Synthetic, spectroscopic and superoxide dismutase studies of some copper(II)-zinc(II) containing heterobimetallic complexes of tetradeinate \(\text{N}_2\text{O}_2\) donor Schiff bases

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Heterobimetallic complexes containing copper(II)-zinc(II) ions with a series of Schiff bases viz., \(\text{N},\text{N}^\prime\)-hexylene/heptylene/octylene/dodecaline bis(acetylace-tonimine) (~L4 respectively) containing \(\text{N}_2\text{O}_2\) donor atoms have been prepared and characterized by elemental analyses, magnetic moments, conductance measurements, IR, electronic and ESR spectral data. The complexes derived from \(\text{L}1\) and \(\text{L}3\) have also been evaluated for their superoxide dismutase (SOD) activity using alkaline dimethylsulphoxide as superoxide generating system and nitroblue tetrazolium chloride (NBT) as superoxide scavenger.

Binuclear complexes are of extensive investigation in recent years owing to their biological and industrial application1. Heterobinuclear complexes particularly those comprising of copper(II) and zinc(II) within the same ligand framework are gaining momentum due to their mimicking behaviour with active centre of copper-zinc superoxide dismutase enzyme2,3.

The present work is a part of our continued effort in the area of synthetic dinuclear chemistry4,5. A systematic variation of alkyl chain has been made to study their effect on the geometry and SOD activity of the complexes in the light of earlier reports6,7.

Experimental
All the chemicals used were purchased from S D Fine Chemicals (India). The other chemicals were of AR grade and were used as such. The solvents used were purified by standard methods8.

General procedure
The Schiff bases (\(\text{L}1\)-\(\text{L}4\)) were prepared by the procedure of Martell et al9. The complexes were prepared adopting the following general method.

A methanolic solution of \(\text{CuCl}_2\), \(\text{ZnCl}_2\) (each 0.50 mmol in 50 ml methanol) was added separately to a 50 ml solution (methanol-chloroform, 50% v/v) of respective Schiff bases (1 mmol) with constant stirring under nitrogen atmosphere over a period of 20 min followed by the addition of 5-6 drops of triethylamine.

The respective reaction mixtures were boiled under reflux on a steam bath for 2 h followed by the reduction of their volumes to 20 ml under reduced pressure. The reaction mixtures were then stored in a refrigerator for overnight. The blue-green microcrystalline solids thus obtained were filtered and washed successively with small volumes of methanol followed by chloroform and diethyl ether and then dried in vacuo over anhydrous \(\text{CaCl}_2\).

The infrared spectra (KBr pellets, 4000-400 cm\(^{-1}\) nujol mull 400-200 cm\(^{-1}\)) were recorded on JASCO FT/IR-5300 and Perkin Elmer 883 infrared spectrophotometers respectively. The electronic spectra (nujol mull) were recorded on Cary 2390 spectrophotometer. The powder and solution (in dil. glacial acetic acid) ESR spectra were recorded (at room temperature and liquid nitrogen temperature) on a Varian E 109 ESR spectrometer at the Chemistry Department, University of Leicester, U.K.

The elemental analyses were carried out at the CDRI, Lucknow, while metals and chlorine were estimated by literature procedure10. The molar conductance values in DMSO (~10 \(^{-3}\) M) were recorded on a Scientronic digital conductivity meter. The magnetic susceptibilities were measured on Cahn-Faraday electrobalance and magnetic moments were calculated making diamagnetic corrections using appropriate Pascal's constants11. The superoxide dismutase activity of two of the complexes viz. [\(\text{CuZn(L}4\).2MeOH\)] and [\(\text{CuZn(L}3\).2MeOH\)] were measured by the literature procedure2.

Results and discussion
The elemental analyses of Schiff bases and their metal complexes along with their electronic and magnetic moment data are reported in Table 1. The molar conductance values (32.6-11.5 ohm\(^{-1}\)
cm$^2$ mol$^{-1}$) for complexes suggested their non-electrolytic nature$^{12}$.

