Reprints
Metal-ion directed synthesis of N2O2 type chelate complexes of Ni(II), Cu(II) and Zn(II): Spectral, thermal and single crystal studies

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Highlights
- Central metal ion is coordinated with azomethine nitrogen and phenolic oxygen atoms.
- Ni(II) and Cu(II) are square-planar whereas Zn(II) is octahedral in geometry.
- Exocyclic –OCH3 facilitates deprotonation of phenolic oxygen by resonance.
- Single crystal studies of Ni(II) complex reveal monoclinic crystal system.

Abstract
A set of Ni(II), Cu(II) and Zn(II) complexes of Schiff base have been synthesized by one pot condensation reaction of 2-hydroxy-4-methoxybenzophenone with 1,3-diaminopropane in 1:2:1 molar ratio. They have been characterized by elemental analysis, conductance measurement, thermal analysis (TGA/DTA), FT-IR, 1H-NMR, EPR spectra, ESI–MS and electronic spectral studies. In order to establish the geometry, a single crystal X-ray structure for [Ni(L)] complex was determined. It crystallizes in monoclinic system having unit cell parameters $a = 14.015(5)$ Å, $b = 13.391(5)$ Å, $c = 14.931(5)$ Å and $\alpha = 90.000(5)^\circ$, $\beta = 112.237(5)^\circ$, $\gamma = 90.000(5)^\circ$ with $P 21/c$ space group. No $\pi-\pi$ stacking interaction was obtained in molecular packing diagram. A square-planar geometry has been confirmed for Ni(II) complex. Furthermore, on the basis of elemental analysis, IR, UV–visible and EPR data a square-planar geometry for Cu(II) and a distorted octahedral geometry for the Zn(II) complex has been established. In case of Zn(II) complex NO$_3$ group was found to be coordinated in monodentate fashion. The low molar conductivity values of the complexes measured in chloroform and DMSO suggest their non-ionic nature.

Introduction
Schiff bases derived from the condensation of amines with aldehyde/ketone are multifunctional macrocyclic ligands and quite often they mimic the biological molecules [1]. They may be symmetrical or highly unsymmetrical. It has been reported that Schiff base complexes of the metal ions with completely filled d orbitals such as, Zn(II) and Cd(II) can be used as an effective emitting layer showing photophysical properties [2]. They have also been shown to exhibit antitumor, anti HIV and antimicrobial properties [3]. Singh and co-workers have shown that Zn(II), Cd(II), Sn(II) and Pb(II) complexes with Schiff base derived from carboxaldehyde and 2-amino phenol are four coordinated. The phenolic group is coordinated after deprotonation. Molecular structure of these complexes has been optimized and suggested tetrahedral geometry for them [4].

The property of the complexes depends on the nature of metal and the ligand. The Schiff base derived from the condensation of diamines with ketone generally, gives a macrocyclic ligand with cavity of different dimensions. Sometimes, it is made very selective for certain metal ions owing to their ionic radii which allow them...
to be appropriately fitted in the cavity. On the other hand the Schiff bases derived from the condensation of an aldehyde with monoamines are unsymmetrical and open at one end. Their selectivity is therefore, lost and metal ions of varying ionic radii may be coordinated [5–7].

It has been shown from a study of Ni(II) and Cu(II) complexes of thiosemicarbazone derived from hydroxybenzophenone and 3,4-methylthiosemicarbazide that the ligand coordinates in three different modes. Mononuclear and polymeric complexes of Cu(II) with thiosemicarbazone act as models for galactose oxidase and as a redox catalyst [8]. Complexes of lanthanides with tripodal ligands containing OH group has been reported. On the basis of their interaction with DNA it has been shown that they have potential as therapeutic agent and DNA probes [9].

In a very recent paper [10] it has been reported that the Mn(II), and Cu(II) complexes with thiocarbazide derivatives have different stereochemistry. The Mn(II) is octahedral while the Cu(II) has been reported to be square-planar. They are nano crystalline in nature.

The tetradentate N2O2 type Schiff base complexes with Cu(II), Ni(II) and Zn(II) ions are square-planar [11]. They have been shown to be active against Staphylococcus aureus, Pseudomonas aeruginosa and Escherichia coli. The activity of Schiff base against microbes is enhanced after complexation with metal ions. Bimetallic complexes with Schiff bases have been studied mainly to explore their stereochemistry and activity against bacteria and fungi. The homobimetallic Cu(II) complexes are of special interest so as to correlate the spin–spin interaction between the two metal ions. They also exhibit enzymatic properties [12]. Intelligent design of Schiff base may lead to the formation of supramolecule which may be symmetrical or unsymmetrical and can be used as spin cross over molecular magnetic material [13,14].

In this project we are reporting the synthesis of a novel symmetrical N2O2 tetradentate open ended Schiff base ligand and its complexes with Ni(II), Cu(II) and Zn(II) by in situ condensation of the two essential components of the ligand 2-hydroxy-4-methoxybenzophenone (Sigma) and 1,3-propanediamine (Fluka), M(NO3)2.nH2O (BDH) were used as supplied. 2-Hydroxy-4-methoxybenzophenone (Sigma) and 1,3-propanediamine (Fluka), M(NO3)2.nH2O (BDH) were used as supplied. 2-Hydroxy-4-methoxybenzophenone (Sigma) and methanol were of analytical grade.

Elemental analysis was carried out with Carlo Erba 1106. The molar conductivity was measured with a CM-82 ELICO conductivity bridge in chloroform and DMSO. The IR spectra (600–4000 cm⁻¹) were recorded on a Spectrolab Interspec FT/IR-2020 spectrometer as KBr disc. Far IR spectra (200–500 cm⁻¹) were recorded using CsBr. Electronic spectra were recorded at room temperature on a Perkin Elmer Lambda-35 UV–vis spectrophotometer in chloroform and DMSO solutions. ¹H NMR spectrum of the ligand was recorded on Bruker Advance 500 MHz Spectrometer in CDCl₃ at IIT, Madras. The EPR spectrum of the copper complex was recorded at liquid N₂ temperature in DMSO with JEOLE FA 200 EPR spectrometer operating at X-band microwave frequency region (8.65–9.75 GHz) with 100 kHz modulation frequency using DPPH as standard g marker at University of Hyderabad, India. The TGA/DTA was done with a Simultaneous DTG–60H thermal analyzer under static nitrogen atmosphere at a heating rate of 10 °C/min, using Al₂O₃ as reference. The ESI–MS were recorded with a Waters Micromass Q-Tof Micro LC-MS system at SAIF, Punjab University, Chandigarh, India.

