CHAPTER-IV

CHLOROSULPHATES
There are few reports on chemistry of chlorosulphates as compared to that of fluorosulphates. Metal chlorosulphates, e.g., mono- (80, 81, 200, 201), bis- (83), tris- (88), chloro(chlorosulphates) of the VIb group elements, tin and antimony (90), titanium (92), bismuth (94), organosilicon (96) and mixed chlorosulphates have been reported. There is, however, no report on the preparation and characterization of the coordination complexes of the metal chlorosulphates with donor molecules. In the present work, the preparation and characterization of cobalt(II), copper(II), nickel(II) and zinc(II) chlorosulphates, dichlorobis(chlorosulphato)titanium(IV), tetrachloro(chlorosulphato)antimony(V) and their coordination complexes with nitrogen and oxygen donors, have been carried out.

4.1 Infrared Spectra of Metal Chlorosulphates

Like ionic fluorosulphates, chlorosulphates can also be thought of having $C_{3v}$ symmetry. This would result in six Raman or i.r. active vibrations, namely; an $SO_3$ symmetric stretch ($\nu_1$), an $SO_3$ asymmetric stretch ($\nu_4$) and $SO_3$ symmetric band ($\nu_3$), an $SO_3$ asymmetric bend ($\nu_5$), $\nu_{S-Cl}$ ($\nu_2$) and a $S-Cl$ wagging ($\nu_6$) (52). Waddington and Klanberg (111) assigned the spectra of $(CH_3)_4N(SO_3Cl)$ and $PCl_4(SO_3Cl)$ by comparison with the spectra of fluorosulphates (105), however, the Raman study by Gillespie and Robinson (52) showed that a band at
Fig. 4.1 - Infrared spectra of copper(II) and zinc(II) chlorosulphate

A - cu\((SO_3Cl)_2\)
B - zn\((SO_3Cl)_2\)
540 cm\(^{-1}\) assigned by Waddington and Klanberg to the S-Cl stretching mode was in fact the SO\(_3\) symmetric stretching vibration. The four bands at 533, 555, 600 and 640 cm\(^{-1}\) observed in the i.r. spectrum of NaSO\(_3\)Cl by Steger and Ciurea (202) were assigned in terms of removal of expected degeneracy of the asymmetric bend to give 533 and 555 cm\(^{-1}\) frequencies and a Fermi resonance interaction between symmetric SO\(_3\) bend and a combination band of the S-Cl stretch (392 cm\(^{-1}\)) and the S-Cl wag. (220 cm\(^{-1}\)) (52) to give the 600 and 640 cm\(^{-1}\) frequencies.

Ciruna and Robinson (200) also studied the infrared spectra of alkali and alkaline earth metal chlorosulphates. They observed that apart from \(\nu_6\) (S-Cl wag.) and \(\nu_2\) (\(\nu_{\text{SO}_3}\) S-Cl), which are not determined directly, the remaining fundamental frequencies are consistent with the expected C\(_{3v}\) symmetry of the chlorosulphate anion.

4.1.1 Metal chlorosulphates: The i.r. spectra of M(SO\(_3\)Cl)\(_2\), where M = Co, Ni, Cu and Zn, indicate the presence of only one type of chlorosulphate group in these compounds. The infrared frequencies are listed in Table 39 together with the tentative assignments.

Table 39 shows that cobalt(II), nickel(II) and zinc(II) chlorosulphates show six fundamental frequencies without any splitting in E modes indicating C\(_{3v}\) symmetry of the chlorosulphate group (Fig. 4.1). The frequencies in cobalt(II), nickel(II) and
### Table 39

**Chlorosulphate Vibrations in Cobalt(II), Copper(II), Nickel(II) and Zinc(II) Chlorosulphates**

<table>
<thead>
<tr>
<th></th>
<th>Co(SO₃Cl)₂</th>
<th>Cu(SO₃Cl)₂</th>
<th>Ni(SO₃Cl)₂</th>
<th>Zn(SO₃Cl)₂</th>
<th>Assignments*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1220 vs</td>
<td>1420 s</td>
<td>1220 s</td>
<td>1225 vs</td>
<td></td>
<td>ν₄ (E)</td>
</tr>
<tr>
<td>1070 vs</td>
<td>1060 s</td>
<td>1080 s</td>
<td>1080 vs</td>
<td></td>
<td>ν₁ (A₁)</td>
</tr>
<tr>
<td>575 m</td>
<td>565 m</td>
<td>570 m</td>
<td></td>
<td></td>
<td>ν₅ (E)</td>
</tr>
<tr>
<td>540 m</td>
<td>550 m</td>
<td>540 m</td>
<td>545 m</td>
<td></td>
<td>ν₃ (A₁)</td>
</tr>
<tr>
<td>380 m</td>
<td>395 s</td>
<td>395 m</td>
<td>375 s</td>
<td></td>
<td>ν₂ (A₁)</td>
</tr>
<tr>
<td>350 m</td>
<td>330 s</td>
<td>350 s</td>
<td>345 s</td>
<td></td>
<td>ν₆ (E)</td>
</tr>
</tbody>
</table>

* vs = very strong; s = strong; m = medium; w = weak
zinc(II) chlorosulphates can well be compared with those of their corresponding fluorosulphates (132). The $C_3v$ symmetry in these compounds is maintained not due to ionic chlorosulphate but because all the three oxygen atoms of chlorosulphate are coordinated to metal ion in an equivalent manner thus giving hexacoordination to the metals. In case of copper(II) chlorosulphate, nine fundamental frequencies (Fig. 4.1) with all the doubly degenerate modes ($E$ modes) splitted are observed. This indicates $C_5$ symmetry of the chlorosulphate group. In case of $\text{Cu(SO}_3\text{Cl)}_2$, the symmetry lowering is due to a form of chlorosulphate coordination in which two oxygen atoms of each chlorosulphate group are more strongly bonded to the metal ion than the third as in the case of $\text{Cu(SO}_3\text{F)}_2$ (132). S-Cl stretching frequencies of copper(II), cobalt(II) and nickel(II) chlorosulphates at 395, 380 and 375 cm$^{-1}$ respectively are in agreement with the values reported earlier (108).

4.1.2 Tetrachloro(chlorosulphato)antimony(V) : Likhacheva (203) reported the formation of $\text{SbCl}_4(\text{SO}_3\text{Cl})$ by the reaction of $\text{SoCl}_3$ in $\text{SO}_2\text{Cl}_2$ with 5% solution of $\text{SO}_3$ in $\text{SO}_2\text{Cl}_2$. Lehmann and Riesel (90) carried out the reaction between antimony(V) chloride with sulphur trioxide and chlorosulphuric acid respectively. They reported the Raman spectra of the adduct $\text{SbCl}_5\cdot\text{OSO}_2$. In the present investigations tetrachloro(chlorosulphato)antimony(V) has been obtained by refluxing antimony(V) chloride and chlorosulphuric acid in sulphuryl chloride. It is a white crystalline,
Fig. 4.2 - Infrared spectra of dichlorobis(chlorosulphato)titanium(IV)
very hygroscopic solid soluble in acetone, acetonitrile and nitrobenzene and decomposes ca.260°.

The 3-O stretching and deformation modes of vibrations in SbCl₄(SO₃Cl) (Table 40) compare well with the corresponding modes in SbCl₄(SO₃F), and, therefore, bidentate bridging chlorosulphate group in SbCl₄(SO₃Cl) is envisaged.

The inconsistent molecular weight results of SbCl₄(SO₃Cl) in nitrobenzene rule out the possibility of predicting precisely, whether the molecule is a dimer or a polymer.

4.1.3 Dichlorobis(chlorosulphato)titanium(IV): Dichlorobis(chlorosulphato)titanium(IV) has been prepared by the reaction of titanium(IV) chloride and chlorosulphuric acid (1:2 mol ratio) in sulphuryl chloride (93). The compound formed is yellow hygroscopic solid, insoluble in common organic solvents. It decomposes ca.260°.

The i.r. spectrum of dichlorobis(chlorosulphato)titanium(IV) reported by Frazer et al. (93) showed strong bands at 555-585, 625-665 and 1075-1175 cm⁻¹, but were not properly assigned. The i.r. spectrum of TiCl₂(SO₃Cl)₂ was recorded in the range 2000-200 cm⁻¹. The salient features are given in Table 41.

