



Synthesis and Spectroscopic Characterization of Some Copper(II) Trinuclear Complexes involving Nitrogen as Bridging Atoms

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The following Schiff bases were employed as ligands in synthesizing Cu(II) trinuclear complexes: 1,2-bis-(2-aminobenzylideneamino) ethane (L_1), 1,2-bis-(2-aminobenzylideneamino)propane (L_2), 1,3-bis-(2-aminobenzylideneamino)propane (L_3), 1,2-bis-(2-aminobenzylideneamino)benzene (L_4). The ligands were obtained by reacting 2-aminobenzaldehyde with 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane and 1,2-diaminobenzene, respectively. Four trinuclear coordination complexes were synthesized and structurally characterized by elemental analysis, molar conductivity, FT-IR, UV-Visible, magnetic and EPR spectral studies. The results suggest that the complexes are trinuclear and ionic in nature.

Key Words: Schiff base, Trinuclear complexes, 2-Aminobenzaldehyde, Cu(II) complexes.

INTRODUCTION

Schiff bases have found wide applications in the field of coordination chemistry¹ and these are widely employed as ligands in preparing coordination complexes^{2,3}. These ligands are readily available, versatile and depending on the starting materials (primary amines and carbonyl precursors), they exhibit functionalities. The number, the nature and the relative position of the donor atoms of the Schiff base ligands allow the good control over the number of the metal ions within homo and heteropolynuclear complexes⁴. All these advantages make Schiff bases a good ligand in synthesizing metal complexes.

2-Aminobenzaldehyde and its derivatives are useful carbonyl precursors for the synthesis of a large variety of Schiff bases which result by reacting with (a) monoamines, (b) diamines carrying two amino groups⁵. In the last case, the condensation leads to tetradentate N_4 Schiff base⁶. Additional coordinating groups attached to 2-aminobenzaldehyde increase its ability to generate polynuclear complexes. Here in we have reported some tetradentate Schiff base ligands derived from 2-aminobenzaldehyde and their trinuclear complexes with copper(II).

EXPERIMENTAL

Elemental analysis was carried out by Perkin-Elmer CHN analyzer, where as the metal content was determined spectrophotometrically¹³ after digesting the complexes with conc.

H_2SO_4 and nitrogen estimation was done by Kjeldhal's method¹⁴. Jasco-IR-700 double beam spectrophotometer was used for recording the IR spectra of the complexes in the range 4000-400 cm^{-1} . The electronic spectra of the complexes in acetonitrile were recorded in HITACHI UV-2001 spectrophotometer. The molar conductance of complexes in DMSO (10^{-3} M) was determined at 25 °C using a Systronics direct reading conductivity bridge. EPR spectra of the complexes were recorded on a JEOL spectrometer equipped with variable temperature facility operating at X-band frequencies. The magnetic susceptibility of the trinuclear copper complex $[Cu(CuL_3)_2]^{2+}$ has been determined in the temperature range of 79 to 296 K.

The ligands used were prepared by the reaction of 2-aminobenzaldehyde with various diamines. The diamines used were 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane and 1,2-diaminobenzene. 2-Aminobenzaldehyde was prepared by the reduction of 2-nitrobenzaldehyde using ferrous sulphate in an ammoniacal medium⁷. The product was then separated by steam distillation. 2-Aminobenzaldehyde as obtained was converted into the tetraamines by condensing it with the appropriate diamine. These ligands were then used for the synthesis of mononuclear complexes. By using these mononuclear complexes, trinuclear complexes were prepared.

Preparation of ligands⁶⁻¹⁰: The ligands were prepared by following the procedure of Green and Tasker.

Preparation of 1,2-bis-(2-aminobenzylideneamino) ethane: (L_1): A solution of 1,2-diaminoethane (0.005 mol)

and freshly prepared 2-aminobenzaldehyde (0.01 mol) in 50 mL of ethanol was heated under reflux for 1 h. The Schiff base separated as white flakes on cooling and recrystallized from ethanol.