Synthesis of ligand (H₂L)

The ligand H₂L (L = 1-Phenyl-1-(2-hydroxy-4’-methoxy)methyldiene-1,3-propanediamine) was synthesized (Scheme 1) by refluxing for 4 h a methanolic (15 ml) solution of 1,3-propanediamine (1 mmol, 0.083 ml) and 15 ml solution of 2-hydroxy-4-methoxybenzophenone (2 mmol, 0.456 g) in the same solvent. A yellow precipitate appeared under reflux. It was cooled to room temperature, filtered and washed with cold methanol and dried in vacuum over CaCl₂.

Synthesis of complexes

The complexes were synthesized by direct method (Scheme 2). To a boiling methanolic (15 ml) solution of hydrated metal nitrates (1 mmol), was added 2-hydroxy-4-methoxybenzophenone (2 mmol, 0.456 g) (20 ml) drop wise followed by the addition of one mmmol of 1,3-propanediamine (0.083 ml) dissolved in methanol. In case of Ni(II) the resulting solution was refluxed for about 20 h. The product was monitored by TLC and when a single spot was obtained the clear solution was left for seven days which yielded good quality single crystals. However, in the case of Cu(II) and Zn(II) violet and white precipitates were obtained after 10 h of refluxing. It was cooled to room temperature and filtered. They were washed with cold methanol and dried in vacuum over anhydrous CaCl₂.

X-ray crystallographic study and structure refinement

Single crystal X-ray data of complex [Ni(L)] were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite monochromator MoKα radiation (λ = 0.71073 Å). The linear absorption coefficients, scattering factors for the atoms and the
analomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [15]. The data integration and reduction were carried out with SADABS [17] and the space group was determined using the program SHELXTL-97 [19]. The structure was solved by the direct methods using SHELXTL-97 and refined on $F^2$ by full-matrix least-squares. The analytical data is consistent with their composition (Table 2). The molar conductance in free and ligated states. The elemental analysis is consistent with their composition (Table 2). The molar conductance in free and ligated states.

**Results and discussion**

Reaction of Ni(II), Cu(II) and Zn(II) nitrate with 2-hydroxy-4-methoxybenzophenone and 1,3-propanediamine in 1:2:1 ratio results into complex formation. The Schiff base was separately synthesized and characterized in order to ensure the spectral data is consistent with their composition (Table 2). The molar conductance in free and ligated states. The elemental analysis is consistent with their composition (Table 2). The molar conductance in free and ligated states.

The IR spectrum (Table 3) of the ligand shows a band in 3200–3350 cm$^{-1}$ region corresponding to phenolic OH groups. Ni(II) and Cu(II) complexes also show a band in this region corresponding to phenolic OH groups. However, in the case of Ni(II) and Cu(II) complexes, this band is shifted to a lower frequency indicating complexation.

**Table 1**

Crystal data and structure refinement of [Ni(L)].

<table>
<thead>
<tr>
<th>[Ni(L)]</th>
<th>C$_2$H$_8$N$_2$NiO$_4$</th>
<th>Color/shape</th>
<th>Dark green/square shaped/Block</th>
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<td>Crystal size</td>
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<td></td>
</tr>
<tr>
<td>Formula weight</td>
<td>531.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>$P 2_1/c$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (K)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Cell lengths</td>
<td>$a = 14.015(5)$ Å, $b = 13.391(5)$ Å, $c = 14.931(5)$ Å</td>
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<td></td>
</tr>
<tr>
<td>Cell angles</td>
<td>$\alpha = 90.000(5)^\circ$, $\beta = 112.237(5)^\circ$, $\gamma = 90.000(5)^\circ$</td>
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<tr>
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<td>GOOF</td>
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<tr>
<td>$F(000)$</td>
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<tr>
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<tr>
<td>$\theta_{\text{min}}$</td>
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<td>$\mu$ (mm$^{-1}$)</td>
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<td>Diffractometer/scan</td>
<td>Bruker SMART CCD</td>
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<td></td>
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<td>Radiations used, graphite monochromator</td>
<td>Mo Kα ($\lambda = 0.71073$)</td>
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<td>Refl. collected</td>
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<td>Index ranges</td>
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<tr>
<td>Data completeness</td>
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<td>Final R indices</td>
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</table>

**Table 2**

Analytical data.

<table>
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<tr>
<th>S. No.</th>
<th>Complexes</th>
<th>Yield (%)</th>
<th>M.P. (°C)</th>
<th>Color</th>
<th>Analysis (%) (calcd.) found</th>
<th>Am (cm$^2$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H$_2$L</td>
<td>65</td>
<td>230</td>
<td>Yellow</td>
<td>(75.19) 74.86 (5.60) 5.94 (5.65) 4.89 (3.85)</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>[Ni(L)]</td>
<td>35</td>
<td>300</td>
<td>Dark green</td>
<td>(67.31) 66.96 (5.42) 5.03 (5.06) 5.23 (5.26)</td>
<td>20.20</td>
</tr>
<tr>
<td>3</td>
<td>[Cu(L)]</td>
<td>54</td>
<td>330</td>
<td>Violet</td>
<td>(66.87) 67.01 (5.03) 4.97 (5.03) 5.15 (5.15)</td>
<td>19.22</td>
</tr>
<tr>
<td>4</td>
<td>[ZnH$_2$L(NO$_3$)$_2$]</td>
<td>50</td>
<td>120</td>
<td>White</td>
<td>(54.56) 55.01 (4.10) 4.31 (8.21) 7.90 (7.90)</td>
<td>35.46</td>
</tr>
</tbody>
</table>

**Infrared spectra**

The IR spectrum (Table 3) of the ligand shows a band in 3200–3350 cm$^{-1}$ region corresponding to phenolic OH groups. Ni(II) and Cu(II) complexes also show a band in this region corresponding to phenolic OH groups. However, in the case of Ni(II) and Cu(II) complexes, this band is shifted to a lower frequency indicating complexation.
and its deprotonation was facilitated. The new bands observed in the region 560–570 cm\(^{-1}\) and 480–510 cm\(^{-1}\) are assigned to \(\text{m}(\text{M–O})\) and \(\text{m}(\text{M–N})\) respectively [25,26]. It is known that the \(\text{NO}_3\) coordinates as symmetrical or asymmetrical chelating bidentate, bridging bidentate or as monodentate ligand. For both types of coordination three well separated bands appear in about 1020–1510 cm\(^{-1}\) region. When the difference between the two highest frequencies is very large (\(\Delta 200\) cm\(^{-1}\)) the \(\text{NO}_3\) ion is supposed to act as bidentate ligand while a difference of approximately 100–115 cm\(^{-1}\) refers to monodentate nature of \(\text{NO}_3\). We have observed three bands at 1509, 1394 and 1104 cm\(^{-1}\). The difference between the two highest peaks in our case comes out to be 113 cm\(^{-1}\) [27] which suggests that \(\text{NO}_3\) is acting as a monodentate ligand in the present case.

