lattice water of the clay (26). DTA-TG-DTG curves of [Ni(den)$_2$]-Mnt composite are shown in Fig.3.25. The DTA curve shows five peaks and the TG curve exhibits only three mass loss curves. The first DTA curve shows a very broad endotherm from 75 to 140°C with a peak at about 111°C. TG curve remains unchanged up to about 75°C and then exhibits a mass loss of about 6.0 % up to 140°C and has been attributed to loss of interlayer water. At 273°C, the DTA curve shows the first exothermic peak and the TG curve exhibits a mass loss of about 5.5 % in the temperature range 210 - 330°C, which may be due to the oxidation of the organic hydrogen and partial decomposition of the metal complex. Thus, conversion of the octahedral [Ni(den)$_2$]-Mnt (187-189) to lower [Ni(den)]-Mnt species takes place. Similar observation was also reported earlier (189). Comparing the decomposition temperature of the free salt of the metal-complex, it reveals that such metal complex, when intercalated into layered Mnt clay, gets an extra thermal stability of about 50°C. This enhanced thermal stability of the metal complex may be due to shielding effect by the alumino-silicate layer structure of the clay. The DTA curve shows second and third exothermic peaks at 354 and 456°C respectively. The TG curve does not show any sharp mass loss but exhibits a very small mass loss in the temperature range 350-470°C and may be due to oxidation of the residual carbon left over the clay as charcoal during the oxidation of the den molecule at lower temperature (around 273°C) as well as partial oxidative decomposition of [Ni(den)]-Mnt. The exothermic peak of the
Fig. 3.25. TG-DTG-DTA curves of [Ni(den)_2]-Mnt composite.
DTA curve observed for the composite prepared by the interaction between Ni-Mnt and den reported earlier (189) differs from the above and is perhaps due to difference in packing of the metal complex in the interlamellar spacing and rate of heating of the composite. The DTA curve shows the fourth exothermic peak at 557°C, which may be due to oxidation of carbon remained as charcoal on the clay and also oxidative decomposition of the metal complex converting to NiO. The endothermic dehydroxylation peak of Mnt (Fig. 3.24) expected near 500°C is not observed because it overlaps with the exothermic peak. The TG curve shows a mass loss of about 6.0 % in the temperature range 500-700°C which may be attributed to the mass loss by oxidation of residual carbon and dehydroxylation of layered structure of Mnt.

The major thermal changes that occur with mass loss of the intercalated composite may be presented as -

\[
\begin{align*}
[Ni(den)_2]-Mnt \times H_2O & \quad \xrightarrow{111^\circ C} \quad [Ni(den)_2]-Mnt + x H_2O \\
& \quad \text{Endothermic}
\end{align*}
\]

\[
\begin{align*}
[Ni(den)_2]-Mnt & \quad \xrightarrow{273^\circ C} \quad [Ni(den)_{2-x}]-Mnt + (den)_x \\
& \quad \text{Exothermic}
\end{align*}
\]

\[
\begin{align*}
[Ni(den)_{2-x}]-Mnt & \quad \xrightarrow{557^\circ C} \quad [NiO]-Mnt + \text{Other products} \\
& \quad \text{Exothermic}
\end{align*}
\]

The DTA, TG and DTG curves of [Ni(tpy)_2]-Mnt composite are shown in Fig. 3.26. The DTA and TG curves show five and four peaks respectively. The
Fig. 3.26. TG-DTG-DTA curves of [Ni(tpy)₂]-Mnt composite.
DTA curves show an endothermic peak in a temperature range of 50-140°C. The TG curve shows mass loss of about 6.0% in the same temperature range, which may be attributed to loss of water from the interlayer of the clay matrix. The DTA curve shows the first exothermic peak at 340°C and the TG curve shows a very little loss of mass in this temperature range indicating some oxidative decomposition of the organic moiety from the metal complex. At about 400°C, the DTA curve shows the second exothermic peak. The TG curve shows a mass loss of about 3.5% in the temperature range 390 - 410°C, which may be due to the oxidation of the organic hydrogen and partial decomposition of the metal complex. The free salt of the metal complex, i.e., [Ni(tpy)₂]X₂ (where X = halide or other anions) (190) are only stable up to about 200°C and converts to [Ni(tpy)]X₂ by losing one tpy molecule. This clearly indicates that the metal complex gets extra thermal stability by about 150-200°C upon intercalation into interlamellar spacing of the layered Mnt clay. This enhancement of thermal stability is probably due to combined effects of π-interaction between the aromatic rings of tpy and oxygen plan of the alumino silicate layer of Mnt (191) as well as the shielding effects of the layered Mnt clay. But in case of [Ni(den)₂]-Mnt, the enhancement of thermal stability is only about 50°C since there is no π interaction between den and the oxygen plan of Mnt. The DTA curve shows the third exothermic peak at 505°C and therefore, the endothermic dehydroxylation peak of Mnt at around 500°C (Fig.3.24) is perhaps overlapped with the exothermic peak.
The TG curve shows a mass loss of about 8.5 % in the temperature range 500 - 560°C which may be attributed to the conversion of the monoligated metal complex into metal oxide i.e. NiO with simultaneous oxidative decomposition of the tpy molecule and partial dehydroxylation of the layered clay structure. The fourth and fifth exothermic peak of the DTA curve occur at about 575°C and 645°C, respectively, and the TG curve shows very little mass loss in those temperature range, which may indicate the gradual oxidation of the carbon deposited during oxidative decomposition of the organic moiety on the clay as charcoal. The major thermal changes that occur with mass loss of the intercalated composite may be presented as:

\[
\begin{align*}
\text{[Ni(tpy)\textsubscript{2}]-Mnt.x H\textsubscript{2}O} & \quad \xrightarrow{110^\circ C} \quad \text{[Ni(tpy)\textsubscript{2}]-Mnt + x H\textsubscript{2}O} \quad (5) \\
\text{[Ni(tpy)\textsubscript{2}]-Mnt} & \quad \xrightarrow{397^\circ C} \quad \text{[Ni(tpy)\textsubscript{2-x}]-Mnt + (tpy)\textsubscript{x}} \quad (6) \\
\text{[Ni(tpy)\textsubscript{2-x}]-Mnt} & \quad \xrightarrow{505^\circ C} \quad \text{[NiO]-Mnt + other products} \quad (7) \\
\text{[NiO]-Mnt} & \quad \xrightarrow{574 & 645^\circ C} \quad \text{Unknown products} \quad (8)
\end{align*}
\]
3.4.2.2 X-ray Diffraction studies

XRD patterns along with basal spacing \((d_{001})\) data of the intercalated metal-complex-Mnt composites are shown in Fig. 3.27. It reveals from Fig. 3.27a that the cationic \([\text{Ni(den)}_2]^{2+}\) is intercalated into the Mnt clay, because the observed basal spacing i.e. 14.5\(\text{Å}\) of the intercalated composite is the summation of the thickness (9.6\(\text{Å}\)) of the clay layer and the diameter (about 4.5\(\text{Å}\)) of the metal complex cation (188) as shown in Fig. 3.23. The basal spacing \((d_{001})\) value gradually decreases as the temperature of drying increases (Fig. 3.27 b-h). The decrease of the basal spacing \((d_{001})\) from 14.5 to 14.1\(\text{Å}\) during heating at 150\(\degree\)C (Fig. 3.27c), is attributed to loss of water molecules from the interlayer spacing. At about 250\(\degree\)C (Fig. 3.27e), the basal spacing \((d_{001})\) decreases to 13.5\(\text{Å}\) which is not adequate to accommodate the octahedral structure of the metal complex in the interlayer spacing and thus may indicate presence of a slightly distorted octahedral structure. In the temperature range of 300 - 350\(\degree\)C (Fig. 3.27 b, f & g), the interlayer spacing was further reduced to about 3.5 \(\text{Å}\) revealing transformation of the octahedral metal-complex into other lower species, possibly to pseudo-octahedral \([\text{Ni(den)}]^{2+}\) complex (187). And at about 400\(\degree\)C (Fig. 3.27h), the interlayer spacing is almost collapsed showing a basal spacing \((d_{001})\) of about 10 \(\text{Å}\) exhibiting multiple XRD peaks which may indicate mixture of different products containing intercalated NiO.
Fig. 3.27. XRD patterns and basal spacing ($d_{001}$) of oriented samples intercalated [Ni(den)$_2$]-Mnt (a-h) and [Ni(tpy)$_2$]-Mnt (i-p) composites heated at different temperature (50-400°C) for 1hr in air atmosphere.
The product obtained from the interaction of bulky cationic species \([\text{Ni(tpy)}_2]^2^+\) and Mnt shows basal spacing \((d_{001})\) (Fig. 3.23 and 3.27i) of about 19.4Å at 50°C indicating that the cationic species is intercalated into the clay platelets because the summation of the layer thickness (9.6Å) and dimension (about 9.5Å) of the metal complex matches well with the observed basal spacing \((d_{001})\) value i.e. 19.4 Å. On drying the composite with raising temperature, the basal spacing \((d_{001})\) decreases slightly to 19.3 Å up to 150°C, which is attributed to loss of water from the interlayer structure. On further raising the temperature up to 350°C, the basal spacing \((d_{001})\) of the composite gradually reduces to 19.0Å (Fig. 3.27o), which may still indicate the presence of the octahedral structure of the \([\text{Ni(tpy)}_2]^2^+\) species in the interlamellar spacing of the layered Mnt clay matching its shape with the hexagonal hollows of the clay surface (167). But, at about 400°C (Fig. 3.27p) the basal spacing \((d_{001})\) value decreases to about 12Å indicating that the metal complex is either decomposed oxidatively to \(\text{Ni}^{2^+}/\text{NiO}\) and/or converted into other lower monoligated species like \([\text{Ni(tpy)}]^2^+\). It is known that the salt of \([\text{Ni(tpy)}_2]^2^+\) is stable up to 200°C in free state and above it, the metal complex converts to monoterpyridine \(\text{Ni(tpy)}^2^+\) species (190). Therefore, XRD data reveal that the intercalated cationic species gets an extra thermal stability of about 150-200°C, which may be due to \(\pi\) interaction between the oxygen plane of Mnt and the aromatic rings of tpy as well.
as thermal shielding by the clay platelets (191). The above observations corroborate the data of thermal analyses.