Preparation of 1,2-bis-(2-aminobenzylideneamino)propane: (L₂): 2-Aminobenzaldehyde (0.01 mol) and 1,2-diaminopropane (0.005 mol) dissolved in ethanol were reacted under refluxing conditions. After 1 h refluxing, the mixture was poured on crushed ice and a white amorphous solid formed was separated out.

Preparation of 1,3-bis-(2-aminobenzylideneamino)propane: (L₃): About 0.005 mol of 1,3-diaminopropane was added to a solution of 0.01 mol of 2-aminobenzaldehyde in 50 mL of ethanol and the contents were refluxed for about 1 h. After partial evaporation of the solvent the Schiff base formed was filtered.

Preparation of 1,2-bis-(2-aminobenzylideneamino)-benzene: (L₄) 0.01 mol of 2-aminobenzaldehyde in 30 mL of ethanol was added to a solution of 0.005 mol of 1,2-diaminobenzene and refluxed. After the refluxing was stopped, the contents were poured into the crushed ice. The yellow coloured solid formed was filtered.

Preparation of complexes: For the synthesis of trinuclear complexes the mononuclear complexes were prepared first^{9,11,12}. They were then converted to trinuclear complexes. 1 mol of mononuclear complex [Cu(L₁)] was dissolved in hot ethanol. To this ethanolic solution of 0.5 mol of Cu(II) perchlorate hexahydrate was added and refluxed for 3½ h. The mixture was allowed to cool. The brown coloured solid formed was filtered and dried (**Scheme-I**).

A similar procedure was adopted for the synthesis of trinuclear complexes using the mononuclear complexes [Cu(L₂)], [Cu(L₃)] and [Cu(L₄)].

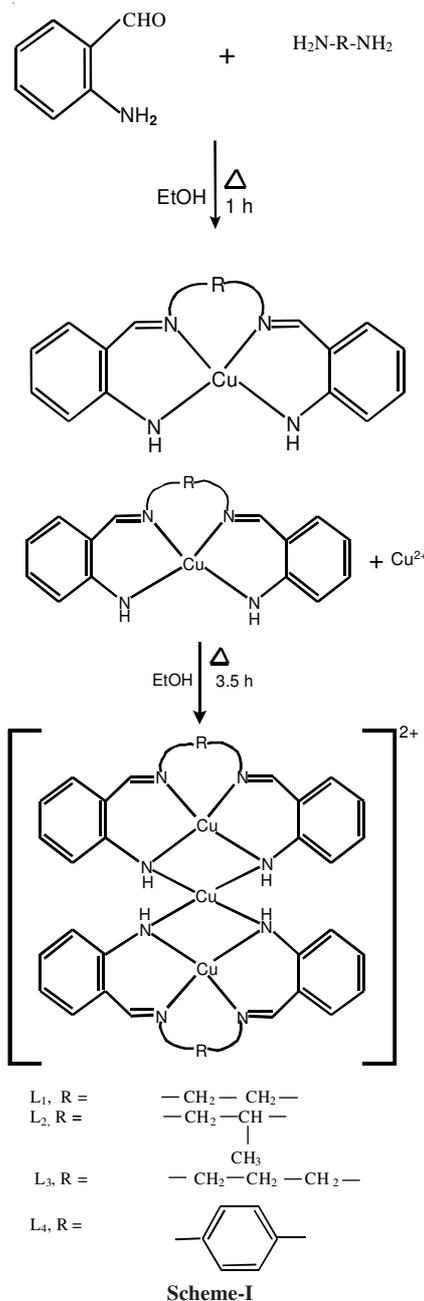
RESULTS AND DISCUSSION

All the complexes were negligibly soluble in water and completely soluble in DMF, DMSO, ethanol, methanol, acetone and acetonitrile. The elemental composition of the complexes prepared shows good agreement with the calculated values (Table- 1).