The \(\text{1}H\)-NMR spectrum of ligand was recorded in CDCl\(_3\) (Fig. 1). The spectrum showed multiplet in \(\delta 7.1–7.2\) ppm region due to symmetric aromatic protons of the ligand. The methoxy protons showed a singlet at \(\delta 3.8\) ppm. However, aliphatic protons of methylene group attached to amine nitrogen resonate at \(\delta 3.55\) ppm [28,29]. A signal at \(\delta 15.88\) ppm is assigned to phenolic –OH proton. Since this phenolic proton has less electron density due to resonance effect of \(m\)-methoxy group, it is far downfield shifted. Two double doublets in \(\delta 6.44–6.64\) ppm region have been assigned to asymmetric aromatic protons.

Electronic spectra

The UV–vis spectra of Ni(II) and Cu(II) complexes [Fig. 2S:(a),(b)] were recorded in chloroform and that of Zn(II) complex in DMSO. The absorption band observed in the region 255–300 nm and 310–410 nm were assigned to \(\pi\rightarrow\pi^*\) and \(n\rightarrow\pi^*\) transitions respectively of azomethine group and are due to ligand to metal charge transfer. The wavelengths of absorption maxima and band assignment for the proposed geometries of the complexes are given in Table 4.

The light green Ni(II) ion in aqueous medium exhibits weak band in the visible region of the spectrum. The \(d\rightarrow d\) band in our case in chloroform, appears as twin peaks around 587 nm assigned to the \(3\text{T}_{1g}(P)\rightarrow3\text{A}_{2g}(F)\) suggesting square-planar geometry for the complex. A set of two peaks at 675 nm and 687 nm may be attributed to \(3\text{T}_{1g}(F)\rightarrow3\text{A}_{2g}(F)\) and \(3\text{T}_{1g}(F)\rightarrow3\text{A}_{2g}(F)\) transitions, respectively [30,31]. We observed a peak at 410 nm which is generally obscured for Ni(II) ion in aqueous medium.

The Cu(II) complex showed a broad peak at 548 nm corresponding to \(3\text{B}_{1g}\rightarrow3\text{E}_g\) transition indicating square-planar geometry around the Cu(II) ion [32,33].

ESI–Mass spectra

The ESI–MS of complexes and the ligand has been recorded using the positive ion mode. They display prominent peaks corresponding to the molecular ion fragments. Their intensity gives an

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Complex</th>
<th>(\nu(\text{OH}))</th>
<th>(\nu(\text{C–O}))</th>
<th>(\nu(\text{CH}_2))</th>
<th>(\nu(\text{C=O}))</th>
<th>(\nu(\text{CH}_3))</th>
<th>(\nu(\text{N–O}))</th>
<th>(\nu(\text{M–O}))</th>
<th>(\nu(\text{M–N}))</th>
<th>(\nu(\text{NO}_3^-))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\text{H}_2\text{L})</td>
<td>3200–3350</td>
<td>1261</td>
<td>2932</td>
<td>1602</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>[\text{Ni}(\text{L})]</td>
<td>–</td>
<td>1214</td>
<td>2942</td>
<td>1569</td>
<td>560</td>
<td>514</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>[\text{Cu}(\text{L})]</td>
<td>–</td>
<td>1218</td>
<td>2964</td>
<td>1578</td>
<td>563</td>
<td>493</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>[\text{Zn}(\text{H}_2\text{L})(\text{NO}_3)_2]</td>
<td>3257–3100</td>
<td>1171</td>
<td>2955</td>
<td>1576</td>
<td>566</td>
<td>482</td>
<td>1509,1394,1104</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

**Table 3**

Infrared spectral data.

**Table 4**

Electronic spectral data.

**Fig. 1.** \(\text{1}H\)-NMR of ligand (\(\text{H}_2\text{L}\)).
idea of the molecular ion peak and has been used to confirm the proposed formula and stability of fragments. In the present investigation, the mass spectrum of H2L shows a molecular ion peak at m/z 493 [M+] corresponding to C32H28N2O4 ion. The molecular ion peak for Cu(II) complexes is observed at m/z 557 [M+] along with many other intermediary fragment peaks. The mass spectrum of the Zn(II) complex (Fig. 3S) is discussed here in detail. It displays a molecular ion peak at m/z 681 due to [M+] and other intermediate fragments, at m/z 435 corresponding to [C6H5)2C2N2(CH2)3-/Zn(NO3)2]+, at m/z 190 due to [Zn(NO3)2]+ and at m/z 124 due to [(NO3)2]+ respectively, showing usual degradation pattern. The complex has two nitrate ions axially coordinated to the Zn(II) metal. Likewise, the peaks are attributable to other complexes.

**TGA and DTA**

TGA was carried out between 30–800 °C at a heating rate of 10 °C/min in a static nitrogen atmosphere. The TGA and DTA of all the complexes show three stages of decomposition (Fig. 2). Since all the complexes decompose in a similar pattern the result of the Zn(II) complex is discussed here in detail. The first step (50–295 °C) shows a loss of 53.49% which is close to the calculated value (54.38%) corresponding to benzylidene-1,3-propanediamine and two nitrates. The second step shows a weight loss of 28.48% (calc. 27.48%) between (275–550 °C), which is consistent with the loss of (C6H5OH)2 group. The bent part of the graph in the range 550–600 °C corresponds to –OCH3 equal to loss of 8.48%. The flat of the thermogram which remains constant up to 800 °C corresponds to Zn metal as residue.

**EPR spectrum**

X-band EPR spectrum of Cu(II) complex recorded at liquid nitrogen temperature exhibits three well resolved peaks with low intensities in the low field region and one intense peak in the high field region (Fig. 3). From the spectral data it is found that g∥ (2.40, 2.25, 2.14), g⊥ (2.05, 1.96) > 2.003 which supports the d2−y2 as ground state which is consistent with distorted square-planar...
geometry for the Cu(II) complex. The absence of any half field signal suggests the presence of only one Cu(II) ion in the complex. The axial symmetry parameter (G) is related by the expression,

\[ G = \frac{(g_{\|} - 2.0023)}{(g_{\perp} - 2.0023)} = \frac{2.40136 - 2.0023}{2.05898 - 2.0023} = \frac{0.39836}{0.05598} = 7.11 \]

It measures the extent of exchange interaction between the copper centers in polycrystalline solid. Since the calculated G > 4, the exchange interaction between Cu–Cu ions in the complex is ruled out [34,35].

The extent of geometrical distortion is measured by the \( g_{\|}/A_{\|} \) ratio [31]. It is known that this ratio for square-planar complex falls between 105–135 cm\(^{-1}\) and, for tetragonally distorted complex it is 135–250 cm\(^{-1}\) [36]. The present complex has \( g_{\|}/A_{\|} = 120 \text{ cm}^{-1} \) showing square-planar geometry.

