

PII: S0277-5387(96)00277-X

# Study of Cu<sup>II</sup> binuclear complexes of binucleating hexadentate ligands

C. A. Sureshan and P. K. Bhattacharya\*

Department of Chemistry, Faculty of Science, M.S. University of Baroda, Baroda 390 002. India

(Received 8 December 1995; accepted 3 June 1996)

Abstract—Three types of tridentate binucleating Schiff base ligands have been synthesised by condensation of 5,5'-methylenebis-salicylaldehyde with aminoalcohols, aminoacids or aminoethylpyridine. These ligands have two sets of tridentate phenolate  $O^-$ , azomethine N and  $O^-$ ,  $COO^-$  or pyridyl nitrogen coordination sites. The binuclear Cu<sup>II</sup> complexes of these ligands have been prepared and their spectral, magnetic and electrochemical properties have been studied. On the basis of these experimental results long range spin exchange interaction between two copper centres has been indicated. Copyright © 1996 Elsevier Science Ltd

*Keywords*: copper(II) complexes; binuclear complexes; hexadentate ligands; Schiff base; binucleating ligands; magnetic interactions.

In recent years the study of binuclear copper(II) complexes has been a subject of considerable interest because of their structural, magnetic, ESR and electrochemical properties.

In our laboratory Cu<sup>II</sup> complexes of binucleating ligands with two bidentate sites separated by aromatic rings have been studied earlier [1-3]. In such complexes with  $\pi$  delocalised bridges, the spin exchange has been suggested to be through  $\sigma$  bonds [4,5]. Spin exchange interaction between Cu<sup>II</sup> centres separated by  $\sigma$  bonding aliphatic chain has also been studied [6– 9]. In the present study, binucleating ligands with two tridentate coordination sites have been synthesised. They are of three types. The first type of ligand was obtained by the condensation of 5,5'-methylenebissalicylaldehyde (MBS) and aminoalcohols. These ligands have phenolate O<sup>-</sup>, azomethine N and alkoxide O<sup>-</sup> coordination sites. The second type of ligands was prepared by the condensation of above mentioned dialdehyde (MBS) and aminoacids and have phenolate O<sup>-</sup>, azomethine N and carboxylate COO<sup>-</sup> coordination sites. The third type of ligands was prepared by the condensation of MBS with aminoethylpyridine and have phenolate O<sup>-</sup>, azomethine N and pyridyl N coordination sites. Binuclear complexes of these ligands with Cu<sup>2+</sup> ions have been prepared and characterized by spectral, magnetic and electrochemical studies.

### **EXPERIMENTAL**

Chemicals

5'5-Methylenebis-salicylaldehyde (MBS) was prepared by the method reported earlier [10]. Glycine (gly),  $\alpha$ -alanine ( $\alpha$  ala), phenylalanine (pha), valine (val), ethanolamine (ea), propanolamine (pa), 2-aminobutanol (L<sub>2</sub>ab), aminoethylpyridine, methanol, dimethylformamide, tetrabutylammonium tetrafluoroborate and CuCl<sub>2</sub>·2H<sub>2</sub>O used were of A.R. grade.

Preparation of binucleating ligands using MBS and aminoalcohols (I)

5'5-Methylenebis-salicylaldehyde (5 mmol) was dissolved in 50 cm<sup>3</sup> of benzene and to this 10 mmoles of aminoalcohol (ea, pa,  $L_2ab$ ) solution in 20 cm<sup>3</sup> of benzene was added dropwise. The solution was refluxed for 3 h and the azeotrope was separated. Excess benzene was distilled out and the solid obtained was washed thoroughly with benzene and recrystallized from benzene. Yield : compound I<sub>A</sub> 1.1 gm (62%); compound I<sub>B</sub> 1.2 gm (65%); compound I<sub>C</sub> 1.2 gm (63%).

# Preparation of binucleating ligand using MBS and aminoacids (II) or aminoethylpyridine (III)

MBS (5 mmol) was suspended in 150 cm<sup>3</sup> of methanol. To this 10 mmoles of aminoacid (gly, ala, val or

<sup>\*</sup> Author to whom correspondence should be addressed.

pha) or aminoethylpyridine were added. The solutions were stirred for about five hours. The volumes of methanol were reduced to ~20 cm<sup>3</sup>. The yellow crystalline products separated were washed with benzene and recrystallized from methanol. Yield: compound II<sub>A</sub> 1.1 gm (62%); compound II<sub>B</sub> 1.2 gm (60%); compound II<sub>D</sub> 1.9 gm (70%); compound III<sub>A</sub> 1.2 gm (53%).