A well defined i.r. spectrum has been obtained (Fig. 4.2). The comparison of S-O stretching and deformation modes of vibrations of TiCl₂(SO₃Cl)₂ and TiCl₂(SO₃F)₂ suggest that chlorosulphate in TiCl₂(SO₃Cl)₂ behaves as bidentate bridging group. Thus,
<table>
<thead>
<tr>
<th>SbCl$_4$(SO$_3$Cl)</th>
<th>SbCl$_4$(SO$_3$F)</th>
<th>SbF$_4$(SO$_3$F)</th>
<th>Assignments **</th>
</tr>
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<tbody>
<tr>
<td>1380</td>
<td>1365</td>
<td>1400</td>
<td>$\nu_4$(E)</td>
</tr>
<tr>
<td>1230</td>
<td>1160</td>
<td>1216</td>
<td></td>
</tr>
<tr>
<td>1210</td>
<td>1165</td>
<td>1067</td>
<td>$\nu_1$(A$_1$)</td>
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<tr>
<td>570</td>
<td>675</td>
<td>670</td>
<td>$\nu_5$(E)</td>
</tr>
<tr>
<td>515</td>
<td>555</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>550</td>
<td>545</td>
<td>560</td>
<td>$\nu_3$(A$_1$)</td>
</tr>
<tr>
<td>433</td>
<td>865</td>
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<td>$\nu_2$(A$_1$)</td>
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<td></td>
<td>830</td>
<td></td>
<td>$\nu_6$(E)</td>
</tr>
<tr>
<td>- (404)</td>
<td>448</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>- (384)</td>
<td>400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>345 (-)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>320 (-)</td>
<td></td>
<td></td>
<td>$\nu$(Sb-Cl)</td>
</tr>
<tr>
<td>- (172)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- (150)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- (122)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- (72)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The Raman spectrum was taken in the lower region and it is given in parentheses.

** s = strong; m = medium; w = weak
**TABLE 41**

INFRARED DATA OF TiCl$_2$(SO$_3$Cl)$_2$ AND SOME RELATED COMPOUNDS

<table>
<thead>
<tr>
<th>TiCl$_2$(SO$_3$Cl)$_2$</th>
<th>TiCl$_2$(SO$_3$F)$_2$</th>
<th>Assignments$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1340</td>
<td>1340</td>
<td>$\nu_4$(E)</td>
</tr>
<tr>
<td>1240</td>
<td>1195</td>
<td></td>
</tr>
<tr>
<td>1110</td>
<td>1080</td>
<td>$\nu_1$(A$_{1g}$)</td>
</tr>
<tr>
<td>470</td>
<td>850</td>
<td>$\nu_2$(A$_{1g}$)</td>
</tr>
<tr>
<td>665</td>
<td>616</td>
<td>$\nu_5$(E)</td>
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<tr>
<td>600</td>
<td>518</td>
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<td>$\nu_3$(A$_{1g}$)</td>
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<td>445</td>
<td>$\nu_6$(E)</td>
</tr>
<tr>
<td>390</td>
<td>418</td>
<td></td>
</tr>
<tr>
<td>920</td>
<td>720</td>
<td>Other modes</td>
</tr>
<tr>
<td>860</td>
<td>390</td>
<td></td>
</tr>
<tr>
<td>780</td>
<td>363</td>
<td></td>
</tr>
</tbody>
</table>

$^*$ s = strong; m = medium; w = weak
the following structure for $\text{TiCl}_2(\text{SO}_3\text{Cl})_2$ is proposed:

\[
\begin{array}{c}
\text{Cl} \\
\text{Ti} \\
\text{Cl}
\end{array}
\begin{array}{c}
\text{C} \\
\text{S} \\
\text{Cl}
\end{array}
\begin{array}{c}
\text{O} \\
\text{Cl} \\
\text{Ti}
\end{array}
\begin{array}{c}
\text{Cl} \\
\text{C} \\
\text{Cl}
\end{array}
\]

4.2 Infrared Spectra of Coordination Complexes of Metal Chlorosulphates

As the anion of a strong acid, the chlorosulphate ion might be expected to coordinate weakly to metal ions in complex compounds. However, there are no reports about the coordinating properties of this anion.

In the present investigations coordination complexes of $\text{Co(SO}_3\text{Cl})_2$, $\text{Ni(SO}_3\text{Cl})_2$, $\text{Cu(SO}_3\text{Cl})_2$, $\text{Zn(SO}_3\text{Cl})_2$, $\text{TiCl}_2(\text{SO}_3\text{Cl})_2$ and $\text{SbCl}_4(\text{SO}_3\text{Cl})_2$ with pyridine, quinoline, acetonitrile, tetramethylurea, dimethylsulphoxide and acetylacetone have been prepared and characterized.

4.2.1 Pyridine Complexes: The chlorosulphates, $\text{Co(SO}_3\text{Cl})_2$, $\text{Ni(SO}_3\text{Cl})_2$, $\text{Cu(SO}_3\text{Cl})_2$, $\text{Zn(SO}_3\text{Cl})_2$, $\text{TiCl}_2(\text{SO}_3\text{Cl})_2$ and $\text{SbCl}_4(\text{SO}_3\text{Cl})_2$ form complexes with pyridine of the compositions $\text{Co(Py)}_4(\text{SO}_3\text{Cl})_2$, $\text{Ni(Py)}_4(\text{SO}_3\text{Cl})_2$, $\text{Cu(Py)}_4(\text{SO}_3\text{Cl})_2$, $\text{Zn(Py)}_4(\text{SO}_3\text{Cl})_2$, $\text{TiCl}_2(\text{SO}_3\text{Cl})_2\cdot\text{Py}$ and $\text{SbCl}_4(\text{SO}_3\text{Cl})_2\cdot\text{Py}$. All these complexes are hygroscopic solids. The complexes of cobalt(II), nickel(II),
copper(II) and zinc(II) chlorosulphates with pyridine are soluble in acetonitrile and the complex SbCl$_4$(SO$_3$Cl)$_4$·Py is soluble in acetonitrile as well as in nitrobenzene. The complex TiCl$_2$(SO$_3$Cl)$_2$·Py is insoluble in common organic solvents.

4.2.1.1 Pyridine Vibrations: The positions of the principal infrared bands (2000-200 cm$^{-1}$) observed in the spectra of pyridine complexes are given in Table 42. The assignment of the various bands has been made by a comparison between the spectrum of coordinated pyridine and that of the free base.

Qualitatively coordinated pyridine (139) is usually readily distinguished from the free base by the presence of a weak band between 1235 and 1250 cm$^{-1}$, by a shift in the strong 1578 to 1600 cm$^{-1}$ (this band appears with a shoulder in the spectrum of the free base); and by the shifts of the 601 and 403 cm$^{-1}$ bands to 625 and 420 cm$^{-1}$. Between 990 and 1217 cm$^{-1}$ there is a group of five strong bands in the spectrum of pyridine. In the spectra of coordinated pyridine there is the same group of five bands, occasionally with slight splitting and with an extra moderate to weak band between 1235 and 1250 cm$^{-1}$. According to Greenwood and Wade (140) this group of bands is shifted to higher frequencies when pyridine is acting as a ligand.