TABLE-1
ANALYTICAL DATA OF THE COMPLEXES

Complex	m.f.	Found (calculated) (%)			
		M	C	H	N
[Cu(CuL ₁) ₂] ²⁺	C ₃₂ H ₃₂ N ₈ O ₈ Cl ₂ Cu ₃	20.94 (20.76)	41.80 (41.20)	3.49 (3.52)	12.25 (12.20)
[Cu(CuL ₂) ₂] ²⁺	C ₃₄ H ₃₆ N ₈ O ₈ Cl ₂ Cu ₃	20.08 (20.14)	43.19 (42.82)	3.81 (3.90)	12.02 (11.84)
[Cu(CuL ₃) ₂] ²⁺	C ₃₄ H ₃₆ N ₈ O ₈ Cl ₂ Cu ₃	20.22 (20.14)	48.12 (47.91)	2.98 (3.05)	11.49 (11.84)
[Cu(CuL ₄) ₂] ²⁺	C ₄₀ H ₃₂ N ₈ O ₈ Cl ₂ Cu ₃	18.17 (18.79)	47.32 (47.41)	3.45 (3.16)	11.51 (11.05)

The ligands have two primary amino groups and two azomethine groups and hence are expected to bind to the metal ions through these four ligating atoms^{6,8,9,11}. In the mononuclear complex, the deprotonation of the primary amine group has been observed to give rise to a neutral complex^{8,11}. When another metal ion is reacted with the mononuclear complex,



the lone pair of electrons of the -NH group can be used to bind the metal ion. As a result, molecules such as 1,2-bis-(2-aminobenzylideneamino)ethanecopper(II) can function as metallo ligands. It is well known that Cu²⁺ forms complexes considered basically to be square planar¹⁵. In keeping with this view, the reaction between Cu²⁺ and the complexes are expected to yield trinuclear complexes [Cu(CuL)₂]²⁺. A fairly good agreement was obtained between the experimental and calculated values of CHN and metal contents of the mononuclear and trinuclear complexes.

Conductivity studies: One of the measurements commonly employed in the determination of the charge type is the determination of its equivalent conductance at infinite dilution. These data are mainly used in obtaining information about the nature of the complex in solution. Most useful data are obtained in non-aqueous solvents such as nitrobenzene, acetonitrile, DMSO and DMF. The conductivity of the

complexes was determined in acetonitrile solution. The molar conductance values of the mononuclear and trinuclear complexes are given in Table-2.

TABLE-2
CONDUCTANCE DATA OF THE MONONUCLEAR
AND TRINUCLEAR COMPLEXES

Complex	Molar conductance (S cm ² mol ⁻¹)	Type of electrolyte
CuL ₁	68	Non-electrolyte
CuL ₂	61	Non-electrolyte
CuL ₃	76	Non-electrolyte
CuL ₄	74	Non-electrolyte
[Cu(CuL ₁) ₂] ²⁺	234	1:2
[Cu(CuL ₂) ₂] ²⁺	253	1:2
[Cu(CuL ₃) ₂] ²⁺	278	1:2
[Cu(CuL ₄) ₂] ²⁺	261	1:2

The values of the mononuclear complexes indicate that they are non-electrolytes. The trinuclear complexes are electrolytes. The values on comparison with ranges suggested by Geary¹⁶ show that the trinuclear copper complexes exist as 1:2 electrolytes. Hence in these complexes, two perchlorate ions are counter ions based on the reactants. This is in agreement with the formula proposed for the complexes on the basis of analytical data.

Infrared spectral studies: The infrared spectra of the copper(II) complexes are recorded in the 4000-400 cm⁻¹ region. The data collected from the IR spectra of the mono and trinuclear copper(II) complexes are tabulated in Table-3.

TABLE-3
INFRARED SPECTRAL DATA OF MONONUCLEAR
AND TRINUCLEAR COMPLEXES

Complex	-NH (cm ⁻¹)	C=N (cm ⁻¹)	ClO ₄ ⁻ (cm ⁻¹)
CuL ₁	3454	1608	-
CuL ₂	3451	1618	-
CuL ₃	3450	1612	-
CuL ₄	3456	1608	-
[Cu(CuL ₁) ₂] ²⁺	3438	1618	1142,1117,1086,627
[Cu(CuL ₂) ₂] ²⁺	344	1604	1143,1118,1086,626
[Cu(CuL ₃) ₂] ²⁺	3436	1611	1140,1118,1086,626
[Cu(CuL ₄) ₂] ²⁺	3447	1606	1141,1118,1088,625