#### Method I

#### Synthesis of binuclear complexes of ligand I and II

(a) To 2 mmol of binucleating ligand I or II in 50 cm<sup>3</sup> methanol, were added 8 mmoles of lithium methoxide, to raise the pH. This solution was added to 4 mmoles of  $CuCl_2 \cdot 2H_2O$  in 10 cm<sup>3</sup> methanol. The resulting product was stirred for 1 h, filtered, washed thoroughly with methanol and dried *in vacuo*.

(b) To 2 mmol of MBS and 4 mmol of aminoalcohol (ea, pa,  $L_2ab$ ) or aminoacid (gly, ala, pha, val) in 50 cm<sup>3</sup> of methanol, 8 mmol of lithium methoxide were added to raise the pH. The solutions were stirred for 2 h, 4 mmol of CuCl<sub>2</sub> · 2H<sub>2</sub>O in 20 cm<sup>3</sup> of methanol were added. The reaction mixture was further stirred for one hour, the complex formed was filtered, washed with methanol and dried *in vacuo*.

### Method II

# (a) Synthesis of binuclear complex of ligand III with $ClO_4^-$ counter ion

2 mmol of ligand III were dissolved in 25 cm<sup>3</sup> of methanol and to this were added 4 mmol of  $Cu(ClO_4)_2 \cdot 6H_2O$  in 15 cm<sup>3</sup> methanol. The solution was stirred for 1 h. The solid obtained was filtered and washed with methanol and dried *in vacuo*.

# (b) Synthesis of binuclear complex of ligand III with $Cl^-$ counter ion

2 mmol ligand III were dissolved in 25 cm<sup>3</sup> methanol and to this were added 4 mmol of  $CuCl_2 \cdot 2H_2O$  in 15 cm<sup>3</sup> methanol. The solution was stirred for  $\sim 10$  h. The solid obtained was filtered and washed with methanol and dried *in vacuo*.

### Physical measurements

C and H analyses were performed on Coleman analyzer model-33 and nitrogen was estimated by Dumas' method. Copper was estimated gravimetrically as copper oxide. Magnetic measurements were carried out using a Gouy balance at room temperature. The analytical data have been presented in Table 1. IR spectra (as KBr pellets) were recorded on a Shimadzu IR 408 spectrophotometer. The electronic spectra were recorded on a Shimadzu UV-vis spectrophotometer UV-240. Their diffuse reflectance spectra were recorded on the same instrument, equipped with spherical reflectance assembly, using BaSO<sub>4</sub> as a reference material. Thermogravimetric studies were carried out by using as thermal analyser, a Shimadzu D.T. 30 instrument. The ESR spectra were recorded by using a Varian E-15 spectrometer and TCNE was used as the marker.

The electrochemical unit consisted of model 174A polarographic analyzer, universal programmer, x-y recorder, platinum working electrode and Pt wire auxiliary electrode. Ag/AgNO<sub>3</sub> was used as the reference electrode.

#### **RESULTS AND DISCUSSION**

The analyses of the complexes correspond to the following binuclear formula (Fig. 1).

#### Electronic spectra

The electronic spectra of complexes II<sub>B</sub>, II<sub>C</sub>, II<sub>D</sub> and III<sub>A</sub> in DMF solution exhibit a broad band in the region 630–690 nm and four bands at 500, 380, 270 and 240 nm. Similar bands are observed in reflectance spectra of the complex also. The band in the 630–690 nm region corresponds to d-d transitions and is

Table 1. Preparative yields, analytical, magnetic and TGA data for the binuclear complexes"