The spectra of pyridinium salts are very different from those of other pyridine complexes. Although the ion retains the same ($C_2v$) symmetry as pyridine the presence of an extra hydrogen
<table>
<thead>
<tr>
<th>Complex</th>
<th>$v_{1+6b}$ or $v_{8a}$</th>
<th>$v_{19a}$</th>
<th>$v_{19b}$</th>
<th>$v_{13a}$</th>
<th>$v_{15}$</th>
<th>$v_{12}$</th>
<th>$v_{1}$</th>
<th>$v_{6}$</th>
<th>$v_{4}$</th>
<th>$v_{11}$</th>
<th>$v_{6a}$</th>
<th>$v_{16b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1627</td>
<td>1578</td>
<td>1478</td>
<td>1436</td>
<td>-</td>
<td>1217</td>
<td>1145</td>
<td>1031</td>
<td>991</td>
<td>942</td>
<td>747</td>
<td>700</td>
</tr>
<tr>
<td>Co(Py)$_4$(SO$_3$Cl)$_2$</td>
<td>1630</td>
<td>1515</td>
<td>1480</td>
<td>-</td>
<td>1240</td>
<td>1220</td>
<td>1160</td>
<td>1045</td>
<td>1010</td>
<td>970</td>
<td>750</td>
<td>690</td>
</tr>
<tr>
<td>Ni(Py)$_4$(SO$_3$Cl)$_2$</td>
<td>1630</td>
<td>1610</td>
<td>1485</td>
<td>1448</td>
<td>-</td>
<td>1220</td>
<td>1150</td>
<td>1035</td>
<td>1015</td>
<td>970</td>
<td>755</td>
<td>690</td>
</tr>
<tr>
<td>Cu(Py)$_4$(SO$_3$Cl)$_2$</td>
<td>1635</td>
<td>1615</td>
<td>1490</td>
<td>-</td>
<td>1240</td>
<td>1220</td>
<td>-</td>
<td>1047</td>
<td>1020</td>
<td>965</td>
<td>760</td>
<td>690</td>
</tr>
<tr>
<td>Zn(Py)$_4$(SO$_3$Cl)$_2$</td>
<td>1630</td>
<td>1605</td>
<td>1490</td>
<td>1450</td>
<td>-</td>
<td>1220</td>
<td>1160</td>
<td>1045</td>
<td>1019</td>
<td>970</td>
<td>760</td>
<td>690</td>
</tr>
<tr>
<td>TiCl$_2$(SO$_3$Cl)$_2$·Py</td>
<td>1630</td>
<td>1615</td>
<td>1480</td>
<td>1465</td>
<td>1240</td>
<td>1225</td>
<td>1155</td>
<td>1040</td>
<td>1010</td>
<td>-</td>
<td>755</td>
<td>690</td>
</tr>
<tr>
<td>SbCl$_4$(SO$_3$Cl)·Py</td>
<td>1635</td>
<td>1600</td>
<td>1485</td>
<td>-</td>
<td>1235</td>
<td>-</td>
<td>-</td>
<td>1040</td>
<td>1010</td>
<td>-</td>
<td>760</td>
<td>680</td>
</tr>
</tbody>
</table>
atom on the nitrogen increases the number of vibrational modes. Pyridinium salts have symmetrical N-H stretching frequencies near 3200 cm$^{-1}$ in non-hydrogen bonded salts and near 2300 cm$^{-1}$ in the hydrogen bonded salts. Below 2000 cm$^{-1}$ the major differences between the spectra of pyridinium and pyridine derivatives are as follows: The bands at 1640, 1327, 1295 and 1250 cm$^{-1}$ in the spectrum of pyridinium salts do not appear in the spectra of pyridine complexes. The band at 1490 cm$^{-1}$ in the spectra of pyridinium salts is much stronger than the 1430 cm$^{-1}$ band in the spectra of pyridinium salts are more complicated than those of pyridine complexes.

A study of Table 42 reveals that the peak at 1240 cm$^{-1}$ appears in almost all the pyridine complexes and $\nu_{6a}, \nu_{6a}$ and $\nu_{16b}$ are found at 1500-1615, 625-650 and 420-435 cm$^{-1}$ which indicate that the nitrogen of pyridine is coordinated to the metal atom. In the above coordination complexes five strong bands between 990 and 1217 cm$^{-1}$ are reproduced with slight increase in frequency as compared to pure pyridine. The band $\nu_{1+6b}$ or $\nu_{6a+12}$ which is found at 1627 cm$^{-1}$ in pure pyridine is observed in the above coordination complexes in the range 1630-1635 cm$^{-1}$. The absence of $\nu_{N-H}$ around 3200 and 2300 cm$^{-1}$ and 1640, 1327, 1295 cm$^{-1}$ frequencies rule out the formation of pyridinium salts.

4.2.1.2 Chlorosulphate Vibrations: Complexes of cobalt(II), nickel(II) and copper(II) chlorosulphates with pyridine are
octahedral as has been established by their electronic spectra (page 151, 157, 152). This indirectly shows that the chlorosulphate groups are monodentate. The S-O stretching and deformation modes (Table 43) in these complexes and also in zinc(II) chlorosulphate complex compare well with the corresponding fluorosulphate complexes (122), where fluorosulphate groups act as monodentate ligands. The reduced symmetry (C₅) of chlorosulphate groups in these complexes is obvious from the splitting of the E modes. The magnitude of ν₄(E) splitting is of the order of ca.110-140 cm⁻¹ which suggests weak interaction between the metal and the chlorosulphate group. Similar observations have been made in the fluorosulphate complexes (122).

Chlorosulphate groups in SbCl₄(SO₃Cl) and TiCl₂(SO₃Cl)₂ (Table 40 and 41) behave as a bidentate bridging group. However, chlorosulphate vibrations undergo enormous changes (Table 43) when it is coordinated with pyridine. The positions of ν₄(E) and ν₁(A₁) suggest the monodentate nature of the chlorosulphate groups having reduced symmetry (C₅) giving hexacoordination to the metals. The magnitude of ν₄(E) splitting in both these complexes is of the order of 100 cm⁻¹ which again shows a weak interaction between metal and the chlorosulphate group.

4.2.2 Quinoline Complex: Dichlorobis(chlorosulphato)titanium(IV) forms complex with quinoline of the composition TiCl₂(SO₃Cl)₂·Q. It is a yellow coloured hygroscopic solid, decomposes ca. 260° and is insoluble in common organic solvents.
### TABLE 43

CHLOROSULPHATE GROUP VIBRATIONS IN $\text{Co(Py)}_4(\text{SO}_3\text{Cl})_2$, $\text{Ni(Py)}_4(\text{SO}_3\text{Cl})_2$, $\text{Cu(Py)}_4(\text{SO}_3\text{Cl})_2$, $\text{Zn(Py)}_4(\text{SO}_3\text{Cl})_2$, $\text{TiCl}_2(\text{SO}_3\text{Cl})_2\cdot\text{Py}$ and $\text{SbCl}_4(\text{SO}_3\text{Cl})_2\cdot\text{Py}$

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_4 (E)$</th>
<th>$\nu_1 (A_1)$</th>
<th>$\nu_5 (E)$</th>
<th>$\nu_3 (A_1)$</th>
<th>$\nu_2 (A_1)$</th>
<th>$\nu_6 (E)$</th>
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</thead>
<tbody>
<tr>
<td>$\text{Co(Py)}_4(\text{SO}_3\text{Cl})_2$</td>
<td>1300vs</td>
<td>1085</td>
<td>600</td>
<td>-</td>
<td>400</td>
<td>370</td>
</tr>
<tr>
<td></td>
<td>1190w</td>
<td></td>
<td>565</td>
<td></td>
<td></td>
<td>320</td>
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<tr>
<td>$\text{Ni(Py)}_4(\text{SO}_3\text{Cl})_2$</td>
<td>1300s</td>
<td>1095</td>
<td>595</td>
<td>555</td>
<td>405</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td>1190s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>270</td>
</tr>
<tr>
<td>$\text{Cu(Py)}_4(\text{SO}_3\text{Cl})_2$</td>
<td>1300s</td>
<td>1100s</td>
<td>600s</td>
<td>543</td>
<td>390</td>
<td>365</td>
</tr>
<tr>
<td></td>
<td>1180s</td>
<td></td>
<td>560s</td>
<td></td>
<td></td>
<td>290</td>
</tr>
<tr>
<td>$\text{Zn(Py)}_4(\text{SO}_3\text{Cl})_2$</td>
<td>1300s</td>
<td>1100s</td>
<td>590s</td>
<td>545</td>
<td>400</td>
<td>325w</td>
</tr>
<tr>
<td></td>
<td>1190s</td>
<td></td>
<td>560s</td>
<td></td>
<td></td>
<td>290w</td>
</tr>
<tr>
<td>$\text{TiCl}_2(\text{SO}_3\text{Cl})_2\cdot\text{Py}$</td>
<td>1368m</td>
<td>1080m</td>
<td>670</td>
<td>555</td>
<td>470</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1270s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>340</td>
</tr>
<tr>
<td>$\text{SbCl}_4(\text{SO}_3\text{Cl})_2\cdot\text{Py}$</td>
<td>1400</td>
<td>1050</td>
<td>650</td>
<td>550</td>
<td>415</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td></td>
<td>570</td>
<td></td>
<td></td>
<td>340</td>
</tr>
</tbody>
</table>

* $s =$ strong;  $m =$ medium;  $w =$ weak
4.2.2.1 Quinoline Vibrations: Some bands in the spectrum of quinoline are associated with the carboxylic ring while the others are associated with heterocyclic ring. The effect of coordination is not probably transmitted to the carboxylic ring and consequently there is very little or no change in the spectrum of the bands arising out of carboxylic rings.