The most common band observed in all the spectra of the complexes is in the 3460-3430 cm⁻¹ region. A band in this region is typically indicative of the presence of -NH group¹⁷. The bands in the region 1600-1450 cm⁻¹ are expected for the aromatic ring. In addition to these bands for the aromatic ring, there is an extra band observed in all the spectra in the 1600-1620 cm⁻¹ region. Green and Tasker^{6,9} have assigned separate stretching frequencies to the C=N group and the aromatic system of the ligand. The former are distinctly lower energy than those in a variety of Schiff bases^{18,19}. The compounds containing azomethine group generally absorb in the 1690-1480 cm⁻¹ region. The exact position depends on the compound considered²⁰. Hence the band in the 1650-1600 cm⁻¹ region is assigned to C=N stretching vibration²¹. When the spectra of the mononuclear copper(II) complexes are examined, it is found that the bands typically assignable to the primary amino group and the azomethine are shifted to lower frequencies.

This shift is indicative of the involvement of the primary amine and azomethine groups of the ligand in binding to the metal^{11,22}.

On comparison of the mono- and trinuclear copper(II) complexes, the trinuclear complexes show a downward shift of about 10-20 cm⁻¹ for the -NH stretching vibration. This shift indicates that the nitrogen atoms of the -NH groups in the mononuclear complexes bind to the third metal ion added in the formation of the trinuclear complexes^{22,23}. Another important absorption observed around 1100 cm⁻¹ in the spectra of the trinuclear copper(II) complexes is due to the perchlorate ion²⁴, which is the counter ion in this system. For the compounds in which perchlorate ion is a counter ion, bands typically assignable to the perchlorate ion²⁵ are observed in the 1100 cm⁻¹ and 625 cm⁻¹. The splitting of this band and the appearance of other bands are indications of the nature of the perchlorate ion (*i.e.*) whether it is free or coordinated and the mode of coordination²⁶.

Hathaway *et al.*²⁷ examined the infrared spectra of the transition metal perchlorates. They have reported that in ionic perchlorates, ν_1 at 620 cm⁻¹ is inactive while ν_3 mode at 1110 cm⁻¹ appears as a strong band. When the perchlorate is coordinated, ν_1 also becomes allowed and can be seen, while the triple degeneracy of ν_3 is partially lifted and consequently the band at 1110 cm⁻¹ appears as a doublet or triplet.

In the present trinuclear complexes, the bands in the 1110 cm⁻¹ are split into 3 bands around 1140, 1110 and 1090 cm⁻¹ as well as the band in the 625 cm⁻¹ was also found. In addition, the band corresponding to ν_1 mode at 930 cm⁻¹ has acquired sufficient intensity to be observable in the spectra, when the intensity of the absorption of bands at 1110 cm⁻¹ are very high. The splitting of the bands and the appearance of the band at 930 cm⁻¹ support the coordinated nature of the perchlorate ion in the solids²⁸.

Electronic spectral studies: The electronic spectra are concerned with the energy difference between the ground state and the excited electronic states. All the complexes show absorptions at *ca.* 215 nm, *ca.* 235 nm and *ca.* 260 nm, assignable to the internal ligand transitions. Similarly the band at *ca.* 307 nm in the spectra of the copper complexes is also due to an internal ligand transitions²⁹. The band at *ca.* 330 nm in the (2-aminobenzylideneamine) complexes is attributed to a $\pi \rightarrow \pi^*$ transition involving molecular orbitals which originate from the azomethine group and benzene ring^{30,31}. In accord with the assignment in anilines³² and in benzaldehyde³³ Schiff bases the band at *ca.* 260 nm is assigned to the benzenoid $\pi \rightarrow \pi^*$ transition³⁴. The weak band at *ca.* 410 nm in some of the complexes is assigned to $n \rightarrow \pi^*$ transition involving the lone pair of electrons of the azomethine nitrogen atom and the π^* orbital associated with the azomethine group³³. The near IR region showed no absorption up to 1000 nm. The copper(II) complexes absorb strongly in the UV and in addition show at least one peak in the visible region. The band at *ca.* 480 nm appears to arise from charge transfer involving ligand and metal orbitals³⁵.