**Description of crystal structure**

The ORTEP diagram for [Ni(L)] is depicted in Fig. 4. The crystal structure showed a discrete type complex in which nickel atom is coordinated to N2O2 donor set of the ligand leading to the formation of four six membered chelate rings which increases the stability of the complex. The [Ni(L)] crystallizes in monoclinic system having space group P2\(_1\)/c. The two cis-coordinated phenolic oxygen and two imine nitrogen atoms exhibit almost regular square-planar geometry, as there are no considerable differences in bond lengths and bond angles of the donor atoms coordinated to central metal ion. The complex is dsp\(^2\) hybridized which is supported by the diamagnetic behaviour of Ni(II) ion. The crystallographic data and structural refinement are summarized in Table 1. The selected bond angles and bond lengths are given in Tables 2 and 3 respectively. The nickel oxygen distances, Ni–O1 (1.828 Å) and Ni–O2 (1.836 Å) are shorter than nickel nitrogen distances Ni–N1 (1.881 Å) and Ni–N2 (1.888 Å) as a consequence of negative charge borne by the phenolic oxygen atoms. Although the two phenyl rings are identical, nevertheless one of them is slightly tilted where the other stays in the plane (Fig. 5). The molecular packing diagram has shown four formula units per unit cell (Fig. 6) with no π–π stacking interaction.

**Conclusion**

The complexes have been found to be N2O2 type chelates in which Ni(II) and Cu(II) are coordinated through azomethine nitrogen and phenolic oxygen of the ligand exhibiting square-planar geometry which has been supported by IR, EPR, Electronic spectra and X-ray crystallographic studies. In case of Zn(II) complex two nitrate ions were also found to be coordinated as monodentate ligand conferring an octahedral geometry to the metal.

**Acknowledgements**

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**Appendix A. Supplementary data**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.08.004.

**References**


Please cite this article in press as: S. Yadav et al., Metal-ion directed synthesis of N2O2 type chelate complexes of Ni(II), Cu(II) and Zn(II): Spectral, thermal and single crystal studies, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy (2012), http://dx.doi.org/10.1016/j.saa.2012.08.004.
Please cite this article in press as: S. Yadav et al., Metal-ion directed synthesis of N2O2 type chelate complexes of Ni(II), Cu(II) and Zn(II): Spectral, thermal and single crystal studies, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy (2012), http://dx.doi.org/10.1016/j.saa.2012.08.004
Synthesis and characterization of heterobimetallic complexes of the type \([\text{Cu}(\text{pn})_2][\text{MCl}_4]\) where \(\text{M} = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}, \text{Cd(II)}, \text{and Hg(II)}\)

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1. Introduction

Although diamines are well known chelating agents, they also behave as bridging ligand either with cis or trans conformation. The 1,3-diaminopropane is known to form six membered chelate ring with the metal ions (Miyoshi et al., 1972; Allmann et al., 1990). \([\text{Cu}(\text{pn})_2]\text{Cl}_2\) is known to have a tetragonally distorted pseudooctahedral unit with \(C_{2v}\) symmetry where chloride ions are weakly bonded and remain uncoordinated (Davey and Stephens, 1971). Chemistry of tetrahalogeno complexes is well established. Such complexes are strictly termed as halide complexes (Hald and Rasmussen, 1978a,b; Ohba and Rasmussen, 1994). After a closer examination of \(\text{M(en)}\text{Cl}_2\) X-ray powder photographs and vibrational data it has been pointed out that \(\text{Zn(en)}\text{Cl}_2\) and \(\text{Cd(en)}\text{Cl}_2\) should not be formulated as \([\text{Zn(en)}_2]\text{[ZnCl}_4]\) or \([\text{Cd(en)}_2]\text{[CdCl}_4]\) nevertheless, this type of formulations are reported in the older literature (Sukarova et al., 1993; Fatmi et al., 2007).

Gerken and coworkers have reported the synthesis and stabilization of tetrachloroaarsonium and tetrabromoarsonium cations using weakly coordinating bulky anions as counter anions. It has been reported that \([\text{AsCl}_4]\text{[As(OTeF}_5]_3]\) is stable while \([\text{AsBr}_4]\text{[As(OTeF}_5]_3]\) undergoes slow decomposition at room temperature but kinetically more stable than \(\text{AsF}_6\) and \([\text{AsF(OTeF}_5]_3]\) salt, which rapidly decomposes upon warming at room temperature. The synthesis and stabilization of such complexes are recent matter of concern (Pastorek et al., 2011; Nami et al., 2010; Beznischenko et al., 2009; Pryma et al., 2003; Gerken et al., 2000; Casteel et al., 1996).

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A family of cyanobridged Copper(II)–Copper(I) mixed valence polymers containing diamine ligands of formula [Cu(pn)₂][Cu₂(CN)₄] has been prepared with the aim of analyzing how their architecture may be affected by steric constraints imposed by the diamine ligands (Cui et al., 2011; Colacio et al., 2002). Since the stabilization of tetrachloro-metallate ion by bis-propanediamine cupric ion has not been reported, it is, therefore, considered worthwhile to study and evaluate the phenomenon associated with the formation and stabilization of relatively larger [MCl₄]²⁻ anion by [Cu(pn)₂]²⁺ cation (Ha, 2010; Kim et al., 1998; Sundberg and Ugge, 1997). In continuation of our earlier work on heterobinuclear complexes, we are reporting in this paper, a series of novel bimetallic transition metal complexes of the type [Cu(pn)₂][MCl₄], (M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)) (Siddiqi et al., 1993a–d). The ionic nature has been established from their molar conductance in DMF.

2. Experimental

1,3-Diaminopropane (Fluka), MCl₂ (M = Co, Ni, Cu, Zn, Cd and Hg) (BDH) were used as supplied. DMF (Merck), MeOH and Et₂O used in this work were of analytical grade.

2.1. Preparation of [Cu(pn)₂]Cl₂

[Cu(pn)₂]Cl₂ was synthesized by literature method with a slight modification (Siddiqi et al., 1993a–d). To a hot solution of CuCl₂·2H₂O (1.66 g, 0.01 mol) in MeOH (25 cm³) was added dropwise 1,3-diaminopropane (1.671 ml, 0.02 mol) dissolved in the same solvent. The dark blue precipitate formed instantaneously was refluxed for 5–6 h (Scheme 1) and left for nearly ten days which yielded dark blue flakes. It was washed with MeOH followed by Et₂O and dried in vacuum for seven days. Any attempt to prepare such complexes with Cr(II), Mn(II) and Fe(III) was unsuccessful. The quantity used and per cent yield of all the complexes are given below.

![Scheme 1] Synthesis of [Cu(pn)₂]Cl₂.