Compound no.	Yield	С	Н	N	Cu	$\mu_{ m B}$	% Weight loss	Temperature range
I <sub>A</sub>	0.68 g 68%	45.2 (45.5)	4.6 (4.4)	5.5 (5.5)	24.9 (25.3)	1.3	7	180-200
IB	0.66 g 63%	47.5 (47.6)	4.7 (4.9)	5.1 (5.3)	23.7 (24.0)	1.1	7	170-190
Ic	0.73 g 65%	49.1 (49.2)	5.9 (6.1)	4.9 (5.0)	22.4 (22.6)	1.1	6	180-210
IIA	0.70 g 66%	42.9 (43.1)	3.5 (3.5)	5.1 (5.3)	23.8 (24.0)	1.3		
IIB	0.70 g 63%	45.2 (45.1)	3.9 (3.9)	4.9 (5.0)	23.2 (22.7)	1.3	7	190-220
II <sub>C</sub>	0.76 g 62%	51.4 (51.6)	5.3 (5.2)	4.8 (4.8)	21.4 (21.8)	1.2		
IID	0.85 g 60%	55.6 (55.8)	4.4 (4.2)	3.9 (3.9)	17.6 (17.9)	1.3	5	190-210
III <sub>A</sub>	0.91 g 55%	42.5 (42.2)	3.9 (3.6)	6.7 (6.8)	15.1 (15.4)	1.2		
III <sub>B</sub>	0.61 g 46%	53.0 (52.7)	4.2 (3.9)	8.3 (8.5)	19.0 (19.2)	1.2	1	100-110

"Calculated values are in parentheses.



indicative of square planar geometry around the metal ion. The ligand occupies three positions with one water molecule completing the fourth coordination position [11,12]. The band at around 500 nm is a charge transfer band from phenolate oxygen to Cu<sup>II</sup>. The bands 380, 270, 245 nm have previously been assigned to ligand related  $\pi_1^* \leftarrow \pi$  and  $\pi_2^* \leftarrow \pi$  transition [13,14] and appear in all spectra. They are consistent with dianionic form of Schiff base formed by salicylaldehyde and amino acids and their complexes previously reported [15-17]. This confirms the presence of the salicylaldimine group. The complexes  $I_A$ ,  $I_B$ ,  $I_C$  and  $II_A$  are insoluble and hence only reflectance spectra could be recorded. The bands appearing at 630-690 nm, 500, 380, 270 and 245 nm are similar to the spectra for the complexes  $II_B$ ,  $II_C$  and  $II_D$ . The reflectance spectrum of complex III<sub>B</sub> shows d-d band in the region 830-860 nm. Compared to the perchlorate containing complex III<sub>A</sub> and neutral complexes I and II the bands in the complex III<sub>B</sub> occurs at lower energy. Further, the spectra of II<sub>B</sub>, II<sub>C</sub> and II<sub>D</sub> in DMF and III<sub>A</sub> in DMF or dioxan/water solution do not show significant change from the reflectance spectra, whereas  $III_B$  on dissolution in water/dioxan exhibits spectra different from that in solid phase. A broad *d*-*d* band is observed in the range 630–690 nm similar to all other complexes in solution. This shows that there may be chloride bridges in the  $III_B$  complexes resulting in tetranuclear complexes. The chloride bridges break on dissolution in water with consequent change in the spectrum. The fact that the neutral complexes I and II and perchlorate complex III<sub>B</sub> show no significant change on dissolution, indicates the absence of interdinuclear complex interaction in these complexes.

## IR spectra

The IR spectra obtained for these complexes are in agreement with proposed structures. For the IR spectrum of the complex III<sub>A</sub> perchlorate band is observed at 1100 cm<sup>-1</sup>. The band at ~900 cm<sup>-1</sup> is absent and there is no splitting of the 1100 cm<sup>-1</sup> band indicating that perchlorate is tetrahedral and is outside the coordination sphere.

## Magnetic and ESR data

Room temperature magnetic measurements showed  $\mu_B 1.1-1.3$  for binuclear complexes. These lower magnetic moments indicate antiferromagnetic interaction between the two metal centers at room temperature. The ESR spectra of samples I<sub>C</sub>, II<sub>A</sub>, II<sub>B</sub> and II<sub>D</sub> were carried out at room temperature in powder form and for III<sub>A</sub> the spectra were recorded at room temperature in powder form as well as frozen solution spectra in DMF. The *g* values are shown in Table 2 and one spectrum is shown in Fig. 2. Observation of

Table 2. Electrochemical data and ESR parameters of some complexes

	Cathodic pe			
Compound no.	$E_{\rm PC}^{\rm I}$	$E_{ m PC}^2$	$g_{\parallel}$	$g_{\perp}$
I <sub>C</sub>		_	2.042	2.18
IIA			2.045	2.19
IIB	-0.97	-1.40	2.043	2.19
IIc	-0.98	-1.42		
IID	-0.98	-1.43	2.014	2.191
III <sub>A</sub>	-0.92	1.24	2.038	2.189

"Potentials are given in volts.