The bands of low intensity in the visible region are assigned to *d-d* transitions. All the mononuclear and trinuclear copper(II) complexes exhibit a characteristic shoulder in the range 575-590 nm which is assigned to spin-allowed *d-d*

transitions³⁶. The shoulder in this region suggest a square-planar geometry around the copper(II) ion. But the trinuclear complexes, in addition to the shoulder at 575-590 nm, show a shoulder at 730-790 nm. Tetrahedral copper(II) generally possess their crystal field absorption in the range 530-590 nm³⁷. So the shoulder at 730-790 nm for the trinuclear copper(II) complexes is assigned to the *d-d* transition of the copper(II) in tetrahedral geometry. Hence in the trinuclear copper(II) complexes, the two terminal copper ions are in a square planar geometry and the central copper(II) may be in a tetrahedral arrangement.

The similarity of the electronic spectra of all the trinuclear copper(II) complexes suggest a similar coordination environment in these complexes.

Variable temperature electron spin resonance spectral studies: The ESR spectra of the mononuclear and trinuclear copper(II) complexes in ethanol are recorded in the X-band at room temperature and in frozen ethanol glass at liquid nitrogen temperature. The two major components of the *g*-tensor in the axially symmetric field g_{\perp} and g_{\parallel} values are computed from the spectra. The hyperfine coupling constant A_{\parallel} are measured directly from the spectra. The spin Hamiltonian values are tabulated in Table-4.

TABLE-4
ESR SPECTRAL DATA OF MONONUCLEAR AND TRINUCLEAR COMPLEXES

Complexes	g_{\parallel}	g_{\perp}	g_{ave}	A_{\parallel} (mT)
CuL ₁ RT	2.119	2.010	2.065	8.673
LNT	2.219	1.980	2.109	19.33
CuL ₂ RT	-	-	-	-
LNT	2.203	1.988	2.096	18.922
CuL ₃ RT	2.148	2.032	2.090	8.462
LNT	2.249	2.000	2.124	16.02
CuL ₄ RT	-	-	-	-
LNT	2.280	1.994	2.107	19.078
[Cu(CuL ₁) ₂] ²⁺ RT	2.118	2.013	2.065	8.196
LNT	2.213	1.995	2.103	18.92
[Cu(CuL ₂) ₂] ²⁺ RT	2.142	2.026	2.084	8.264
LNT	2.210	1.921	2.100	19.55
[Cu(CuL ₃) ₂] ²⁺ RT	2.125	2.011	2.068	7.671
LNT	2.232	2.002	2.117	19.40
[Cu(CuL ₄) ₂] ²⁺ RT	2.293	2.070	2.182	21.96
LNT	2.150	2.012	2.081	8.723
LNT	2.438	2.066	2.252	8.494
	2.159	-	-	11.60

All the copper(II) complexes containing an unpaired electron should exhibit four equally spaced lines in the first derivative ESR spectra arising from the interaction of the unpaired electron with ⁶³Cu (I=3/2) nucleus^{38,39}. These signals will be further split depending on the nuclear magnetic moment of the donor atoms around Cu²⁺. The mononuclear copper(II) complexes exhibit four line hyperfine interaction signals with the nuclear spin 3/2 of copper. The hyperfine coupling constant A_{\parallel} related to I = 3/2 nuclear spin of copper was measured from the splitting of four well-resolved signals. The g_{\parallel} values are greater than g_{\perp} values. Generally for copper(II) ion if the unpaired electrons occupy the $d_{x^2-y^2}$ orbital as the ground state, there would be elongation of copper(II) ion and the esr spectrum would show $g_{\parallel} > g_{\perp}$. On

the other hand, if d_{z^2} is the ground state, then there would be compression and the esr would show $g_{\parallel} < g_{\perp}$ ³⁸. The majority of copper(II) complexes show $g_{\parallel} > g_{\perp}$, which means that $d_{x^2-y^2}$ is commonly the ground state. It is seen from the Table-4 that $g_{\parallel} > g_{\perp}$ for all the copper(II) complexes which implies that the 3d unpaired electron of copper(II) ion should occupy the $d_{x^2-y^2}$ orbital⁴⁰.