2.2. Preparation of [Cu(pn)₂][MCl₄]

To a methanolic solution (15 cm³) of [Cu(pn)₂]Cl₂ (0.01 mol) was added divalent metal chloride dissolved in the same solvent (0.01 mol). On stirring the mixture for ten min dark colored precipitates (Table 1) were obtained (Scheme 2). It was filtered and washed with MeOH followed by Et₂O and dried in vacuum over anhydrous CaCl₂ for 7 days. Any attempt to prepare such complexes with Cr(II), Mn(II) and Fe(III) was unsuccessful. The quantity used and per cent yield of all the complexes are given below.

2.3. No. of moles, weight (g) of the reactants and per cent yield of the products

(1) Cu(pn)₂Cl₂ + CoCl₂·6H₂O → [Cu(pn)₂][CoCl₄]
   0.01 mol (1.66 g) 0.01 mol (2.59 g) yield 32%
(2) Cu(pn)₂Cl₂ + NiCl₂·6H₂O → [Cu(pn)₂][NiCl₄]
   0.01 mol (1.66 g) 0.01 mol (2.71 g) yield 41%
(3) Cu(pn)₂Cl₂ + CuCl₂·2H₂O → [Cu(pn)₂][CuCl₄]
   0.01 mol (1.66 g) 0.01 mol (1.70 g) yield 45%
(4) Cu(pn)₂Cl₂ + ZnCl₂ → [Cu(pn)₂][ZnCl₄]
   0.01 mol (1.66 g) 0.01 mol (1.66 g) yield 45%
(5) Cu(pn)₂Cl₂ + CdCl₂ → [Cu(pn)₂][CdCl₄]
   0.01 mol (1.66 g) 0.01 mol (1.82 g) yield 57%
(6) Cu(pn)₂Cl₂ + HgCl₂ → [Cu(pn)₂][HgCl₄]
   0.01 mol (1.66 g) 0.01 mol (2.71 g) yield 54%

2.4. Physical measurements

Elemental analyses were carried out with Carlo-Erba 1106. Molar conductance was measured with ELICO Conductivity Bridge CM 183. The IR spectra (600–4000 cm⁻¹) were recorded with Interspec 2020 FTIR SPECTROLAB, UK as KBr pellet. Far IR spectra (200–500 cm⁻¹) were recorded using CsBr. Electronic spectra were recorded with UV–vis spectrophotometer UV min-1240. Chlorine was analyzed as AgCl. The TGA was done with Mettler Stare SW 8.10 under nitrogen atmosphere using Al₂O₃ as reference.
3. Results and discussion

The elemental analysis is consistent with the proposed formulation of the complexes and they decompose only above 200 °C (Table 1). The reaction of [Cu(pn)₂]Cl₂ with MCl₂ leads to the formation of [Cu(pn)₂][MCl₄]. The complex [Cu(pn)₂]Cl₂ may be pseudo octahedral. It is apparent that during its reaction with MCl₂, the chloride ion may be transferred in order to maintain equilibrium between the two species. In such complexes, the central metal ion in cationic form explicitly exists in square-planar environment although the larger anionic counterpart maintains its ubiquitous tetrahedral configuration and is stabilized by [Cu(pn)₂]²⁺ cation. The structure of [Cu(pn)₂]²⁺ is known to be square-planar (Kang et al., 2007; Mondal et al., 2001). There is no speculation about it. They are moderately soluble in DMSO and DMF, stable to heat and light and can be stored in an open atmosphere without any decomposition.

It evident by their room temperature molar conductivity (1 mM) measured in DMF (60–90 Scm⁻² mol⁻¹) that [Cu(pn)₂]Cl₂ behaves as 1:2 electrolyte while [Cu(pn)₂][MCl₄] is 1:1 electrolyte in the same solvent. It is known that molar conductance of 1 mM solution of 1:1 electrolyte falls between 120 Scm⁻² mol⁻¹ for ionic compounds of this type, such as tetra phenyl borate the conductance is as low as 115 Scm⁻² mol⁻¹ (Geary, 1971). Since the molar conductance of [Cu(pn)₂]Cl₂ is 120 Scm⁻² mol⁻¹, it is suggested to be 1:2 electrolyte (Table 1). The quantitative estimation of Cl⁻ ion as AgCl confirms the presence of four chloride ions in the bimetallic species. Formation of the bimetallic complex by transfer of chloride ion is also evidenced by reaction of [Cu(pn)₂]Cl₂ with [M(PPh₃)₂Cl₂] where M = Co(II), Ni(II) (Scheme 3). Precipitation of triphenyl phosphine in this reaction indicates that it is replaced by chloride ions of the precursor.

3.1. Electronic spectra

Two types of absorption bands were observed for all the complexes in their UV–visible spectra (Figs. 1a, 1b). The intense band ranging from 250 to 300 nm is unambiguously attributed to the L → M charge transfer (Bernhardt et al., 2001). All compounds of Cu(II) with diamines exhibit a band around 250 nm which is assigned to ligand to metal charge transfer. Zelenak and co-workers have recently reported from the electronic spectral study and crystal structure that the UV band at 250 nm in [Cu(pn)₂]Cl₂ is attributed to ligand to metal charge transfer (Zelenak et al., 2006). Intraligand charge transfer does not occur in such complexes. Secondly, the Laporte-forbidden d–d transition (400–800 nm) is due to d⁹ of Cu(II) ion (Nami et al., 2010). The precursor complex [Cu(pn)₂]Cl₂ shows a broad d–d band at 630 nm which indicates an octahedral structure.