### 3.4.2.3 Infrared spectroscopic studies

FT-IR spectra (600 - 1500 cm\(^{-1}\)) of the intercalated composites are shown in Fig.3.28. Four major bands are observed at about 3626, 1635, 1040 and 917 cm\(^{-1}\) (Fig. 3.28a) which are due to \(\nu_(OH)\), \(\delta_(OH)\), (SiO) and Al-OH-Al deformation bands, respectively, of the aluminosilicate layers of Mnt. The other OH deformations occur near 800 cm\(^{-1}\) as very weak bands. The \(\nu(CH_2)\) bands at 2920 and 2872 cm\(^{-1}\) of the metal complex in \([Ni(den)_2]-Mnt\) composite are observed (Fig.3.28b) as weak bands. The bands at 1447, 1380 and 1336 cm\(^{-1}\) are attributed to \(\delta(CH_2)\), \(\omega(CH_2)\) and \(\omega(NH_2)\) respectively for the metal coordinated ligand in the intercalated composites (Fig. 3.28 b). The multiple bands in the region 600 - 800 cm\(^{-1}\) due to \(\rho(NH_2)\), skeletal vibration etc. of the free metal complex are not clearly observed, but only two weak bands at 783 and 694 cm\(^{-1}\) are found which are difficult to identify. FT-IR spectra (600-1500 cm\(^{-1}\)) of the intercalated \([Ni(den)_2]-Mnt\) composite at different temperatures are shown in Fig. 3.29(a-e). Up to about 250\(^0\)C, intensity of the characteristic bands remained almost unchanged. The formation of hydrogen bond between N-H group the ligand moiety of the metal complex and oxygen plane of Mnt is likely and may be one of the reasons for the enhancement of thermal stability of the composite. As the intercalated compound is heated to about 350\(^0\)C, the intensity of the characteristic
Fig. 3.28. FT-IR spectra (600-4000 cm\(^{-1}\)) of Na-Mnt, [Ni(den)\(_2\)]-Mnt and Ni(tpy)\(_2\)]-Mnt composite.
bands of the metal complex decreases considerably (Fig.3.29d) indicating the decomposition of the metal complex into other lower species. Similarly, the new CH\textsubscript{2} bands at 2920 and 2872 cm\textsuperscript{-1} (Fig. 3.28 b) of the composite are stable up to 250° C, but at about 350° C, the intensity of the bands are reduced to minimum. At about 400° C the characteristic bands of the metal complex are almost vanished and thus indicating complete decomposition of the metal complex.

The ring stretching (C-H in-plane ring stretching vibrations) occurring below 1500 cm\textsuperscript{-1} are observed in the [Ni(tpy)\textsubscript{2}]-Mnt composite (Fig.3.28 c) as distinct bands. The C-H out-of-plane deformation vibrations of the heterocyclic tpy rings in the region 650-800 cm\textsuperscript{-1} are also observed as distinct band in intercalated composite (Fig.3.28 c). As the intercalated composite is heated, the band layer 1635 cm\textsuperscript{-1} at room temperature due to δ(OH) gradually shifts to lower wave number up to 1604 cm\textsuperscript{-1} at about 400° C. This shift may be an indication that some π interaction between the aromatic tpy and oxygen plane of Mnt occurs. The FT-IR (600-1500 cm\textsuperscript{-1}) spectra of [Ni(tpy)\textsubscript{2}]-Mnt composite heated at different temperature are shown in Fig.3.29 (f-j). When the intercalated compound is heated up to 350° C (Fig.3.29 i), the intensity and the peak positions of the IR bands remain almost the same as that of unheated composite indicating the stable state of the metal complex in the interlamellar spacing but at about 400° C (Fig.3.29 j), the intensity of the peaks are decreased considerably indicating the
Fig. 3.29. FT-IR spectra (600-1500 cm\(^{-1}\)) of the intercalated [Ni(den)\(_2\)]-Mnt (a-e) and Ni(tpy)\(_2\)]-Mnt (f-j) composites heated at different temperature (50-400°C) for 1 hr in air atmosphere.
transformation of the octahedral metal complex into other forms. All these observations corroborate the data of thermal and XRD analyses.

The thermal stability of the [Ni(den)$_2$]-Mnt and [Ni(tpy)$_2$]-Mnt composites studied by thermal, XRD and IR spectroscopic analyses indicate that the latter composite containing metal complex with aromatic backboned ligand (tpy) gains higher thermal stability than those containing aliphatic backboned ligand (den) upon intercalation into layered clay matrix of Mnt. Thus, suitable metal complexes may provide intercalated metal-complex-clay composite exhibiting comparatively higher thermal stability for developing microporous materials.