The IR spectra showed that in schiff bases, $\nu \text{N} - \text{H}$ observed in the range 3445-3474 cm$^{-1}$ was shifted to 3424-3439 cm$^{-1}$ in the complexes while $\delta \text{N} - \text{H}$ (1608-1612 cm$^{-1}$) in schiff bases shifted to 1579-1584 cm$^{-1}$ in the corresponding complexes. The doublets observed for $\nu \text{C} - \text{H}$ in the range 2930-2997 and 2851-2860 cm$^{-1}$ in the free schiff bases were shifted to 2922-2924 and 2851-2855 cm$^{-1}$ respectively in complexes. The peak observed in the range 1566-1575 cm$^{-1}$ (ref. 13) due to $\nu \equiv \text{C} = \equiv \text{O}$ in free schiff bases shifted to 1521-1530 cm$^{-1}$ on complexation. Furthermore, $\rho (\text{N} - \text{H})$ and $\rho (\text{CH}_2)$ of free schiff bases observed between 864-887 and 783-800 cm$^{-1}$ respectively shifted to 881-938 and 781-791 cm$^{-1}$ in the complexes$^{13}$. The coordination of methanol in all complexes was supported by the observation of a band in the region 3575-3610 cm$^{-1}$ (ref. 14).

In the complexes, weak bands observed between 425-440 and 415-420 cm$^{-1}$ were assigned to $\nu \text{Cu} - \text{N}$ and $\nu \text{Zn} - \text{N}$ respectively$^{15}$ while peaks in far IR region observed at 342-346 and 325-315 cm$^{-1}$ were assigned to $\nu \text{Cu} - \equiv \text{O} = \equiv \text{C}$ and $\nu \text{Zn} - \equiv \text{O} = \equiv \text{C}$ respectively$^{16}$. The peaks observed at 310 and 285 cm$^{-1}$ could be assigned to $\nu \text{M} - \equiv \text{Cl}$ where $\text{M} = \text{Cu(II)}$ and $\text{Zn(II)}$. The presence of bridged chlorine was considered on the basis of peak observed in 275-270 cm$^{-1}$ region$^{17}$.

The effective magnetic moments of the complexes (2.04-2.17) are in the range reported for other Cu(II) species in distorted octahedral coordination environment$^{18}$. The magnetically silent Zn(II) has no effect on magnetic moment value of Cu(II) in complexes. The electronic spectra of the complexes exhibited bands in the range 700-712 nm [low intensity and 490-566 nm (high intensity)] which were assigned to $d-d$ and charge transfer transitions respectively. The range of $d-d$ bands agreed well with the tetragonally distorted octahedral coordination around Cu(II) reported in the literature$^{19}$. The red shift in $d-d$ transitions may be a consequence of increasing extent of distortion due to stepwise increase in polymethylene chain length connecting the two halves of the ligands as reported by Bereman et al. and others for similar type of systems$^{6,7}$.

In order to observe the effect of increasing polymethylene chain length on the distortion of coordination geometry around Cu(II) in complexes, ESR spectra of the complexes at room temperature and liquid nitrogen temperature were re-
Table 2 – Electron spin resonance values for Cu(II) complexes