The spectral data reveal (Table 20) that on coordination, the bands at 1408 and 1339 cm$^{-1}$ associated with carboxylic ring do not show any significant change. The band at 1449 cm$^{-1}$ associated with the heterocyclic ring of quinoline exhibits a shift to a higher frequency of the order of ca. 60 cm$^{-1}$. The other modes of vibrations associated with the heterocyclic ring such as $\nu_{ab}$, $\nu_{19a}$ and $\nu_{12}$ also show an upward trend in TiCl$_2$(SO$_3$Cl)$_2$·Q. These observations indicate that the nitrogen of quinoline is coordinated to titanium. The C-H vibrations ($\nu_{9b}$ and $\nu_{15}$) on coordination move to higher frequencies but the magnitude of the shifts is small as compared to that in the ring vibrations. A smaller shift indicates that only little effect of coordination which is responsible for larger shifts in the ring frequencies involving C-C and C-N is transmitted to C-H bands. All the out-of-plane C-H vibrations ($\nu_5$, $\nu_{10}$, $\nu_{11}$) show an upward trend in TiCl$_2$(SO$_3$Cl)$_2$·Q (Table 20).

4.2.2.2 Chlorosulphate Vibrations: Various bands of the i.r. spectrum of chlorosulphate group in TiCl$_2$(SO$_3$Cl)$_2$·Q are given in Table 21. The chlorosulphate group vibrations indicate the
Fig. 4-3: Infrared spectra of tetrakis(acetonitrile)bis(chlorosulphato)cobalt(II) and tetrakis(acetonitrile)bis(chlorosulphato) zinc(II).

A - Cu(CH₃CN)₄(SO₂Cl)₂
B - Zn(CH₃CN)₄(SO₂Cl)₂
reduced symmetry \((C_s)\) of the chlorosulphate group. The \(v_4(E)\) splitting in \(\text{TiCl}_2(\text{SO}_3\text{Cl})_2\) is of the order ca.175 cm\(^{-1}\) indicating rather strong interaction between metal and the anion.

4.2.3 Acetonitrile Complexes: Cobalt(II), nickel(II), copper(II), and zinc(II) and tetrachloro(chlorosulphato)antimony(V) form complexes with acetonitrile of the compositions \(\text{Co(CH}_3\text{CN})_4(\text{SO}_3\text{Cl})_2\), \(\text{Ni(CH}_3\text{CN})_4(\text{SO}_3\text{Cl})_2\), \(\text{Cu(CH}_3\text{CN})_4(\text{SO}_3\text{Cl})_2\), \(\text{Zn(CH}_3\text{CN})_4(\text{SO}_3\text{Cl})_2\) and \(\text{SbCl}_4(\text{SO}_3\text{Cl})\cdot\text{CH}_3\text{CN}\). All these complexes are hygroscopic solids.

The complexes of cobalt(II), nickel(II), copper(II) and zinc(II) chlorosulphates are soluble in acetonitrile and complex of \(\text{SbCl}_4(\text{SO}_3\text{Cl})\) is soluble in acetonitrile as well as in nitrobenzene.

4.2.3.1 Acetonitrile Vibrations: The positions of the principal infrared bands observed in the spectra (4000-200 cm\(^{-1}\)) of acetonitrile complexes are given in Table 44 and 25 (Fig. 4.3). The assignments of the various bands have been made by a comparison between the spectrum of coordinated acetonitrile and that of the free base.

The Lewis base character of acetonitrile can arise either by donation of the \(\pi\)-electron from the C-N triple bond or from the lone pair localized on the nitrogen atom. In case of metal halide complexes with acetonitrile the bonding is of the latter type (146). Niobium and tantalum(V) chlorides and bromides and antimony(V) chloride form 1:1 adduct with acetonitrile (147,148). The \(\nu_{C-N}\) in all these complexes show an increase. This increase in frequency upon coordination is explained on the kinematic
<table>
<thead>
<tr>
<th></th>
<th>(\text{Co(} \text{CH}_3\text{CN)}_4 \text{(SO}_3\text{Cl)}_2)</th>
<th>(\text{Ni(} \text{CH}_3\text{CN)}_4 \text{(SO}_3\text{Cl)}_2)</th>
<th>(\text{Cu(} \text{CH}_3\text{CN)}_4 \text{(SO}_3\text{Cl)}_2)</th>
<th>(\text{Zn(} \text{CH}_3\text{CN)}_4 \text{(SO}_3\text{Cl)}_2)</th>
<th>\text{CH}_3\text{CN}</th>
<th>\text{Assignments}^*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(299\text{cm})</td>
<td>(299\text{cm})</td>
<td>(298\text{cm})</td>
<td>(298\text{w})</td>
<td>(300\text{cm})</td>
<td>(300\text{cm})</td>
<td>(\nu_5(\text{e})\text{CH}_3\text{asy.st.})</td>
</tr>
<tr>
<td>(294\text{cm})</td>
<td>(292\text{cm})</td>
<td>(293\text{cm})</td>
<td>(294\text{cs})</td>
<td>(294\text{vs})</td>
<td>(294\text{cs})</td>
<td>(\nu_1(\text{a}_1)\text{CH}_3\text{asy.st.})</td>
</tr>
<tr>
<td>(2315\text{vs})</td>
<td>(232\text{vs})</td>
<td>(232\text{vs})</td>
<td>(232\text{vs})</td>
<td>(2289)</td>
<td>(229\text{vs})</td>
<td>(\nu_4(\text{A}_1))</td>
</tr>
<tr>
<td>(2298\text{vs})</td>
<td>(230\text{vs})</td>
<td>(230\text{vs})</td>
<td>(229\text{vs})</td>
<td>(2289)</td>
<td>(229\text{vs})</td>
<td>(\nu_2(\text{a}_1)\text{CN st.})</td>
</tr>
<tr>
<td>(140\text{cm})</td>
<td>(140\text{vs})</td>
<td>(-)</td>
<td>(-)</td>
<td>(140\text{cm})</td>
<td>(140\text{cm})</td>
<td>(\nu_6(\text{e})\text{CH}_3\text{asy.def})</td>
</tr>
<tr>
<td>(137\text{cs})</td>
<td>(137\text{vs})</td>
<td>(137\text{cs})</td>
<td>(-)</td>
<td>(144\text{vs})</td>
<td>(144\text{vs})</td>
<td>(\nu_3(\text{a}_1)\text{CH}_3\text{sy.def})</td>
</tr>
<tr>
<td>(1040\text{vs})</td>
<td>(104\text{vs})</td>
<td>(104\text{vs})</td>
<td>(105\text{vs})</td>
<td>(1047\text{vs})</td>
<td>(1047\text{vs})</td>
<td>(\nu_7(\text{e})\text{CH}_3\text{Rock.})</td>
</tr>
<tr>
<td>(94\text{cs})</td>
<td>(94\text{vs})</td>
<td>(94\text{vs})</td>
<td>(94\text{vs})</td>
<td>(918\text{vs})</td>
<td>(918\text{vs})</td>
<td>(\nu_4(\text{a}_1)\text{CC st.})</td>
</tr>
<tr>
<td>(890\text{w})</td>
<td>(88\text{os})</td>
<td>(88\text{os})</td>
<td>(84\text{os})</td>
<td>(750)</td>
<td>(750\text{w})</td>
<td>(2 \times \nu_8(\text{A}_1))</td>
</tr>
<tr>
<td>(-)</td>
<td>(42\text{os})</td>
<td>(42\text{os})</td>
<td>(42\text{os})</td>
<td>(375)</td>
<td>(375\text{vs})</td>
<td>(\nu_8(\text{e})\text{CCN def.})</td>
</tr>
</tbody>
</table>

* \(\text{v.s.} = \text{very strong}; \ s = \text{strong}; \ m = \text{medium}; \ w = \text{weak}\)
coupling and ionic contribution to the C-N bond (146). So, the increase in i.r. active C-N stretching frequency is diagnostic of complex formation via the lone pair on the nitrogen atom. As seen in Tables 25 and 44, the C-N stretching frequency which in acetonitrile appear at 2251 cm\(^{-1}\) shifts to ca. 2300 cm\(^{-1}\) in these complexes. This increase shows that nitrogen of the acetonitrile is coordinated to the metal atom.