3.4.3 Conclusion

Thermal behaviour of the intercalated [Ni{Di(2-aminoethyl)amine}$_2$]-Mnt (I) and [Ni(2,2':6',2"-terpyridine)$_2$]-Mnt (II) composites studied by thermal (TG, DTA, DTG) analyses supplemented by XRD and IR spectroscopy show that these are stable up to 273°C and 397°C respectively which are about 50°C and 150°C higher compared to melting / decomposition of their respective free metal complex salts. Metal complex with aromatic backboned ligands gets higher thermal stability than that of aliphatic one upon intercalation into Mnt. XRD data show that the basal spacing ($d_{001}$) of the I composite i.e. 14.5 Å at 50°C show a gradual decrease on increasing the temperature and reached a value of about 13.5 Å at 250°C. This corresponds to a distorted octahedral intercalated complex in the interlamellar spacing. On the other hand, the II composite shows a
basal spacing (d_{001}) of 19.4 Å at 50°C and decreases slightly to 19.0 Å at about 350°C indicating presence of octahedral metal complex in the interlamellar spacing and thus the XRD data corroborate the observation made by the thermal analyses. The characteristic bands of IR spectra of the composites I and II in the temperature range 50 - 400°C also show that these are stable up to about 250°C and 350°C respectively which also support the data of thermal as well as XRD analyses. Such metal-complex-clay composites may be utilized for developing microporous layered materials exhibiting comparatively higher thermal stability.
3.5 Phosphate-bridged Montmorillonite clay and its intercalation reaction

3.5.1 Introduction

Layered clay minerals, particularly Mnt has been widely used as catalysts (50), adsorbents (17, 94, 192, 193) etc. But such materials sometimes need modification for improving its textural property. The layer structure of the clay consists of an octahedral alumina sheet sandwiched by two tetrahedral silica sheets. The interlayer is generally occupied by alkali ions which balance the layer charge arising from isomorphous substitution in the clay structure. Mnt exhibits swelling behaviour due to extensive hydration of the interlayer cations and undergoes dispersion in polar solvents like water. The aluminate edges in the clay layers are reactive and can bind with suitable anions like PO$_4^{3-}$, SO$_4^{2-}$ etc. (6, 27) and may modify the textural behaviour. When phosphate fertilizers are used, a part of the liberated PO$_4^{3-}$ anion bind strongly with the clay minerals invariably present in the soil and become immobile, and therefore cause a drastic change in the texture of the clay. Therefore, there is a need to study the change in behaviour of the phosphate contaminated soil. In view of above, an attempt has been made to bridge up the reactive aluminate edges with PO$_4^{3-}$ unit to modify the matrix of the clay and to evaluate the intercalation/intersalation reaction with bulky cationic complex like $[\text{Ni(phen)}_3]^{2+}$ and their thermal behaviour as well as stability under water.
3.5.2 Results and Discussion

The ortho-phosphoric acid treated Na-Mnt is assumed to exhibit (194, 195) an extensively bridged structure of Mnt where the aluminate edges of clay fragments are covalently bound by $\text{PO}_4^{3-}$ units (Fig.3.30). The $\text{PO}_4^{3-}$ anions are believed to chemisorb on oxides and clay minerals by a binuclear bridging mechanism:

\[
\begin{align*}
>\text{Al-OH} & \quad \rightarrow \quad >\text{Al-O} \\
+ \text{PO}_4^{3-} & \quad \rightarrow \quad >\text{Al-O} \quad \text{PO}_2^- + 2\text{OH}^- \\
>\text{Al-OH} & \quad \rightarrow \quad >\text{Al-O}
\end{align*}
\]

This association is stabilized because of both energy and entropy factors(27).

XRD patterns of Na-Mnt, Po-Mnt, $[\text{Ni(phen)}_3]^2+$-Mnt and $[\text{Ni(phen)}_3]^2+$-Po-Mnt are shown in Fig. 3.31. The basal spacing ($d_{001}$) 12.5 Å of Po-Mnt was enhanced to 17.2 Å on treatment with 0.2 CEC-Eqv. of the metal complex (Fig. 3.31. f,g). It is evident that the oriented film of Po-Mnt retains the original layer structure and the metal complex $[\text{Ni(phen)}_3]^2+$ forms almost a monolayer with slight deviation from perpendicular of their c-axis to the plane of the clay layer. Po-Mnt on treatment with 60 meq (equal to 1 CEC of Po-Mnt) of $[\text{Ni(phen)}_3]^2+$ results in a product which shows a basal spacing ($d_{001}$) of about 17.8 Å (Fig. 3.31 h) indicating a monolayer of the metal complex in the interlamellar spacing with its c-axis perpendicular to the plane of clay layer. Similarly, Na-Mnt on
Fig. 3.30. Schematic presentation of a portion of the structure of Mnt treated with H$_3$PO$_4$
Fig. 3.31. X-ray diffraction patterns and basal spacing ($d_{001}$) of Na-Mnt, Po-Mnt, [Ni(phen)$_3$]$^{2+}$-Mnt and [Ni(phen)$_3$]$^{2+}$-Po-Mnt.
treatment with 114 meq (equal to 1 CEC of Na-Mnt) yields a product having basal spacing \((d_{001})\) of about 17.7Å (Fig. 3.31 c) which indicates adsorption of the metal complex as monolayer in the interlamellar spacing. It is interesting to note that in case of Po-Mnt treatment with excess \((>1\) CEC-Eqv.) metal complex results in intersalation reaction (adsorption of excess metal salt over CEC) (Table 3.6) but the basal spacing \((d_{001})\) remains almost the same as that of the product obtained on treatment with 1 CEC-Eqv. of metal complex. This additional amount of metal complex salt is likely to occupy the interlamellar spacing (Fig. 3.32A) as monolayer laterally with that of already exchanged \([\text{Ni(phen)}_3]^{2+}\). On the other hand, intersalated products formed by treatment of Na-Mnt with increasing dose \((>\text{CEC})\) of metal complex (Table 3.5) exhibit a basal spacing \((d_{001})\) of about 28.9 or 32.1Å (in case of unwashed product) indicating double (Fig.3.32) or pseudo-trilayer (Fig. 3.32C) formation of metal complex in the interlamellar spacing\(169\). In the intersalated product, the excess \((>\text{CEC})\) adsorption is considered to be due to intermolecular interaction and a van der Waals type of attraction between the metal complex salts caused by closeness of the adsorbates in the clay interlayers\(20, 148, 171\). Thus it clearly indicates that expansion of basal spacing in case of Po-Mnt is restricted compared to Na-Mnt clay layers.
Fig. 3.32. Schematic presentation of intersalated monolayer (A), bilayer (B) and pseudo-trilayer (C) products.
The IR spectra of Na-Mnt and Po-Mnt are shown in Fig. 3.33. The bands at 3625 and 3425 cm\(^{-1}\) appearing in both the cases are due to \(v(\text{OH})\) stretching for AlAI\(\text{OH}\), AlMg\(\text{OH}\) and water, and the band at about 1631 cm\(^{-1}\) is assigned for \(\delta(\text{OH})\) bending. IR bands at 1020, 526 and 462 cm\(^{-1}\) are due to Si-O stretching and bending respectively. The bands at 1402, 1130 and 575 cm\(^{-1}\) shown by Po-Mnt are absent in Na-Mnt and are assigned to different vibrations of PO\(_4^{3-}\) and HPO\(_4^{2-}\) groups. The bands at 791 and 691 cm\(^{-1}\) are due to out-of-plane and in-plane vibrations OH groups in the clay structure(129, 196, 197).