 $g_{\parallel}$  and  $g_{\perp}$  indicates tetragonal distortion and supports square planar structure. Even though the antiferromagnetic interaction is there the  $\Delta ms = 2$  i.e., half field signals are not observed, probably due to large zero field splitting [6,18].

As the two metal atoms are far apart and the molecule is not flexible, the interaction can be through  $\sigma$ and  $\pi$  orbitals over the bridging atom. The  $p_x$  orbitals of the two phenoxo O<sup>-</sup> combine with two Cu<sup>II</sup>  $d_{x^2-y^2}$ orbitals with unpaired electron. This results in the formation of two bonding and two antibonding molecular orbitals. The ligand atom orbitals which have less energy are comparable with the bonding molecular orbitals and ligand electrons occupy the bonding molecular orbitals. The two metal atom electrons occupy the antibonding molecular orbitals. They may be singly occupied in the two antibonding molecular orbitals, resulting in triplet state. If there is significant separation between the two antibonding orbitals there is pairing of electrons in the lower energy antibonding molecular orbital, resulting in antiferromagnetic spin coupling and a singlet state. The extent of spin exchange depends on the separation between the energies of singlet and triplet state  $(^{2}J)$ . There is a temperature-dependent mixture of the singlet and triplet states and consequent lowering in the magnetic moment at room temperature. Long range spin exchange in bridges with delocalised  $\pi$  orbitals



Fig. 2. The ESR spectra of a complex  $III_A$  in DMF at LNT.



Fig. 3. Cyclic voltammogram of a complex III<sub>A</sub> at 0.1 M. Electrolyte (tetrabutyl ammonium tetrafluoroborate) concentration in DMF.

have been extensively studied and in these cases also the exchange interaction is considered to be through  $\sigma$  orbitals [4,5]. In binuclear complexes with aliphatic bridges also spin exchange has been observed and X-ray crystal structure study shows that there is no interdinuclear complex interaction in such complexes [8,9], and hence antiferromagnetic interaction has been attributed to spin polarization of  $\sigma$  electrons. However, in the absence of X-ray and variable temperature magnetic data, attributing such a low magnetic moment, in the present study, to interaction through --CH<sub>2</sub>-- bridge is tentative and formation of tetranuclear structure, involving interdinculear interaction [19,20] cannot be ruled out.

#### Electrochemical studies

Cyclic voltammetric data of the complexes were recorded in DMF medium. The Schiff base ligands do not exhibit any redox peaks in the potential range investigated 0--1.7 V. The C.V. of mononuclear complex Cu (sal, ala) H<sub>2</sub>O shows one quasireversible peak at  $\sim -0.92/0.64$  corresponding to Cu<sup>II</sup>/Cu<sup>I</sup> couple. The electrochemical properties of four binuclear complexes  $II_B$ ,  $II_C$ ,  $II_D$  and  $III_A$  were studied. The electrochemical data are given in Table 2. A representative cyclic voltammogram is shown in Fig. 3. All these complexes exhibit completely irreversible behaviour. The binuclear complexes exhibit two reduction peaks which correspond to the stepwise reduction of two Cu<sup>II</sup> centers to Cu<sup>II</sup>:

$$Cu''Cu'' \xrightarrow{+1e} Cu^{1}Cu'' \xrightarrow{+1e} Cu^{1}Cu^{1}$$
.

The possibility that these two peaks correspond to simultaneous reduction of the two copper centres to  $Cu^{I}$  and finally to  $Cu^{0}$  is ruled out, since the mononuclear complex Cu (sal, ala)  $H_2O$  shows only one step reduction  $Cu^{II} \rightarrow Cu^{I}$ . The two-step reduction in the binuclear complexes indicates interaction between the two paramagnetic  $Cu^{II}$  centers [21]. This is in agreement with the magnetic data showing antiferromagnetic interaction.