4.2.3.2 Chlorosulphate Vibrations: The chlorosulphate vibrations in cobalt(II), nickel(II), copper(II), zinc(II) chlorosulphate and tetrachloro(chlorosulphato)antimony(V) complexes with acetonitrile are tabulated in Table 45 (Fig. 4.3). The octahedral nature of these complexes has been established from their electronic spectra (pages 57, 97, 112). This indirectly shows that the chlorosulphate groups behave as monodentate ligands in these complexes. The S-O stretching and deformation modes (Table 45) in these complexes and zinc(II) chlorosulphate complex compare well with the corresponding modes in fluorosulphate complexes (121), in which fluorosulphate group acts as a monodentate ligand. The reduced symmetry (C\(_5\)) of chlorosulphate groups in these complexes is obvious from the splitting of the \(E\) modes. The magnitude of \(\nu_4(E)\) splitting in cobalt(II) and nickel(II) complexes is of the order of ca. 100 cm\(^{-1}\) and copper(II) and zinc(II) complexes it is of the order of 40-60 cm\(^{-1}\). The magnitude of the splitting of \(\nu_4(E)\) modes suggest the weak interaction between the metal and the chlorosulphate group.
TABLE 45

CHLOROSULPHATE GROUP VIBRATIONS IN ACETONITRILE COMPLEXES OF Co(SO$_3$Cl)$_2$, Ni(SO$_3$Cl)$_2$,
Cu(SO$_3$Cl)$_2$, Zn(SO$_3$Cl)$_2$, and SbCl$_4$(SO$_3$Cl)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_4$(E)</th>
<th>$\nu_1$(A$_1$)</th>
<th>$\nu_5$(E)</th>
<th>$\nu_3$(A$_1$)</th>
<th>$\nu_2$(A$_1$)</th>
<th>$\nu_6$(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(CH$_3$CN)$_4$(SO$_3$Cl)$_2$</td>
<td>1310s</td>
<td>1050b</td>
<td>595s</td>
<td>535m</td>
<td>400s</td>
<td>375s</td>
</tr>
<tr>
<td></td>
<td>1220s</td>
<td></td>
<td>555s</td>
<td></td>
<td></td>
<td>290m</td>
</tr>
<tr>
<td>Ni(CH$_3$CN)$_4$(SO$_3$Cl)$_2$</td>
<td>1290</td>
<td>-</td>
<td>580m</td>
<td>540sh</td>
<td>408</td>
<td>340</td>
</tr>
<tr>
<td></td>
<td>1155</td>
<td></td>
<td>555m</td>
<td></td>
<td></td>
<td>270</td>
</tr>
<tr>
<td>Cu(CH$_3$CN)$_4$(SO$_3$Cl)$_2$</td>
<td>1270</td>
<td>1100w</td>
<td>575m</td>
<td>540m</td>
<td>390m</td>
<td>370s</td>
</tr>
<tr>
<td></td>
<td>1230</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>345w</td>
</tr>
<tr>
<td>Zn(CH$_3$CN)$_4$(SO$_3$Cl)$_2$</td>
<td>1300m</td>
<td>1100s</td>
<td>580m</td>
<td>535m</td>
<td>395m</td>
<td>345s</td>
</tr>
<tr>
<td></td>
<td>1240m</td>
<td></td>
<td>545m</td>
<td></td>
<td></td>
<td>310s</td>
</tr>
<tr>
<td>SbCl$_4$(SO$_3$Cl)$\cdot$CH$_3$CN</td>
<td>1410m</td>
<td>1063</td>
<td>650</td>
<td>555</td>
<td>410</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1300m</td>
<td></td>
<td>590</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* s = strong;  m = medium;  b = broad;  sh = shoulder
However, it is apparent that in case of cobalt(II) and nickel(II), the interaction is stronger as compared to that in copper(II) and zinc(II) complexes.

The i.r. spectrum of SbCl₄(SO₃Cl).CH₃CN (Table 45) indicates one kind of chlorosulphate group of reduced symmetry (C₃). The S-O stretching as well as deformation modes indicate the monodentate nature of the chlorosulphate group, leading to hexacoordination of antimony. The magnitude of \( V_4(x) \) splitting of the order of ca.100 cm\(^{-1}\) again suggests a weaker interaction between antimony and the chlorosulphate group.

4.2.4 Tetramethylurea Complex: Tetrachloro(chlorosulphato)antimony(V) forms coordination complex with tetramethylurea of the composition SbCl₄(SO₃Cl).TMU. It is a white crystalline hygroscopic solid, soluble in acetonitrile, acetone, nitromethane, nitrobenzene and tetramethylurea. It decomposes ca.235°.

4.2.4.1 Tetramethylurea Vibrations: A comparison of the i.r. spectrum of the complex SbCl₄(SO₃Cl).TMU with that of pure tetramethylurea exhibits an apparent change in the bands assigned to \( \nu_{C=O} \), \( \nu_{C-N} \) and \( \delta_{N-C=O} \) vibrations of the pure ligand as is obvious from the perusal of Table 27. The \( \nu_{C=O} \) in SbCl₄(SO₃Cl).TMU shifts to higher region by 115 cm\(^{-1}\) and \( \nu_{C-N} \) to a lower region by 100 cm\(^{-1}\). The trend in these shifts may be correlated to the coordination of this ligand through one of its nitrogen atoms rather than through oxygen atom. The formation of the nitrogen
antimony bond increases the electron demand by donor nitrogen atom and blocks the resonance between this nitrogen atom and the carbonyl group. This brings about increased \( \text{C}=\text{O} \) bond character and hence the increase in carbonyl frequency. As a result of the formation of \( \text{N}-\text{Sb} \) bond, this nitrogen to carbon bond increases in length. This greater \( \text{C}-\text{N} \) single bond length shifts \( \nu_{\text{C}=\text{N}} \) to lower frequency. Similar observations have been made by Mizushima et al. (151) when nitrogen of urea acts as a donor atom.

4.2.4.2 Chlorosulphate Vibrations: The i.r. spectrum of \( \text{SbCl}_4(\text{SO}_3\text{Cl})\cdot\text{TMU} \) (Table 26) indicates only one kind of chlorosulphate group of reduced symmetry (\( C_\text{S} \)). The S-O stretching as well as deformation modes indicate that chlorosulphate group acts as a monodentate ligand resulting in hexacoordination of antimony. The magnitude of \( \nu_4(E) \) splitting, of the order of ca.100 cm\(^{-1}\), shows rather weaker interaction between antimony and the chlorosulphate group.

4.2.5 Dimethylsulphoxide Complex: Dichlorobis(chlorosulphato)tinanium(IV) form complex with dimethylsulphoxide of the composition, \( \text{TiCl}_2(\text{SO}_3\text{Cl})_2\cdot\text{DMSC} \). It is yellow hygroscopic solid and decomposes ca.260\(^\circ\).

4.2.5.1 Dimethylsulphoxide Vibrations: The positions of the principal infrared bands observed in the spectra of the complex are given in Table 30. The assignment of the various bands
has been made by a comparison between the spectrum of coordinated dimethylsulphoxide and that of the free base.

Coordination of dimethylsulphoxide has been shown to take place either through oxygen atom or through sulphur atom and the distinction has been made from the trend in the changes in the $\nu_{S=O}$ and $\nu_{C-S}$ stretching frequencies of dimethylsulphoxide on complex formation. Major frequencies corresponding to $\nu_{S=O}$ and $\nu_{C-S}$ have been considered here. In this complex the $\nu_{S=O}$ shifts to lower and $\nu_{C-S}$ to higher frequency region (Table 30). These vibrations in the pure ligand appear at 1050 and 690 cm$^{-1}$ respectively (153). The $\nu_{S=O}$ shifts by 70 cm$^{-1}$ to lower region whereas $\nu_{C-S}$ shifts only 30 cm$^{-1}$ to higher region, indicating coordination through oxygen of $S=O$ group. This indicates the weaker Lewis acid character of the chlorosulphate (154,155).

The direction of shift in this complex, however, justifies the coordination of dimethylsulphoxide through its oxygen atom because coordination through sulphur would increase the $\nu_{S=O}$ as is known in its complexes with platinum(II) and palladium(II) halides (156).

4.2.5.2 Chlorosulphate Vibrations: The S-O stretching and deformation modes (Table 31) indicate the monodentate nature of the chlorosulphate group in the complex, TiCl$_2$(SC$_3$Cl)$_2$·DMSC, whereas the chlorosulphate group in TiCl$_2$(SC$_3$Cl)$_2$ acts as a bicentate bridging ligand.
4.2.6 Acetylacetone Complex: The reaction between dichloro-
bis(chlorosulphato)titanium(IV) and acetylacetone was carried out,
hydrochloric acid gas evolved even at room temperature. A red
orange compound of the formula, Ti(acac)$_2$(SO$_3$Cl)$_2$ was obtained.
It is insoluble in common organic solvents and decomposes ca. 260°.

4.2.6.1 Acetylacetone Vibrations: Acetylacetone can form
chelates with metals in many different ways which have already
been discussed in section 3.2.10.1.

Vibrations due to acetylacetone in Ti(acac)$_2$(SO$_3$Cl)$_2$ are
given in Table 34. With the exception of CH stretching bands
near 2900 cm$^{-1}$, no bands of interest were found in the region
above 1600 cm$^{-1}$. No bands were observed in the 1750-1600 cm$^{-1}$
region either, where ketonic carbonyl modes as well as absorption
due to $\gamma$-carbon bonded ligands would be found. These complexes
have two absorption bands in the region 1600-1500 cm$^{-1}$, which
are assigned mainly due to C=C and C=O stretching modes.