Table 1 Analytical data, color, melting point and conductance.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compounds</th>
<th>Elemental analysis found (Calcd.), %</th>
<th>Color</th>
<th>m.p. (°C)</th>
<th>Molar conductance (Scm² mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
<td>Cl</td>
</tr>
<tr>
<td>1.</td>
<td>[Cu(pn)₂]Cl₂</td>
<td>12.93</td>
<td>3.75</td>
<td>10.01</td>
<td>25.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(12.50)</td>
<td>(4.01)</td>
<td>(9.87)</td>
<td>(26.01)</td>
</tr>
<tr>
<td>2.</td>
<td>[Cu(pn)₂][CoCl₄]</td>
<td>17.01</td>
<td>4.04</td>
<td>12.91</td>
<td>26.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(16.50)</td>
<td>(4.35)</td>
<td>(12.48)</td>
<td>(26.78)</td>
</tr>
<tr>
<td>3.</td>
<td>[Cu(pn)₂][NiCl₄]</td>
<td>17.49</td>
<td>3.96</td>
<td>13.39</td>
<td>27.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(17.06)</td>
<td>(4.35)</td>
<td>(12.80)</td>
<td>(27.12)</td>
</tr>
<tr>
<td>4.</td>
<td>[Cu(pn)₂][CuCl₄]</td>
<td>17.94</td>
<td>4.95</td>
<td>14.08</td>
<td>26.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(17.46)</td>
<td>(4.85)</td>
<td>(13.58)</td>
<td>(27.05)</td>
</tr>
<tr>
<td>5.</td>
<td>[Cu(pn)₂][ZnCl₄]</td>
<td>17.47</td>
<td>5.00</td>
<td>13.34</td>
<td>25.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(17.02)</td>
<td>(5.27)</td>
<td>(13.63)</td>
<td>(26.23)</td>
</tr>
<tr>
<td>6.</td>
<td>[Cu(pn)₂][CdCl₄]</td>
<td>14.86</td>
<td>3.83</td>
<td>11.20</td>
<td>26.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(14.34)</td>
<td>(4.32)</td>
<td>(11.15)</td>
<td>(26.89)</td>
</tr>
<tr>
<td>7.</td>
<td>[Cu(pn)₂][HgCl₄]</td>
<td>13.27</td>
<td>3.40</td>
<td>10.06</td>
<td>27.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(13.20)</td>
<td>(3.89)</td>
<td>(9.48)</td>
<td>(27.83)</td>
</tr>
</tbody>
</table>
geometry. However in bimetallic complex the same band appears at ca. 680 nm, indicating the presence of square-planar geometry (Gaura et al., 1982). The spectra slightly differ from each other with regard to the position of the d–d band, while
the absorption band in the UV region remains nearly unaltered (Table 2). The peak in the visible region varies according to the nature of the metal. The \( \lambda_{\text{max}} \) in the visible region slightly increases with decreasing ionic radii of the metal ions.

**Figure 1b** Visible spectra of complexes.
Talbert et al. (1970), have suggested that \([\text{Cu(pn)}_2]\text{[CuCl}_4\text{]}\) is a complex salt with tetrahedrally coordinated chloro anion. We have observed a broad band at 279 nm in its electronic spectrum which is probably due to charge transfer from ligand to metal. It is also supported by additional (Cu–Cl) bands at 284 cm\(^{-1}\) and 234 cm\(^{-1}\) in its IR spectrum which is in agreement with values previously reported for \([\text{CuCl}_4]^{2-}\) ion (Figgis, 1976). The geometry of \([\text{CuCl}_4]^{2-}\) is, therefore, suggested to be tetrahedral stabilized by \([\text{Cu(pn)}_2]^2+\) ion (Parent et al., 2007).

### 3.2. IR spectra

As a consequence of the reaction of CuCl\(_2\) with 1,3-diaminopropane a square-planar Cu chelate complex is formed bearing

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compounds</th>
<th>(\nu(\text{NH}))</th>
<th>(\nu(\text{C–C}))</th>
<th>(\nu(\text{C–N}))</th>
<th>Ring vib.</th>
<th>(\nu(\text{Cu–N}))</th>
<th>(\nu(\text{M–X}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>([\text{Cu(pn)}_2]\text{Cl}_2)</td>
<td>3404</td>
<td>1027</td>
<td>1440</td>
<td>495</td>
<td>405</td>
<td>268</td>
</tr>
<tr>
<td>2.</td>
<td>([\text{Cu(pn)}_2][\text{CoCl}_4])</td>
<td>3281</td>
<td>1028</td>
<td>1460</td>
<td>500</td>
<td>417</td>
<td>283</td>
</tr>
<tr>
<td>3.</td>
<td>([\text{Cu(pn)}_2][\text{NiCl}_4])</td>
<td>3279</td>
<td>1028</td>
<td>1463</td>
<td>501</td>
<td>416</td>
<td>283</td>
</tr>
<tr>
<td>4.</td>
<td>([\text{Cu(pn)}_2][\text{CuCl}_4])</td>
<td>3283</td>
<td>1028</td>
<td>1455</td>
<td>501</td>
<td>416</td>
<td>284</td>
</tr>
<tr>
<td>5.</td>
<td>([\text{Cu(pn)}_2][\text{ZnCl}_4])</td>
<td>3282</td>
<td>1022</td>
<td>1465</td>
<td>495</td>
<td>401</td>
<td>281</td>
</tr>
<tr>
<td>6.</td>
<td>([\text{Cu(pn)}_2][\text{CdCl}_4])</td>
<td>3270</td>
<td>1022</td>
<td>1462</td>
<td>493</td>
<td>404</td>
<td>234</td>
</tr>
<tr>
<td>7.</td>
<td>([\text{Cu(pn)}_2][\text{HgCl}_4])</td>
<td>3277</td>
<td>1022</td>
<td>1465</td>
<td>491</td>
<td>418</td>
<td>227</td>
</tr>
</tbody>
</table>

![Figure 2](image_url)
The reaction of [Cu(pn)₂]Cl₂ with MCl₂ leads to the formation of [Cu(pn)₃][MCl₄] + 2PPh₃.

Scheme 3 Precipitation of triphenylphosphate.

two chloride ions out of the coordination sphere. The IR spectrum of the 1,3-diaminopropane (Table 3) shows two strong (N-H) absorption bands in 3450–3250 cm⁻¹ region which undergoes a negative shift after chelation with copper(II) forming a six membered ring (Feerrari et al., 1991; Silverstien et al., 1981; Nakamoto, 1986). The in-plane vibration of the six membered rings so formed may be expected to be coupled mechanically to some extent with metal nitrogen vibrational modes.

On the basis of normal coordinate analysis of the [M(en)]²⁺ ion with C₂ᵥ symmetry Omura et al. (1971) have assigned the ν(Cu–N) band in 472–412 cm⁻¹ region. We have noted strong bands in 400–420 cm⁻¹ region for all the complexes (Malik et al., 1983). The M–Cl stretching frequency (Kabanos et al., 1992) in the 250–380 cm⁻¹ region in our case indicates the presence of tetrahedral tetrachlorometallate anion (Exarchos et al., 2001). The bands in the 600–400 cm⁻¹ are assigned to in-plane ring deformation and NH₂ rocking modes (Nami and Siddiqi, 2004). All the ν(Cu–N) and ν(M–Cl) were placed on a firm basis by the initial studies on stretching vibrations of the MX₂⁻. However, it is clear from the previous work on ν(Cd–Cl) that these are invariably below 200 cm⁻¹ in octahedral complexes and only slightly above 200 cm⁻¹ in tetrahedral complexes. An additional IR band is observed in the region 230–350 cm⁻¹ which is assigned to M-Cl stretching frequency of [MCl₄]²⁻ moiety (Clark, 2010).