Table 3.6 Adsorption of [Ni(phen)\(_3\)]\(^{2+}\) on Na-Mnt and Po-Mnt.

<table>
<thead>
<tr>
<th>Type of clay</th>
<th>[Ni(phen)(_3)](^{2+}) added (meq/100 g of clay)</th>
<th>[Ni(phen)(_3)](^{2+}) adsorbed (meq/100 g of clay)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Mnt</td>
<td>22.8</td>
<td>22.8</td>
</tr>
<tr>
<td></td>
<td>114</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td>228</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td>456</td>
<td>296</td>
</tr>
<tr>
<td>Po-Mnt</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>211</td>
</tr>
</tbody>
</table>

The DTA-TG-DTG curves of Na-Mnt and Po-Mnt are shown in Fig. 3.34. Na-Mnt and Po-Mnt each shows the first and second endothermic peaks in the
Fig. 3.33. FT-IR spectra of Na-Mnt and Po-Mnt.
Fig. 3.34. TG-DTG-DTA curves of Na-Mnt and Po-Mnt.
range of 50 to 150°C and 470 to 550°C respectively. These correspond to dehydration from the interlayer water and dehydroxylation of the clay respectively (198). The TG and DTG curves show two mass loss stages. In the first stage up to about 150°C Na-Mnt and Po-Mnt show mass loss of about 13.9 and 13.0 % respectively, which correspond to loss of water from the interlayer spacing. In the second stage Na-Mnt and Po-Mnt exhibit mass loss of about 3.8 and 5.6 % respectively in the temperature range of 470 to 550°C, and is attributed to loss of OH lattice water of the clay (26). The higher mass loss in case of Po-Mnt may be due to presence of some HPO$_4^{2-}$ at the edges of clay layers. TG curves show no mass loss for Na-Mnt and Po-Mnt in the temperature range 890 to 910°C, while DTA curves show exothermic peaks at around 893 and 908°C respectively indicating phase transformation only. It also reveals that the Po-Mnt is thermally more stable than that of Na-Mnt.

SEM-EDX micrographs of Po-Mnt are shown in Fig. 3.35. The broken edge of a thin film of Po-Mnt shows (SEM) that the layers are parallel and are separated by a few microns. The presence of phosphorous on the surface texture of Po-Mnt is evident from the EDX. Thus it reveals that in Po-Mnt, the layer structure is maintained like that of Na-Mnt.

Dried thin film, prepared from Na-Mnt and Po-Mnt were subjected to soaking in water at different temperature for about 12 hrs. Na-Mnt was found to
Fig. 3.35. SEM-EDX micrographs of Po-Mnt.
swell and disperse at room temperature, while Po-Mnt film remained almost intact without swelling up to a temperature of 90°C.

3.5.3 Conclusion

Dispersed Na-Mnt clay upon reaction with orthophosphoric acid produces a phosphate-bridged (Po-Mnt) polymeric product. Interaction of such Po-Mnt with excess (>CEC) [Ni(phen)₃]²⁺ yields an intercalated monolayer composite exhibiting basal (d₀₀₁) spacing of about 17.7Å, while Na-Mnt produces pseudotrilayer (basal spacing about 32.1Å) or bilayer (basal spacing about 28.9Å) composites. The thermal stability of Po-Mnt is higher than that of Na-Mnt. Thin film of the Po-Mnt is found to be stable even on heating under water at 90°C for a few hours.
3.6 Application of clay metal complex composites

3.6.1 Synthesis and application of pillared clay composites useful as solid acid catalysts

3.6.1.1 Introduction

Supported inorganic reagents are rapidly emerging as a new and environmentally accepted materials for improving process efficiency or to replace environmentally unacceptable reagents and catalysts. Attempts are being made to replace highly corrosive HF in olefin alkylation, anhydrous AlCl₃ in Friedel Crafts alkylation etc. by supported solid acid catalyst. All the solid acids are characterized by the presence of protons or coordinatively unsaturated cationic centers on the surface leading to Bronsted and Lewis acidity. Bronsted acidity comes from exchangeable cations which polarize interlayer water molecules. Partial dehydration increases the acidity. Replacement of the exchangeable interlayer Na⁺ ions by high charge density cations such as Al³⁺, Zn²⁺ etc. leads to acidity as high as 10 mol dm⁻³. These highly acidic forms of Mnt clays are the basis of a class of broad spectrum catalysts for organic synthesis. It is also important to note that at high temperatures clays are generally reduced to Lewis acidity only through the loss of interlayer water.