The bands around 1020 and 930 cm$^{-1}$ are assigned to CH$_3$
rocking and skeletal vibrational modes in this compound. The
band at 775 cm$^{-1}$ is assigned to CH bending mode. The band around
670 cm$^{-1}$ may be due to a combination of M-O stretching and
ring deformation modes.

The bands in the region 470 and 290 cm$^{-1}$ are assigned to
metal-oxygen stretching modes (152).

4.2.6.2 Chlorosulphate Vibrations: The i.r. spectrum of
chlorosulphate groups in Ti(acac)$_2$(SO$_3$Cl)$_2$ (Table 35) indicates
only one type of chlorosulphate of reduced symmetry ($C_s$). The
$\nu_4(E), \nu_1(A_1), \nu_5(E), \nu_3(A_1)$ and $\nu_6(E)$ vibrations compare well
with the corresponding fluorosulphate, Ti(acac)$_2$(SO$_3^-$)$_2$,
indicating the monodentate nature of the chlorosulphate group.
The following structure may be assigned to this compound,
assuming monodentate nature of the chlorosulphate groups.

\[
\begin{array}{c}
\text{H}_3\text{C} & \text{C} & \text{O} & \text{SO}_3\text{Cl} \\
\text{H}_3\text{C} & \text{C} & \text{O} & \text{SO}_3\text{Cl}
\end{array}
\]

4.3 Electronic Spectra and Magnetic Properties of Metal
Chlorosulphates and their Coordination Complexes with
Nitrogen Donors

4.3.1 Cobalt(II) Chlorosulphate and its Coordination Complexes:
Cobalt(II), a $d^7$ ion forms tetrahedral and octahedral complexes.
In fact cobalt(II) predominantly forms tetrahedral complexes.
This is because the ligand field stabilization energies favour
the tetrahedral configuration. These two stereochemistries,
namely, tetrahedral and octahedral can be readily distinguished
by a variety of criteria.

(i) Colour: The tetrahedral complexes are usually deep blue to
green in colour while octahedral complexes are pink or reddish
brown. However, there are some exceptions to this general
behaviour, e.g., CoSiO$_4$ is purple and octahedral (204), while
cobalt dipivaloylmethanide is pink and tetrahedral (205).
(ii) Magnetic Properties: The magnetic demeanour is greatly influenced by environmental vagaries as discussed below:

For tetrahedral cobalt(II) the ground term $^4A_2$ is not orbitally degenerate and hence gets no orbital contribution to the magnetic moment value. However, the effective magnetic moment value increases over the spin only value due to the mixing of $^4T_1$ and $^4T_2$ terms with the ground term $^4A_2$ under the action of spin orbit coupling. Substituting the free cobalt(II) ion spin orbit coupling constant ($\lambda$) value of $-178$ cm$^{-1}$ and the lowest $10Dq$ value of $3000$ cm$^{-1}$ of cobalt(II) complexes in the formula:

$$\mu_{\text{eff}} = 2 \left( 1 - 4 \lambda / 10Dq \right) \left[ S(S+1) \right]^{1/2}$$

the magnetic moment value of $4.8$ BM is obtained (176). Thus the theoretical value of magnetic moment for cobalt(II) in tetrahedral environment should be within the limits of $3.9$-$4.8$ BM. However, the experimental results for tetrahedral cobalt(II) complexes show that this value lies in the range $4.1$ - $4.9$ BM at room temperature (206).

In octahedral field, the ground term $^4T_1$ is orbitally degenerate and causes an orbital angular momentum contribution to the magnetic moment which varies with temperature. The magnetic moment is expected to lie within the limits of $3.88$ BM (the spin only value) and $5.2$ BM when full orbital contribution
is considered in the formula:

$$\mu_{\text{eff}} = \left[4S(S+1) + L(L+1)\right]^{1/2}$$

The actual value of the magnetic moment, however, depends upon the amount of $L$, the orbital angular momentum, remaining associated with the ground state orbital triplet. The experimental magnetic moments mostly lie between 4.7 and 5.2 BM at room temperature (182).

(iii) Electronic Spectra: Cobalt(II) being a $d^7$ system, can be treated as a $d^3$ system possessing three positive holes. The various terms spanned by a $d^7$ configuration are: $^4F$, $^4P$, $^2G$, $^2H$, $^2F$, $^2D_a$ and $^2D_g$. A 'β' value of 0.971 kK for the free ion separates the $^2D_a$ term from the $^4F$ term by ca. 54.02 kK (205). All the other terms lie within this energy span. $^4F$ and $^4P$ are the only terms which concern the electronic spectra of a $d^7$ system in a weak or a medium field. Application of a cubic ligand field removes the orbital degeneracy of a number of terms. The $^4F$ term of the free ion originates two terms of triple orbital degeneracy $^4T_{1g}(F)$ and $^4T_{2g}(F)$ and a single orbitally degenerate $^4A_{2g}(F)$ term. The quartet $P$, as usual, gives rise only to a $^4T_{1g}$ term.

In the case of cobalt(II) or in general for any $d^7$ system the ground term is $^4T_{1g}(F)$ or $^2F_g(G)$ depending on the intensity of the ligand field. For ligands such as cyanide ions, which have $\Delta_{\text{oct}}$ ca. 15 kK for cobalt(II) ion, $^4T_{1g}$ does not remain
the ground term. Instead $E_g(G)(t_{2g}^6 e_g^1)$ has the lowest energy. Therefore, the ligand field spectra of six coordinated cobalt(II) complexes vary according to the field strength as to whether it is medium or strong. Usually, an extremely intense field of the order of 15.0 kK ($\Delta_{\text{oct.}}$) is found for anionic nitrogen donors. An oxygen or a neutral nitrogen base creates fields strong enough to give rise to a quartet ground term only.

The electronic spectra of cobalt(II) in a medium of moderately strong field can best be explained in terms of three spin-quartet transitions:

$$
\begin{align*}
4_{T_{2g}}(F) & \leftrightarrow 4_{T_{1g}}(F) \quad \ldots \quad \nu_1 \\
4_{A_{2g}}(F) & \leftrightarrow 4_{T_{1g}}(F) \quad \ldots \quad \nu_2 \\
4_{T_{1g}}(F) & \leftrightarrow 4_{T_{1g}}(F) \quad \ldots \quad \nu_3
\end{align*}
$$

The absorption of radiation corresponding to $\nu_2$ is not allowed by an electronic selection rule because it corresponds to the transition $t_{2g}^3 e_g^4 \leftrightarrow t_{2g}^5 e_g^2$, which involves simultaneous excitation of two electrons. Since the thermal agitation of a molecule occasionally destroys the $C_3v$ symmetry, so an absorption due to $\nu_2$ has been observed in some cases (176). $\nu_1$ and $\nu_3$ have been found to be present usually in the region 5.5 to 21.0 kK in the octahedral derivatives. For example cobalt(II) chloride and bromide (both of which contain octahedral cobalt(II) show absorption bands due to the transitions $\nu_1, \nu_2$ and
The differentiation of a tetrahedral cobalt(II) from an octahedral one is slightly complicated. A tetrahedral cobalt(II) derivative has two absorption bands due to the $^{4}T_{1}(F) \leftrightarrow ^{4}A_{2}(F)$ and $^{4}T_{1}(F) \leftrightarrow ^{4}A_{2}(F)$ transitions. The band due to $\nu_1(t_d)$ occurs in the overtone region of infrared and other two bands $\nu_2$ and $\nu_3$ (for tetrahedral cobalt(II)) appear in 5.5 to 18.3 kK region (132,195,206-209).

Cobalt(II) chlorosulphate is a pink deliquescent solid soluble in acetonitrile giving pink solution. But it does not dissolve in inert organic solvents. Tetrakis(pyridine)bis(chlorosulphato)cobalt(II), Co(Py)$_4$(SO$_3$Cl)$_2$ and tetrakis(acetonitrile)bis(chlorosulphato)cobalt(II), Co(CH$_3$CN)$_4$(SO$_3$Cl)$_2$ are pink crystalline solids and are very hygroscopic. Both the complexes are soluble in acetonitrile.

The electronic spectra of cobalt(II) chlorosulphate and its coordination complexes with pyridine and acetonitrile tabulated in Table 46 were taken from 5-50 kK. The bands at 6.25 ($\nu_1$), 13.5 ($\nu_2$) and 18.2 ($\nu_3$) kK in case of cobalt(II) chlorosulphate (Fig. 4.4) indicate the octahedral arrangement of oxygen atoms around cobalt(II) and these results agree with those obtained by Edwards et al. (108) and to a great extent resemble with cobalt(II) fluorosulphate (69).