3.3. Thermogravimetry

The TGA profile of all the complexes are essentially similar and consists of four well defined stages implying their similar structural features. The weight loss corresponding to various steps in thermogram were compared with those calculated. The thermal analysis of [Cu(pn)₃][MCl₄] was studied (Fig. 2) in the temperature range 50–700 °C at a heating rate of 10 °C min⁻¹. During first break in the temperature range 150–250 °C, the weight loss of ~6.15% (cal. 6.01%) could be accounted for the loss of 3/2 mol of H₂O from the complex which is believed to be absorbed during storage. In the second step (250–340 °C) the weight loss of ~32.65% (cal. 33.33%) corresponds to the elimination of two moles of 1,3-diaminopropane moiety. In the third and fourth step two chloride ions are lost one by one at each step (340–430 °C) a weight loss of ~14.81% (Cal. 15.98%) and (430–700 °C) a weight loss of 13.95% (Cal. 15.98%). In the end the residue 28.63% corresponds to Cu bimetal (Materazzi et al., 2002).

4. Conclusion

The reaction of [Cu(pn)₂]Cl₂ with MCl₂ leads to the formation of [Cu(pn)₃][MCl₄]. As a consequence of the reaction of CuCl₂ with 1,3-diaminopropane a square-planar Cu(II) chelate complex is formed with two chloride ions out of the coordination sphere. The complex [Cu(pn)₂]Cl₂ may be pseudo octahedral but in its reaction with MCl₂, the chloride ion may be transferred to maintain an equilibrium between the two species. In such complexes, the central metal ion in cationic form explicitly exists in square-planar environment, however, the anionic counterpart maintains its ubiquitous tetrahedral configuration.

Acknowledgments

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Please cite this article in press as: Yadav, S. et al., Synthesis and characterization of heterobimetallic complexes of the type \([\text{Cu(pm)}_2][\text{MCl}_4]\) where \(M = \text{Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II)}\). Arabian Journal of Chemistry (2012), http://dx.doi.org/10.1016/j.arabjc.2012.04.045
Kinetics and Mechanism of Nucleophilic Substitution in SnR₂Cl₂ · 2DMSO by Chloride Ions in Micellar Microenvironment

The kinetics of nucleophilic substitution of dimethylsulfoxide by chloride ion in bis-dimethyl sulfoxide dimethylthion(V) dichloride and bis-dimethyl sulfoxide diphenylvin(V) dichloride in micellar microenvironment (1.0 × 10⁻² M SDS in aqueous solution of ethanol (1:1, v/v)) has been studied conductometrically. The reactions have been carried out at 25°C. Substitution follows first order path with respect to chloride ion concentration. A millimolar solution of the complexes in ethanolic solution of 1.0 × 10⁻² M SDS shows an increase in conductance with time due to solution of the molecule. Sn(CH₃)₂Cl₂ · 2 DMSO shows high conductance as compared to Sn(C₆H₅)₂Cl₂ · 2 DMSO. In the presence of the nucleophilic reagents, C₆H₅COCl and CH₃COCl there is a greater enhancement in conductance due to substitution of DMSO by chloride ion. The data of rate constant for solvation (Kₛ) and for nucleophilic substitution (K₁ and K₃) have been calculated. It was found that the solvation is a slower process compared to the substitution by chloride ions i.e., Kₛ, K₃ > Kₛ. A possible mechanism has been suggested.

Key words: Solvation, nucleophilic substitution, sodium dodecyl sulfate, micelles

Kinetik und Mechanismus der nucleophilen Substitution in SnR₂Cl₂ · 2 DMSO durch Cloridionen in mikellarer Mikroumgebung. Die Kinetik der nucleophilen Substitution von Dimethylsulfoxid mit Chlorid in Bis-dimethylsulfoxid-dimethylthion(V)-dichlorid und Bis-dimethylsulfoxiddiphenylvin(V)dichlorid in mikromizellarer Umgebung (1.0 × 10⁻² M SDS in wässriger ethanoler Lösung (1:1, v/v)) wurde konduktometrisch untersucht. Die Reaktionen wurden bei 25°C durchgeführt. Es handelte sich um Reaktionen Erster Ordnung in Bezug auf die Chloridkonzentration. Eine millimolare Lösung des Komplexes in ethanolischer Lösung mit 1.0 × 10⁻² M SDS zeigt eine Zunahme der Leitfähigkeit mit der Zeit aufgrund der Solvatisierung der Moleküle. Sn(CH₃)₂Cl₂ · 2 DMSO hatte im Vergleich zu Sn(C₆H₅)₂Cl₂ · 2 DMSO eine hohe Leitfähigkeit. In Gegenwart der nucleophilen Reagenzien C₆H₅COCl und CH₃COCl ist die Leitfähigkeit stärker erhöht aufgrund der Substitution von DMSO durch Chlorid. Die Geschwindigkeitskonstanten der Solvatisierung (Kₛ) und für die nucleophilen Substitution (K₁ und K₃) wurden berechnet. Es wurde gefunden, dass die Solvatisierung im Vergleich zur Substitution mit Chlorid ein langsamerer Vorgang ist, d.h., Kₛ, K₃ > Kₛ. Ein möglicher Reaktionsmechanismus wurde vorgeschlagen.

Stichwörter: Solvation, nucleophile Substitution, Natriumdodecylsulfat, Micellen

1 Introduction

From green chemistry viewpoint, water/alcohol mixtures would be the perfect solvent to carry out chemical reactions. In many cases, due to hydrophobic effects, water/alcohol system not only accelerates the reaction rates, but also enhances the reaction selectivities, even when the reactants are sparingly soluble or insoluble in this medium. Surfactants which are usually organic compounds that are amphiphilic and contain both hydrophobic (their lipophilic tails called micelles) and hydrophilic groups (called their heads) (Figure 1) have been recently employed to facilitate the reactions in water/alcohol system. A micelle in surfactants sticks with the reactant and due to heavy head settles down into the solvent from surface and thus increases the collision of two reactants and makes a favourable condition for reaction in water/alcohol medium. The behaviour of sodium dodecyl sulphate (SDS) micelles in the presence of n-alkanols has been well documented in literature [1–9]. It has been seen that in aqueous ethanolic solution of SDS micelles are formed which consist of two separate microphases: nonpolar micellar core formed by hydrophobic parts of amphiphiles and the polar surface layer formed by their head groups [10]. The hydrophobic effect mainly contributes to the micellization in aqueous ethanolic solution. The CMC of SDS in dilute aqueous solution of alcohols decreases with increasing concentration of alcohols [11, 12]. The CMC is almost independent of the temperature. Xiang and co-workers [13] have recently reported that CMC of SDS in ethanol continuously decreases with its increasing concentration. The CMC of SDS in pure water (8.491 × 10⁻⁴) becomes to 6.426 × 10⁻⁴ mol L⁻¹ at 1:1 (v/v) ethanol/water ratio. However, extraction of an organic compound becomes more effective with increasing value of ethanol.