Swelling clays with layered structures offer the potential for shape selectivity although the interlayer gap in natural Mnt is quite small. The development of pillared clay based materials has paved the way to overcome this
limitations by offering large interlayer gap (>5Å) coupled with high surface area and high acidity. Therefore, development of Brønsted and Lewis acidity in such pillared materials are expected to be highly useful as solid acid catalysts. Thus, it appears that high and variable acidity, low cost, different types of acidic character, thermal stability and size selectivity make the solid acid catalysts based on smectite clays, particularly Mnt clay, an attractive package.

The replacement of interlayer Na\(^+\) by cations such as Fe\(^{2+}\), Al\(^{3+}\) etc. leads to clay layers of high acidity and are described (38) as broad spectrum catalysts for organic synthesis. But, such catalysts have inherent draw back in respect of interlayer thickness of the materials i.e. the interlayer gap is narrow (about 2Å) for dry materials and therefore restricts their use for reactants having bigger size (>2Å). Replacement of environmentally unacceptable anhydrous AlCl\(_3\), an established catalyst for Friedel Crafts alkylation, by supported AlCl\(_3\) on K-10 Mnt (acid treated clay) has been claimed (199) to be an efficient catalyst. Anchoring of AlCl\(_3\) on the hydroxy groups of the supporting materials may occur (200) through the active group -O-AlCl\(_2\). Such immobilization on expandable Mnt clay will not improve any interlayer expansion i.e. the interlayer surface will not be utilised for such reactions. Smectite clays have been shown to be very effective supports for a number of transitional metal salts. One such example is ZnCl\(_2\) supported on K-10-Mnt which is prepared by digesting methanoic solution of ZnCl\(_2\) with acid treated Mnt. When the loading is very high, the catalytic activity is low and this may be attributed to the aggregation of ZnCl\(_2\) on the support. The metal salt is believed to stay as intact molecule residing within the pores of the
support. Therefore, leaching of the metal salt from the support is very much likely and the catalytic activity is expected to be reduced accordingly. In order to overcome the narrow interlayer distance, a new class of pillared materials have been developed (201) by exchanging Na-Mnt with inorganic polyoxo metal ions like (Al\(_{13}\))\(^{7+}\) of larger size and charge and then calcining at about 450°C for 4 hrs. Metal ion exchanged catalysts were prepared (202) by treating the pillared clay with desired cations. The actual location of the cation exchange site in pillared clays is still not known. Such materials are also called "Pillared Clay" which show higher interlayer spacing (about 10-12Å). Despite their high thermal stability (> 500°C) and high surface area (> 200 \(\text{m}^2/\text{g}\)), pillared clays are less efficient catalysts compared to cations (like Al\(^{3+}\)) exchanged clays.

In this section a new type of pillared clay composite useful as acid catalyst have been described. Such composites are prepared by pillaring the expandable layers of Na-Mnt clay by partial exchange with cationic three dimensional trisdiimine metal complexes like [Ni(phen)]\(^{2+}\) and then exchanging the rest Na\(^+\) ions with multivalent metal cations like Al\(^{3+}\). The experimental details are given in Section 2.1.12 of Chapter 2.

3.6.1.2 Result and Discussion

Interlayer arrangement of metal-metalcomplex-clay composite is represented in Fig. 3.36. The interlayer as well as the external exchange sites of the clay platelets are occupied by Na\(^+\) ions. The Na\(^+\) ions are partially replaced by metal complex cations. The remaining Na\(^+\) ions are than replaced by the active metal ion (Al\(^{3+}\)). It is evident from the figure that on intercalation of the metal
Fig. 3.36. Schematic presentation of metal-metal complex-Mnt composites

$\text{Na}^+ = \text{O}$

$\text{Al}^3+, \text{Cu}^2+, \text{or Cd}^{2+} = \text{Q}$

$[\text{Ni(L-L)}_3]^2+ = \text{N}$

Clay layer

$17.6 \text{Å}$

$12.5 \text{Å}$

Metal Complex

$\text{Al}^3+, \text{Cu}^2+, \text{or Cd}^{2+}$

$\text{Na}^+$
complex cation, the basal spacing increases. The XRD patterns for the metal-metal complex-Mnt composites are shown in Fig. 3.37 for both Mnt$_1$ and Mnt$_2$ clays. The basal spacing of Na-Mnt shows an increase on exchange with Al$^{3+}$ ions (13.5 Å). The metal ion-metal complex Mnt shows $d_{001}$ spacing of 17.7 Å. The distance between two active sites on the clay surface is about 10-15 Å (27) and so the space between two adsorbed cations is large. Therefore, the reactant molecules may get enough interlayer space to react.