The maxima at 6.66, 12.5 and 13.86 kK in case of Co(Py)$_4$(SO$_3$Cl) (Fig. 4.4) have been assigned as $\nu_1$, $\nu_2$ and $\nu_3$. 

$\nu_3$ at 6.6, 13.3, 17.1; 5.3, 13.8 and 16.0 kK respectively.
### Table 46

**Absorption Spectra (KK, and Magnetic Moments of Cobalt(II) Chlorocarbonate and Its Coordination Complexes with Pyridine and Acetonitrile**

<table>
<thead>
<tr>
<th>Complex</th>
<th>$4T_{2g}(f)\leftrightarrow 4T_{1g}(f)$ ($\nu_1$)</th>
<th>$4A_{2g}(f)\leftrightarrow 4T_{1g}(f)$ ($\nu_2$)</th>
<th>$4T_{1g}(p)\leftrightarrow 4T_{1g}(f)$ ($\nu_3$)</th>
<th>Others</th>
<th>$\mu_{\text{eff.}}^{(BM)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co($\text{SO}_3\text{Cl})_2$</td>
<td>6.25</td>
<td>13.5</td>
<td>18.2</td>
<td>20.2sh</td>
<td>4.9</td>
</tr>
<tr>
<td>Co($\text{Py})_4(\text{SO}_3\text{Cl})_2$</td>
<td>6.66</td>
<td>12.5</td>
<td>18.86</td>
<td>26.32</td>
<td>4.9</td>
</tr>
<tr>
<td>Co($\text{CH}_3\text{CN})_4(\text{SO}_3\text{Cl})_2$</td>
<td>6.66</td>
<td>-</td>
<td>20.0</td>
<td>-</td>
<td>4.8</td>
</tr>
</tbody>
</table>
Fig. 4.4 - Reflectance spectra of cobalt(II) chlorosulphate and its coordination complexes

A - Co(SO$_3$Cl)$_2$

B - Co(PY)$_4$(SO$_2$Cl)$_2$

C - Co(CH$_3$CN)$_4$(SO$_3$Cl)$_2$
respectively. In case of Co(CH$_3$CN)$_4$(SO$_3$Cl)$_2$ only $\gamma_1$ and $\gamma_3$ have been observed at 6.66 and 20.0 kK respectively (Fig. 4.4). The magnetic moments (Table 46) of Co(Py)$_4$(SO$_3$Cl)$_2$ and Co(CH$_3$CN)$_4$(SO$_3$Cl)$_2$ are 4.9 and 4.8 BM respectively at room temperature. Thus, the colours, magnetic moments and the electronic spectra suggest that cobalt(II) chlorosulphate and its coordination complexes with pyridine and acetonitrile are octahedral.

4.3.2 Nickel(II) Chlorosulphate and its Coordination Complexes with Pyridine and Acetonitrile: The coordination complexes of pyridine and related ligands with nickel(II) are among the most extensively studied (179, 210-220). Four different types of complexes have been isolated, namely, NiLX$_2$, NiL$_2$X$_2$, NiL$_4$X$_2$ and NiL$_6$X$_2$• Only one complex of NiLX$_2$ type where X = Cl and L = pyridine is known and has been assigned a distorted octahedral structure (210).

Numerous complexes of the second type NiL$_2$X$_2$, where X = Cl, Br, I or NCS and L = pyridine, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine or quinoline are known (178, 211-219). The chloro and bromo complexes of pyridine, 3-methylpyridine, 4-methylpyridine have polymeric octahedral structures while iodo complexes and 2-methylpyridine complexes have tetrahedral structures (178, 211-219).

Nickel(II) complexes of the type NiL$_4$X$_2$ where X = Cl, Br, I, NO$_2$, NCS, ClO$_4$ or BF$_4$ and L = pyridine, 3-methylpyridine,
4-methylpyridine and isoquinoline have also been prepared
(220,221). X-ray analysis (222) has revealed that these complexes
have six coordinate structures in which coordinating anions
occupy trans-position.

Sinha and Ray (223) have reported the isolation of
\[ \text{Ni(Py)}_6(\text{ClO}_4)_2 \]. It has been shown that in the case of substi-
tuted pyridines, in which both the \( \alpha \)-positions are free, upto
six ligands can coordinate to the nickel(II) to form \( \text{NiL}_6X_2 \)
provided the anion \( X \) has a poor donor character, for example,
perchlorate and tetrafluoroborate ion.

Nickel(II) complexes synthesised in the present investi-
gations have the composition \( \text{NiL}_4(\text{SO}_3\text{Cl})_2 \), where \( L \) = pyridine
and acetonitrile. Nickel(II) chlorosulphate and its complexes
namely, \( \text{Ni(Py)}_4(\text{SO}_3\text{Cl})_2 \) and \( \text{Ni(CH}_3\text{CN})_4(\text{SO}_3\text{Cl})_2 \) have light green
colour. In general, nickel(II) octahedral complexes are greenish
or bluish green, while tetrahedral complexes are intense blue
and square planar complexes are yellow to red in colour. The
colour of the complexes under present investigations rules out
the possibility of square planar configurations. These complexes
are soluble in nitrobenzene as well as in acetonitrile but
insoluble in benzene, carbontetrachloride and other non-polar
organic solvents. The differentiation between octahedral and
tetrahedral complexes in case of nickel(II) can be done with
the help of magnetic properties as well as electronic spectra
as discussed below.
(i) **Magnetic Properties**: The nickel(II) ion has 3d$^3$ configuration. From a simple d-orbital splitting diagram, it follows that both octahedral and tetrahedral nickel(II) complexes will have two unpaired electrons and will, therefore, be paramagnetic, whereas, square planar complexes will have no unpaired electron and will be diamagnetic. The spin only magnetic moment in both octahedral and tetrahedral complexes is expected to be 2.8 BM; however, for octahedral complexes, the experimental values range between 2.9 - 3.4 BM at room temperature (221), while for tetrahedral complexes the experimental magnetic moments values range between 3.5 - 4.2 BM (205). This is because the tetrahedral complexes have very high orbital contribution to the magnetic moment whereas in octahedral complexes orbital contribution is more or less quenched.

Nickel(II) chlorosulphate and its complexes are paramagnetic, with magnetic moments in the range of 3.1 - 3.4 BM (Table 47). These values of magnetic moments are well within the range 2.9 - 3.4 BM normally found for octahedral nickel(II) complexes (221). This suggests that in the nickel(II) complexes under present investigations, the nickel(II) experiences octahedral environment.

(ii) **Electronic Spectra**: The electronic spectra of nickel(II) in its various stereochemical configurations are well established. A few important conclusions are mentioned below:

The crystal field spectra of the regular octahedral
Fig. 4-5: Reflectance spectra of nickel (II) chlorosulphate and its coordination complexes

A - Ni\((SO_3Cl)_2\)
B - Ni\((PY)_4(SO_3Cl)_2\)
C - Ni\((CH_3CN)_4(SO_3Cl)_2\)
complexes are characterized by the presence of three moderately intense bands in the range 7-13 ($\nu_1$), 11-20 ($\nu_2$) and 19-27 kK ($\nu_3$) involving three spin allowed transitions from the $^3A_{2g}$ ground term to the three excited triplet terms as shown below (189):

$$
\begin{align*}
3T_{2g}(F) & \leftrightarrow 3A_{2g}(F) \quad \cdots \quad \nu_1 \\
3T_{1g}(F) & \leftrightarrow 3A_{2g}(F) \quad \cdots \quad \nu_2 \\
3T_{1g}(F) & \leftrightarrow 3A_{2g}(F) \quad \cdots \quad \nu_3
\end{align*}
$$

The ratio of $\nu_2 / \nu_1$ of the frequencies of the band maxima in the octahedral complexes lies in most cases between 1.5 to 1.7 (223).

In general, tetrahedral nickel(II) complexes have a multiple visible absorption bands of approximately $\varepsilon_{\text{max}}$ value of 100 1.cm$^{-1}$ mole$^{-1}$ near 16 kK, assignable to the $^3T_1(F) \leftrightarrow ^3T_1(F)$ transition. A near infrared band of intensity about 20 1.cm$^{-1}$ mole$^{-1}$ near 8 kK as assigned to the $^3A_2 \leftrightarrow ^3T_1(F)$ transition.

Majority of square planar complexes exhibit a strong band in the visible region between 15-25 kK and in many cases a second more intense band is observed between 23-30 kK (199).