Octahedral tin(IV) complexes have a wide range of application as catalysts, stabilizers, biocides, wood preservatives, and antitumor and -viral agents [14–23]. The kinetics of nucleophilic substitution of octahedral tin(IV) complexes has been extensively reported in literature [24–28]. To our knowledge, however, no work has been reported in the literature concerning the nucleophilic substitution of octahedral tin(IV) complexes in micellar system. As an extension of our previous work on the kinetics and mechanism of substitution reactions [26–28], we report herein, the kinetics of solvation of the complex SnR₂Cl₂ · 2 DMSO (R = methyl or phenyl) and the mechanism of substitution of dimethylsulphoxide (DMSO) by chloride ion supplied by nucleophilic reagents, such as C₆H₅COCl and CH₃COCl in micellar solu-

Figure 1 Sodium dodecyl sulphate (a common anionic surfactant)
tion. It is quite obvious from the change in conductance that the substitution reaction in micellar system is occurring otherwise the conductance would have been remained constant. When nucleophile is added to the substrate the conductance further increases, which is an additional proof that the reaction is occurring in two steps with changes in conductance that become finally stable. A probable mechanism for substitution has been proposed (Scheme I).

2 Materials and Methods

Kinetic studies were performed with a CM-82T Elico conductivity meter. SnR₂Cl₄, sodium dodecylsulfate, toluene, C₆H₅COCl, CH₃COCl were used as received. Ethanol was distilled before use. Double distilled water was used throughout the experiment.

2.1 Preparation of dimethyl sulfoxide complexes

The complexes were prepared by mixing the appropriate dialkyl- or diaryl-tin dichloride with dimethyl sulfoxide, both dissolved in toluene in 1:2 molar ratios [29]. The complexes, which separate rapidly at room temperature, were collected as stable white crystalline solids about yield 88–90%. Melting point of Sn(CH₃)₂Cl₂·2DMSO and Sn(C₆H₅)₂Cl₂·2DMSO are 110° and 120°C respectively.

Millimolar solution of SnR₂Cl₄·2DMSO (R = methyl or phenyl) was prepared in 1.0 × 10⁻² M SDS containing water-ethanol (1:1, v/v) system and its conductance was measured as a function of time. From the slope of the linear portion of the molar conductance versus time curve (Fig. 2), the specific rate constant for solvation, Kₛ was calculated. The solutions of the nucleophile (benzoyl chloride or acetyl chloride) and the complex were mixed separately in three different molar ratios. The conductance of each set was measured immediately and after 20 minute interval for a period of 220 min. The limiting conductance (Δ₀) was measured after 24 h.

3 Results and Discussion

The conductance of millimolar solutions of the complexes in SDS-water-ethanol system increases with time. The molar

Scheme 1 Proposed mechanism of nucleophilic substitution of dimethyl-sulfoxide by chloride ion in SnR₂Cl₄·2DMSO (where R = CH₃ or C₆H₅)
conductance, AM versus time curve for substitution was similar to those obtained for solution (Figure 2). From the linear portion of the plots of complexes the specific rate constant for solution, Ks were calculated. It was found to be about 1.0 × 10⁻³ S⁻¹.

On plotting log [ΔM/ΔM] against time a linear plot was obtained for different molar ratios of the reactants. In the substitution reaction by Cl⁻ ion, two mutually intersecting linear portions of the graph were obtained (Figure 3). From the slopes of first and second linear portions of the graphs, the specific rate constants, K₁ and K₂, for stepwise replacement of the dimethylsulphoxide from the substrate were estimated respectively using the method of two mutually intersecting lines; the values of K₁ and K₂ are presented in Table 1.

From equation

$$K = \frac{2.303}{t} \log \frac{\Delta M}{\Delta M_s}$$

the first order rate constants were calculated. From Table 1, it is evident that as compared to Sn(C₆H₅)₂Cl₂·2DMSO, Sn(CH₃)₂Cl₂·2DMSO showed high rate constant values (K₁ and K₂) (Table 1). However, the rate constant (K₁ and K₂) of C₆H₅COCl was found greater as compared to CH₃COCl.

In the absence of the nucleophile the rate of increase in molar conductance in the initial stage is low as compared to that in the presence of nucleophile. This may be due to the solution of the complex followed by substitution of DMSO by Cl⁻. The substitution of DMSO by chloride ions supplied by nucleophilic reagents may follow either the first order dissociation of DMSO from the complex followed by a rapid addition of chloride ions or a second order reaction with the simultaneous addition of chloride ions or the dissociation of DMSO. However, in the present case, it was observed that

![Figure 2](image1.png)  
Molar conductance versus time curves: (a) for solvation of (C₆H₅)₂SnCl₂·2DMSO and (b) for solvation of (CH₃)₂SnCl₂·2DMSO in 1.0 × 10⁻² M SDS containing water-ethanol (1:1, v/v) system

![Figure 3](image2.png)  
First order plots for the substitution of Sn(CH₃)₂Cl₂·2DMSO by benzoyl chloride in different molar ratios

<table>
<thead>
<tr>
<th>Complex</th>
<th>Nucleophilic reagent</th>
<th>Ratio</th>
<th>K₁ × 10⁻⁴ (S⁻¹)</th>
<th>K₂ × 10⁻⁴ (S⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)₂SnCl₂·2DMSO</td>
<td>C₆H₅COCl</td>
<td>1:1</td>
<td>4.3</td>
<td>9.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:2</td>
<td>4.3</td>
<td>9.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>large</td>
<td>4.3</td>
<td>9.8</td>
</tr>
<tr>
<td>(CH₃)₂SnCl₂·2DMSO</td>
<td>CH₃COCl</td>
<td>1:1</td>
<td>4.0</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:2</td>
<td>4.0</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>large</td>
<td>4.0</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Table 1 Rate constant for substitution of dimethyl sulphoxide by chloride ion in the complexes Sn(CH₃)₂Cl₂·2DMSO and Sn(C₆H₅)₂Cl₂·2DMSO.
the reaction follows the first order (Sn1) pathway. The rate of increase in conductance during the substitution reactions confirms that the chloride ion is a stronger nucleophile than DMSO. In this study, equilibrium was attained after about 3 h & 40 min.

4 Conclusion

We are reporting for the first time the kinetics of solvation of the complex SnR₂Cl₂ - 2DMSO (R = methyl or phenyl) and the mechanism of substitution of dimethyl sulfoxide (DMSO) by chloride ion supplied by nucleophilic reagents, such as C₂H₅COCl and CH₃COCl in ethanol/water mixture (1:1, v/v) using SDS (1.0 x 10⁻⁴ M) as an anionic surfactant. It is quite obvious from the change in conductance that the substitution reaction is occurring in micellar system. When nucleophile is added to the substrate the conductance further increases, which is an additional proof that the reaction is occurring in two steps with change in conductance that finally becomes stable.

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References


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