The comparison of the reduction potentials of complexes II<sub>B</sub>, II<sub>C</sub> and II<sub>D</sub> with that of complex III<sub>A</sub> shows that the reduction of Cu<sup>II</sup>  $\rightarrow$  Cu<sup>I</sup> in complex III<sub>A</sub> occurs at less negative potential than that of complex II<sub>B</sub>, II<sub>C</sub> and II<sub>D</sub>. This can be explained by  $\sigma$  and  $\pi$  bonding nature of the ligands. In complexes II<sub>B</sub>, II<sub>C</sub> and II<sub>D</sub> there is one phenolate O<sup>-</sup>, one carboxylate COO<sup>-</sup> and one imine coordination, where as in complex III<sub>A</sub> there is one O<sup>-</sup> coordination, one imine and one pyridyl N coordination. As there are two  $\sigma$ bonding in the first case the Cu<sup>II</sup> gets reduced to Cu<sup>I</sup> at more negative potential. In the second case III<sub>A</sub> due to  $\pi$  bonding pyridyl nitrogen the Cu<sup>II</sup>  $\rightarrow$  Cu<sup>I</sup> reduction occurs at less negative potential.

#### Thermogravimetric data

The thermogravimetric analysis (TGA) indicates loss of one water molecule per metal atom in the range of 180–200°C for the complexes. Loss of water at such high temperatures indicates that the  $H_2O$  molecules are coordinated and not lattice held. This is in agreement with C, H, N analysis presented in Table 1.

Acknowledgements—We thank the Department of Science and Technology (New Delhi) for the financial support for this work and Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Bombay for EPR measurements. Our thanks are due to Professor A. C. Shah, Head, Department of Chemistry, M.S. University of Baroda for providing laboratory facilities.

#### REFERENCES

- N. D. Kulkarni and P. K. Bhattacharya, Trans. Met. Chem. 1989, 14, 303.
- N. D. Kulkarni, M. Jacob, K. V. Patel and P. K. Bhattacharya. Synth. and React. Inorg. Met. Org. Chem. 1992, 20, 300.
- B. Trivedi, V. Manjula and P. K. Bhattacharya. J. Chem. Research (S) 1994, 472.

- 4. T. R. Felthouse and D. N. Hendrickson. *Inorg. Chem.* 1978, 17, 2636.
- P. Chaudhuri, K. Oder, K. Wieghardt, S. Ghering, W. Haase, B. Nuber and J. Weiss. J. Am. Chem. Soc. 1988, 110, 3657.
- J. A. Real, M. Mollar, R. Ruiz, J. Faus, F. Lloret, M. Julve and M. P. Levisalles, J. Chem. Soc. Dalton Trans. 1993, 1483.
- S. L. Stefan, M. E. Behairy, S. M. E. Khalil and H. F. A. E. Halim, J. Chem. Res. (S) 1994, 454.
- R. Calvo, C. A. Steren, O. E. Piro, T. Rojo, F. J. Zuniga and E. E. Castellano. *Inorg. Chem.* 1993, 32, 6016.
- J. Glerup, P. A. Goodson, D. J. Hodgson and K. Michelsen. *Inorg. Chem.* 1995, 34, 6255.
- C. S. Marvel and N. Tarkoy, J. Am. Chem. Soc. 1957, 79, 6000.
- 11. N. Arulsamy and P. S. Zacharias, *Trans. Met. Chem.* 1991, **16**, 255.
- M. R. Wagner and F. A. Walker, *Inorg. Chem.* 1983, 22, 3021.
- D. L. Leussing and K. S. Bai, Anal. Chem. 1968, 40, 575.
- D. Heinert and A. E. Martell, J. Am. Chem. Soc. 1963, 85, 188.
- L. A. Zyzyck, H. Frummer and J. F. Villa, J. Inorg. Nucl. Chem. 1975, 37, 1653.
- S. T. Chow, D. M. Johns, C. A. McAuliffe and D. J. Machin, *Inorg. Chim. Acta* 1977, 22, 1.
- L. Casella, M. Gullotti and G. Pacchioni, J. Am. Chem. Soc. 1982, 104, 2386.
- Z. N. Chen, S. X. Liu, J. Qui, Z. M. Wang, J. L. Huang and W. X. Tang, J. Chem. Soc., Dalton Trans. 1994, 2989.
- M. Julve, M. Verdaguer, J. Faus, F. Tinti, J. Moratal, A. Monge and E. Guiterrez-Puebla. *Inorg. Chem.* 1987, 26, 3520.
- 20. J. P. Costes, F. Dahan and J. P. Laurent, *Inorg. Chim. Acta* 1995, **230**, 199.
- E. L. Hasty, L. J. Wilson and D. N. Hendrickson, *Inorg. Chem.* 1978, **17**, 1834.