The band maxima at 12.3 and 23.5 kK in case of nickel(II) chlorosulphate (Fig. 4.5) are assigned to $\nu_2$ and $\nu_3$ indicating
octahedral arrangement around nickel (II). In the complexes $\text{Ni(\text{Py})}_4(\text{SO}_3\text{Cl})_2$ and $\text{Ni(\text{CH}_3\text{CN})}_4(\text{SO}_3\text{Cl})_2$ the $\nu_1$, $\nu_2$ and $\nu_3$ are in the range $7.1 - 8.3$, $11.1 - 14.7$ and $22.2 - 25.0$ cm$^{-1}$ respectively (Fig. 4-5) and $\nu_2/\nu_1$ ratio is found to be in the range $1.55 - 1.76$ (Table 47) indicating the octahedral environment around nickel (II).

4.3.3 Copper(II) Chlorosulphate and its Coordination Complexes with Pyridine and Acetonitrile: A substantial array of copper (II) complexes with pyridine and substituted pyridines have been isolated and characterized by earlier workers. These complexes have the general formula, $\text{CuL}_2\text{X}_2$, where $X = \text{Cl}$, $\text{Br}$, $\text{SCN}$ and $L = \text{pyridine}$, $2$-methylpyridine, $3$-methylpyridine, $4$-methylpyridine, $2$-ethylpyridine, $2,6$-dimethylpyridine and a number of $4$-substituted pyridines and quinolines ($209, 224-230$). It has been established that the halide complexes are polymeric with tetragonal six coordination about copper atom achieved by halide bridges.

Brown et al. (231) have isolated complexes of the general formula $\text{CuL}_4\text{X}_2$, where $X = \text{ClO}_4^-$ or $\text{BF}_4^-$ and $L$ is pyridine, $4$-methylpyridine or quinoline and have suggested coordination of the anion from their infrared spectral studies. The complexes $\text{Cu(\text{Py})}_4(\text{SO}_3\text{Cl})_2$ and $\text{Cu(\text{CH}_3\text{CN})}_4(\text{SO}_3\text{Cl})_2$ obtained in the present investigations are of the type $\text{CuL}_4\text{X}_2$ and their colours are blue and light blue respectively. These complexes are soluble only in acetonitrile. Their structure can partly be established from magnetic and electronic spectral data.
### Table 47

**Absorption Spectra (kHz) and Magnetic Moments of Nickel(II) Chlorsulphate and Its Coordination Complexes with Pyridine and Acetonitrile**

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^3T_{2g}(F)\leftrightarrow^3A_{2g}(F)$</th>
<th>$^3T_{1g}(F)\leftrightarrow^3A_{2g}(F)$</th>
<th>$^3T_{1g}(F)\leftrightarrow^3A_{2g}(F)$</th>
<th>$\nu_2/\nu_1$</th>
<th>$\mu_{\text{eff.}}$ (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ni(SO}_3\text{Cl)}_2$</td>
<td>-</td>
<td>12.30</td>
<td>23.50</td>
<td>-</td>
<td>3.4</td>
</tr>
<tr>
<td>$\text{Ni(Py)}_2(\text{SO}_3\text{Cl})_2$</td>
<td>7.14</td>
<td>11.11</td>
<td>25.00</td>
<td>1.55</td>
<td>3.1</td>
</tr>
<tr>
<td>$\text{Ni(CH}_3\text{CN)}_4(\text{SO}_3\text{Cl})_2$</td>
<td>8.33</td>
<td>14.70</td>
<td>22.22</td>
<td>1.76</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Magnetic Properties: Copper(II) ion has one unpaired electron with spin only magnetic moment of 1.73 BM. The magnetic criterion is relatively unhelpful in elucidating the structure of copper(II) complexes because copper(II) ion still has one unpaired electron regardless of the configuration of the bonds. Despite this drawback, there have been a number of magnetochemical studies of copper(II) complexes.

Figgis (232) has shown that in a perfectly tetrahedral environment around copper(II) the term \(^2T_2\) causes a large orbital contribution to its magnetic moment giving a net value of \(> 2.2\) BM at temperatures above 200\(^\circ\)K and is expected to decrease with temperature. However, a rigorously tetrahedral copper(II) complex is not likely to exist since Jahn-Teller distortion may be expected to split the otherwise degenerate \(2\) ground state and thus to quench some of the orbital contribution resulting in low magnetic moment value.

Octahedral copper(II) having \(\Sigma\) as ground term can get some orbital contribution by mixing up with \(2T_2\) excited state. Substituting \(\lambda\) value of -830 cm\(^{-1}\) for the free copper(II) ion and the 10 \(D\) value of 15,000 cm\(^{-1}\) in copper(II) complexes in equation

\[
\mu_{\text{eff}} = \left( 1 - \frac{2\lambda}{1C \cdot D} \right) \left[ 4S(S+1) \right]^{1/2}
\]

the expected value of magnetic moment comes to be 1.93 BM (176).

The magnetic moment values in case of copper(II) chlorosulphate and its coordination complexes with pyridine anô
acetonitrile are in the range 1.73 - 1.99 BM (Table 48) indicating the octahedral arrangement of atoms around copper(II).

(ii) **Electronic Spectra**: The configuration of complexes of copper(II) presents an interesting problem. Copper(II) having $3d^9$ configuration gives rise to only one free ion term $^2T$ which is tenfold degenerate in spin and orbit. Under the influence of square planar ligand, $d$-$d$ absorption bands have been known to appear in 15-18 kK region for trans-planar complexes (233-235) and near 18 kK for cis-planar complexes (233-236).

For a truly tetrahedral copper(II) complex, the crystal field theory predicts only one transition (236); $^2E \leftarrow ^2T_2$ and therefore, a narrow band would be expected (237).

Liehr (238) has postulated a theory of tetrahedrally coordinated copper(II) ion and has concluded that tetrahedral copper(II) complexes absorb in the region 5-7 kK and bands in visible part of the spectrum (10-20 kK) are not permitted. Nevertheless, Furlani and Morpurgo (239) have shown that the flattening of the coordinated tetrahedron results in the splitting of both the ground and the excited levels. Due to Jahn-Teller distortion, there is no possibility of a truly tetrahedral copper(II) complex and hence copper(II) forms distorted tetrahedral complexes.

The electronic spectra of copper(II) ion in a regular octahedral ($C_h$) environment should consist of a single band, arising from $^2T_{2g} \leftarrow ^2E_g$ transition. However, all the
TABLE 48

ABSORPTION SPECTRA (KK) AND MAGNETIC MOMENTS OF COPPER(II) CHLOROSULPHATE AND ITS COORDINATION COMPLEXES WITH PYRIDINE AND ACETONITRILE

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{2}E \rightarrow ^{2}T_{2}$</th>
<th>$\mu_{\text{eff}} \text{ (BM)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(SO$_3$Cl)$_2$</td>
<td>15.87</td>
<td>1.99</td>
</tr>
<tr>
<td>Cu(Py)$_4$(SO$_3$Cl)$_2$</td>
<td>14.50</td>
<td>1.78</td>
</tr>
<tr>
<td>Cu(CH$_3$CN)$_4$(SO$_3$Cl)$_2$</td>
<td>16.60</td>
<td>1.82</td>
</tr>
</tbody>
</table>
Fig. 4.6—Reflectance spectra of copper (II) chlorosulphate and its coordination complexes

A - Cu(SO$_3$Cl)$_2$
B - Cu(Py)$_4$(SO$_3$Cl)$_2$
C - Cu(CH$_3$CN)$_4$(SO$_3$Cl)$_2$
octahedral copper(II) complexes are apt to be deformed by the Jahn-Teller effect and the absorption band is broadened. A broad band probably involves either two (234) or three (240) overlapping absorptions. Numerous investigators (230,241,242) have observed bands in 11-14 kK region for tetragonally distorted octahedral copper(II) complexes. However, the position of the absorption maxima is dependant on the ligand as \([\text{Cu}(\text{H}_2\text{O})_6]^{2+}\) shows maxima absorption at 12.6 kK while \([\text{Cu}(\text{NH}_3)_6]^{2+}\) at 15.1 kK and \([\text{Cu(En)}_3]^{2+}\) at 16.4 kK.

The broad maxima (Fig. 4.6) observed at 15.8, 14.5 and 16.6 kK in case of \(\text{Cu(SO}_3\text{Cl})_2\), \(\text{Cu(Py)}_4(\text{SO}_3\text{Cl})_2\) and \(\text{Cu(CH}_3\text{CN})_4(\text{SO}_3\text{Cl})_2\) (Table 43) respectively indicate that the chlorosulphate and its complexes are tetragonally distorted octahedrons.