The ESR spectra of the trinuclear copper(II) complexes in ethanol at room temperature are similar to mononuclear copper(II) complexes with the usual 4 lines. But at liquid nitrogen temperature (LNT) in the frozen ethanol glass, the spectra exhibit two sets of 4 lines for the two different copper centers. The trinuclear copper(II) complexes have the copper in two magnetically non-equivalent environments. This is clearly evident in the ESR spectra at LNT, which has 2 sets of 4 lines for the two copper(II) centers with different A_{\parallel} values. The trend $g_{\parallel} > g_{\perp}$ is observed for all the complexes suggest that the unpaired electron is localized in the $d_{x^2-y^2}$ orbital of copper(II) ion. The anisotropic values for g_x and g_y are not well resolved and no A_{\perp} hyperfine coupling constant is observed⁴¹.

For trinuclear copper(II) complexes in the strong interaction limit, the expected states are a quartet and two doublets⁴². When the coupling is antiferromagnetic, one of the doublets is the ground state and the quartet is the lower energy state for ferromagnetically coupled systems. When the coupling is fairly strong, (other than dipolar interaction) a fairly strong variation in the *g*-values is expected as the temperature is varied⁴³. In the present study, the changes in *g*-values from liquid nitrogen to room temperature are small. This indicates that the coupling between the copper centers is rather weak. In weakly coupled systems, the ESR spectra show separate resonances near the *g* values of the individual ions⁴². In keeping with this low temperature ESR shows resonances attributable to individual copper(II) centers. Two resonances can be discerned in the parallel region, while the perpendicular lines are overlapping. It is also seen that one set of the parallel lines is more intense than the other. The stronger signals are assigned to the terminal copper atoms while the weaker signals are due to the central copper.

Variable temperature magnetic susceptibility studies: An important method to study the interaction between metal centers is the determination of magnetic susceptibility. In order to ascertain such information, the magnetic susceptibility of the trinuclear copper complex made from 1,3-bis-(2-amino-benzylideneamino)propane has been determined in the temperature range of 79 to 296 K. The susceptibilities are collected in Table-5. These are the values obtained after applying diamagnetic corrections.

Kahn⁴⁴ has described an orbital mechanism for the interaction between metallic centers in trinuclear complexes. In trinuclear systems, the microscopic nature of the interaction between adjacent centers is rigorously the same as in dinuclear system but the presence of more than two spin carriers may lead to new magnetic behaviour.

The energy difference between the doublets and quartet states is examined as the variation of the magnetic moments as a function of temperature. If the interaction is very strong,

TABLE-5
MAGNETIC SUSCEPTIBILITY VALUES FOR
TRINUCLEAR COPPER(II) COMPLEX

Temperature (K)	χ_{mT} (cm ³ mol ⁻¹ K)
79	0.19745
90	0.20334
100	0.21224
110	0.22257
120	0.22690
130	0.23288
140	0.23539
150	0.24726
170	0.26696
190	0.27975
210	0.29051
230	0.30300
250	0.30735
270	0.32896
296	0.34762

only the lowest energy state will be populated even at room temperature⁴⁵. Then, the magnetic moment will be a constant over the temperature range used in the present study. In the weak coupling limit, magnetic moment will show a slow variation. This is observed in the values of magnetic moments decreasing slowly in the temperature range presently used. This indicates that the interaction between the central copper(II) with the terminal copper(II) is weakly antiferromagnetic. The ground state for such interaction is one of the doublet states. These observations are in consonance with the results of the ESR studies.

Conclusion

Schiff bases and its trinuclear complexes were prepared and characterized using elemental analysis, molar conductivity, FT-IR, UV-visible, magnetic and EPR spectral studies. IR spectral data demonstrates that the nitrogen atoms of the -NH groups in the mononuclear complexes bind to the third metal ion added in the formation of the trinuclear complexes and confirms the presence of perchlorate counter ion. Electronic spectral studies suggest that in trinuclear copper(II) complexes, the two terminal copper ions are in a square planar geometry and the central copper(II) is in a tetrahedral arrangement. EPR and magnetic studies shows that the interaction between the central copper(II) with the terminal copper(II) is weakly antiferromagnetic.

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