When the interlayer cations are exchanged with bigger sized three dimensional cationic metal complex like [Ni(phen)$_3$]$^{2+}$ having a diameter about 8Å (3,20) the basal spacing obtained is about 17.5Å even after heating at about 500°C. Thus, an expansion of the layers by about 8Å is possible by pillaring swelling clays with such metal complexes. This expansion is dependent on the dimension of the intercalating species. Also, pillaring increases the internal surface area for the reactants (Fig.3.36). On the other hand, the restricted space of the composite adds the advantage of selectivity to the reaction.

M$^{n+}$-[Ni(phen)$_3$]$^{2+}$-Mnt composites are very much potent in respect of developing Brønsted and Lewis acids. Brønsted acidity is generated by the polarizing power of the exchanged cations i.e. Al$^{3+}$ ions. Such cations produce Brønsted acid strength by promoting a reaction with water to release H$^+$ ions -

$$[\text{M(H}_2\text{O)}_x]^{n+} \rightarrow [\text{M(H}_2\text{O)}_{x-1}(\text{OH})]^{n+1} + \text{H}^+$$
Fig. 3.37. XRD patterns for, A= Na-Mnt, B= Al-Mnt & C= Al-[Ni(phen)$_3$]-Mnt composites (Mnt$_1$= Neelkanth Mnt, Mnt$_2$= Wyoming Mnt)
As the clay surface loses moisture, the reaction is driven further to the right and the protons are concentrated in a smaller volume of water. Air dried smectite with Al\(^{3+}\) exchange ions are equivalent in acidities to concentrated aqueous solutions of strong acids. When the interlayer water is lost due to heating at higher temperature, the metal ion exchanged Mnt behaves as Lewis acids. Therefore, depending upon the water content of the composites, the strength of acidity changes. Such composites are useful as solid acid catalysts in organic synthesis.

These metal-metal complex-Mnt composites exhibit high surface area (> 100 m\(^2\)/g) and can accommodate reactants having size up to about 8\(\text{Å}\). Most of the unpillared metal ion exchanged clay show very narrow interlayer distance (<2\(\text{Å}\)) for dried materials (Fig.3.36) and hence can not accommodate bigger sized reactants into the interlayer space. These clay composites can be easily converted to Lewis acids by heating up to about 350\(^\circ\)C without destroying the layer arrangement. Moreover, the interlayer distance can be fixed by intercalating with suitable metal complex having desired three-dimensional size. Thus, such clay composites can be used for size selective reactions. The model reaction used for evaluating the catalytic activity of this acid catalyst is the Friedel-Crafts reaction for benzylolation of benzene.

\[
\text{CICH}_2 + \text{Ar} \xrightarrow{\text{Acid catalyst}} \text{ArCH}_2
\]
Usually, the Friedel-Crafts reaction is catalysed by Lewis acids like AlCl₃, FeCl₂, ZnCl₂ etc (4, 18, 34, 50). In the clay supported Al³⁺ or Zn²⁺, the acidity is determined by the hydration state of the clay. Hence, the catalytic activity of the composite is also dependent on the temperature of drying. The benzylation reaction was carried out with Al-[Ni(phen)]₃-Mnt composite dried around 200°C and the results (Gas chromatographic analysis) show (Fig. 3.38) the product diphenylmethane formed in percentage against time of reaction where it is seen that about 12% product was observed within 45 min of reaction which increases to about 63% after 48 hrs of reaction at room temperature.

3.6.1.3 Conclusion

The metal-metal complex-Mnt composites can provide higher surface area (>100 m²/g). The interlayer gap between the layers of the products is about 8 Å and hence can accommodate higher sized reactants. Different types of metal ions may be incorporated into the interlayer spacing for generating Brönsted and Lewis acidity as per the requirement by suitably controlling the water content of the composites. Such products are thermally stable at least up to 350°C and may be used as acid catalysts and also for size selective reactions.

************
Fig. 3.38. Conversion of benzene and benzyl chloride into diphenylmethane in presence of Al-[Ni(phen)$_3$]-Mnt composite as catalyst.
3.6.2 Synthesis of metal-metal complex-Mnt composites useful as deodorants

3.6.2.1 Introduction

Hydrogen sulfide, ammonia and other similar gases, generated by decomposition of proteins or by other means pollute the air. Therefore, removal of such gases at least from indoor air or a refrigerator is essential to bring the concentration well below the pollution level. Several types of deodorants have been developed to arrest such polluting gases from the air (105, 192).