g-values
<table>
<thead>
<tr>
<th>Compounds</th>
<th>Solid</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>Solution</th>
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<td></td>
<td>r.t.</td>
<td>l.n.t.</td>
<td>r.t.</td>
<td>l.n.t.</td>
<td></td>
<td>A values (solution)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[CuZn(L1)2MeOH]</td>
<td>2.2797</td>
<td>2.1009</td>
<td>2.3143</td>
<td>2.0965</td>
<td></td>
<td>$A_{1}^{63}$Cu&lt;sup&gt;10&lt;/sup&gt;-4 (cm&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>148</td>
<td></td>
</tr>
<tr>
<td>[CuZn(L2)2MeOH]</td>
<td>2.3021</td>
<td>2.1165</td>
<td>2.3261</td>
<td>2.0961</td>
<td></td>
<td>$A_{1}^{14}$N (cm&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>147</td>
<td>10</td>
</tr>
<tr>
<td>[CuZn(L3)2MeOH]</td>
<td>2.3140</td>
<td>2.1181</td>
<td>2.3486</td>
<td>2.1145</td>
<td></td>
<td>$A_{1}^{14}$N (cm&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>142</td>
<td></td>
</tr>
<tr>
<td>[CuZn(L4)2MeOH]</td>
<td>2.3379</td>
<td>2.1217</td>
<td>2.3602</td>
<td>2.0769</td>
<td></td>
<td>$A_{1}^{14}$N (cm&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>146</td>
<td></td>
</tr>
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The powder and solution spectra of complexes showed $g_{\|}$ and $g_{\perp}$ pattern only and the corresponding values were found to be consistent with distorted octahedral coordination around Cu(II) in complexes with $d_{x^2-y^2}$ ground state<sup>18</sup>. However, superhyperfine splitting either due to $^{63}$Cu or $^{14}$N could not be observed. The increase in $g_{\parallel}$ values with the corresponding increase in polymethylene chain length further substantiated our speculation derived from electronic spectra of complexes that increase in chain length of polymethylene unit leads to distortion around Cu(II) in the complexes<sup>6,7</sup>. However, room temperature solution ESR spectra of the complexes showed reverse pattern in $g_{\parallel}$ values. This may arise due to bridge cleavage between Cu(II) and Zn(II) in solution resulting into a comparative relief from distortion around metallic centres. But the earlier pattern was resumed in the liquid nitrogen temperature spectra of the complexes where $g_{\parallel}$ values (Table 2) were also found to be consistent with distorted octahedral coordination around Cu(II) in complexes<sup>18</sup>. The ESR spectrum of [CuZn(L4)2MeOH] at liquid nitrogen temperature exhibited four lines in parallel region due to hyperfine splitting caused by $^{63}$Cu values (Table 2) for the complexes. They were found to be in agreement with a recent report by Solomon et al. for copper-zinc superoxide dismutase enzyme<sup>20</sup>. No superhyperfine splitting due to $^{14}$N either in parallel or perpendicular region except in the case of [CuZn(L2)2MeOH] was observed in liquid nitrogen temperature spectra of the complexes. Interestingly, we observed superhyperfine splitting in perpendicular region of liquid nitrogen temperature spectrum of [CuZn(L4)2MeOH]. This splitting could arise due to coupling of hydrogen nuclei (two $-CH_{3}$ groups and one of $=CH$ group) with unpaired spin of Cu(II) as a consequence of spin polarisation<sup>21</sup>. Furthermore, the origin of this superhyperfine splitting due to $^{14}$N was discarded since the total number of lines were found to be eight instead of five.

This observation could be used as another clue for the presence of Zn(II) in the same ligand framework along with Cu(II). Had there not been any ESR silent species like Zn(II) in the present case, there would have been further splitting of eight lines in perpendicular region due to interaction of another seven hydrogen nuclei from seven C−H bonds of another half of the ligand. A single crystal for X-ray studies could not be
grown due to very poor solubility of the complexes in low boiling solvents.

Thus on the basis of above studies a tentative structure (Structure I) has been proposed for the complexes.

![Structure I](image)

The superoxide dismutase activity was assayed by the use of alkaline dimethyl sulphoxide as a superoxide anion generating system in association with nitrobluetetrazolium chloride as scavenger of superoxide. The preferential use of alkaline dimethyl sulphoxide as a source of superoxide ion was based upon earlier reports. The absorbance ($\lambda_{\text{max}}$ 560 nm) was monitored at different concentrations of the complexes. A representative plot of inhibition with increasing concentration of the complex [CuZn(L4).2MeOH] is given (Fig. 1) and the % inhibition was calculated by the relation,

$$\% \text{ inhibition} = \frac{(a) - (b)}{a} \times 100$$

a = absorbance without adding any complex.

b = absorbance in presence of a particular concentration of complex.

Unit superoxide dismutase activity is considered as concentration of complex or enzyme which causes 50% inhibition of alkaline dimethyl sulphoxide mediated reduction of nitrobluetetrazolium chloride (NBT).

The s.o.d. activity observed for [CuZn(L4).2MeOH] at 100 $\mu$M (Fig. 1) as compared to the same activity observed for [CuZn(L4).2MeOH] at 277.5 $\mu$M could be explained in terms of decreasing ligand field strength and increasing distortion in previous complex as compared to the latter.

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References