In general such deodorants are mostly prepared by supporting transition metal salts on supports like activated charcoal, zeolites, silica gel, diatomaceous earth, bentonite clay, fiber etc. (105). In one such method of preparation, the deodorants which was effective against polluting gases generated from fish, meat, or sulfur compounds etc., consisted of fibrous supports like those of traditional Japanese made paper and ordinary paper, fabrics, glass fibre etc. including 5 - 40 wt. % (to the wt. of the support) of one or more of CaSO₄, FeSO₄, ZnSO₄ and MgSO₄. Such deodorants are in general less effective in removing the odorous compounds from air. Another invention (203) discloses preparation of deodorants for ammonia, amine, hydrogen sulfide, mercaptans; which comprises Zn compounds or Cu(II) compounds with different anions supported on porous zeolite or activated charcoal etc (106). In all these inventions the deodorants have a limited surface for the odorous gases. The exchangeable interlayer cations in Mnt clays can be replaced by potent metal cations like Cu²⁺, Cd²⁺, Zn²⁺ etc. These
ions can react with sulphur or nitrogenous gases like H$_2$S, mercaptans, ammonia etc. and arrest them in the clay interlayer space along with the external surfaces also. Earlier works on such deodorants however, restricted the clay interlayer by incorporating the metal ions only (105, 107). In the present study, the basal spacing (d$_{001}$) of the clay has been expanded by pillaring with metal trisdiimine complexes, similarly as described in Section 3.6.1, to promote the access of the gases into the interlamellar space and provide more interaction with the metal ions.

### 3.6.2.2 Result and Discussion

Fig. 3.39 shows the XRD patterns for Cu-[Ni(phen)$_3$]-Mnt composites. The basal spacing of 12.5 Å for Na-Mnt, on intercalation with 0.2 CEC-Eqv. of [Ni(phen)$_3$]Cl$_2$ increases to about 17.3Å which on subsequent exchange with 0.8 CEC-Eqv. of Cu$^{2+}$ ion exhibits a basal spacing 16.7Å. On the other hand, the basal spacing of 0.5 CEC-Eqv. of [Ni(phen)$_3$]Cl$_2$ treated Na-Mnt (17.6Å) remains almost same on further exchange with 0.5 CEC-Eqv. of Cu$^{2+}$ or Cd$^{2+}$ ions. Similar observations are also noticed in case of the metal complex [Ni(bpy)$_3$]Cl$_2$. It has been observed that for 0.2 CEC-Eqv. loading of metal complex, the composite is stable up to about 250$^\circ$C while the composite for 0.5CEC-Eqv. loading of metal complex, is stable up to about 350$^\circ$C. When the clay is exchanged with the Cu$^{2+}$ ions first, the resulting Cu-Mnt does not intercalate the metal complex under the same reaction conditions as Na-Mnt. This may be due to lesser swelling nature of
Fig. 3.39. XRD patterns of A= Na-Mnt, B= [Ni(phen)$_3$]-Mnt & C= Cu-[Ni(phen)$_3$]-Mnt
Cu-Mnt. However, the \([\text{Ni(phen)}_3]\)-Mnt easily incorporates the 0.8 CEC-Eqv. of 
Cu\(^{2+}\) ions; this is evident that the 8Å interlayer gap allows free access to Cu\(^{2+}\) or 
Cd\(^{2+}\) ions which have a small ionic size of 0.73 Å and 0.78 Å respectively.

Intersalation Na-Mnt with such trisdiimine metal complexes may give rise to double and even pseudo-trilayer clay composite with basal spacing 29.6-32 Å (169). Such composites with higher layer of metal complexes in the interlayer space posses high thermal stability (up to about 500°C) but low surface area (3,68). However, stable monolayer is observed for 0.5 CEC-Eqv. of metal complex exchanged Mnt which is found to be of comparable heat stability; in addition, sufficient surface area is obtained for adsorption of the polluting gases. A schematic representation of the interlayer arrangement of the composites is shown in Fig. 3.36. It can be mentioned here that for a loading of 0.1 CEC-Eqv. of metal complex, the composite is stable up to about 200°C. At room temperature the interlayer space of clay contains a certain amount of hydration water which on heating is gradually removed and thereby decreases the Brönsted acidity of the metal cations. On the other hand, the Lewis acidity increases with decreasing water content and the composite becomes a solid Lewis acid. The polluting gases when come in contact with the composite, both at room temperature and high temperature, form the corresponding metal complexes on the clay support. In contact with ammonia, the Cu-composite forms \([\text{Cu(NH}_3)_4]^{2+}\) and turns pale blue in colour (132). On exposure to hydrogen sulphide gas, the
composite turns black due to formation of CuS. Similarly, the Cd-composite turns yellow in contact with \( \text{H}_2\text{S} \) with formation of CdS. The metal-metal complex-Mnt composites retain their deodorising property even after heating to about 250°C. In solution, the Cu\(^{2+}\) or Cd\(^{2+}\) ions react with \( \text{H}_2\text{S} \) in dilute acid solutions (132). It is found that in clay also the interlayer space containing the metal ions possess similar acidic environment (18). Moreover, the interlayer hydrated metal ions are found to be of comparable mobility with metal ions in solution (171) and reactivity can be expected to be similar in both cases. Therefore, it is evident that the interaction of the gases takes place with the clay supported metal ions almost instantaneously.

### 3.6.2.3 Conclusion

The composites \( \text{M-}[\text{Ni(L-L)}_3]\)-Mnt, where, \( \text{M}=\text{Cu, Cd; L-L}=\text{phen, bpy,} \) can arrest large three dimensional odorous/non-odorous molecules and can provide sufficient space (at least 7-8Å gap between the layers) for accommodating coordination compounds formed in-situ by the reaction between the metal cations and the coordinating gaseous molecules. They can provide higher surface area for efficient adsorption and can provide desired interlamellar space-gap (tailor-made) for adsorbing selective polluting gases. These may be utilized for other purposes particularly for suitable catalytic reactions also.

************