Synthesis, Structural, Magnetic and Electrochemical Studies of Antiferromagnetically Coupled Symmetric Oxamidate-Bridged Binuclear Copper(II) Complexes

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The new binuclear copper(II) complexes Cu_2L^{1-3} and $[Cu_2L^{4,5}](ClO_4)_2$ were synthesized by reaction of the monomeric *cis*-*N*,*N′*-bis(3-aminopropyl)oxamidatocopper(II) complex [Cu(oxpn)] with acetylacetone, benzoylacetone, salicylaldehyde, 2-pyridinecarboxaldehyde and diacetyl monoxime in the presence of copper(II) acetate or perchlorate owing to the *trans* isomerisation of the *cis*-oxamidato complex. The crystal structure of Cu_2L^1 consists of centrosymmetric binuclear copper(II) ions which are bridged by an oxamidato group in the *trans* conformation with a copper–copper distance of 5.121 Å. Each copper(II) ion occupies an inner site of the N_2O_2 donor with a distorted square-planar environment. Electrochemical studies showed that two quasireversible one-electron reduction waves are obtained in the cathodic region (E^1_{pc} = –0.48 to –1.02 V, E^2_{pc} = –1.08 to –1.34 V). The conproportionation constants K_{con} for the mixed-valence Cu^ICu^{II} complexes have been determined electrochemically. Room-temperature magnetic-moment studies of binuclear copper(II) complexes reveal the presence of a strong antiferromagnetic interaction (μ_{eff} = 1.14–1.24 μ_B) which is also observed from the broad spectra with g = 2.1. A variable-temperature magnetic-susceptibility study of the complexes **1** and **4** gives J values of –510 cm^{-1} and –497 cm^{-1} respectively.

Introduction

Inorganic chemists are interested in synthesizing bi- and polymetallic complexes to design new molecular materials with unusual magnetic and electrical properties[1–5] and these bi- and polymetallic systems are also attractive as synthetic models of metallo biomolecules[6–8] due to the close proximity of the metal centers. To prepare polynuclear complexes, the use of polynucleating ligands[9,10] and the use of metal complexes as ligands are the most commonly followed strategies.[11–14] Self-assembly of a mononuclear oxamidato complex with a metal ion leads to a novel coordination polymer.[15] Oxamide-based ligands such as *N*,*N′*-bis(3-aminopropyl)oxamide (H_2oxpn) have been of great interest due to their ability to form polynuclear complexes.[16] The oxamide bridge is known to be very efficient in transmitting the exchange interaction between magnetic ions.[17–19] Oxamide ligands with two distinct coordination sites are used in the design of ditopic receptors to allow the translocation of a metal ion driven by pH variation which can lead to mechanical work at the molecular level.[20,21] This possibility gives rise to a new class of potential artificial molecular machines.[22,23] It is also possible to use substituted oxamate and oxamide ligands in the stabilization of unusual high oxidation state transition metal ions.[24,25] Furthermore, the monomeric *cis*-oxamidato complex Cu(oxpn) easily yields binuclear[26,27] and polynuclear[28] complexes by changing its conformation from *cis* to *trans*. It has also been shown that the NH_2 group of *N*,*N′*-disubstituted oxamides can be condensed with a carbonyl group of several compounds to yield new binucleating ligands.[29,30]

The work reported here is concerned with the synthesis, structural, spectral, magnetic and electrochemical properties of disubstituted oxamidate-bridged binuclear copper(II) complexes. These complexes can be used to synthesize polynuclear complexes with suitable multidentate ligands. A schematic diagram of the ligand frames is given in Figure 1.

Results and Discussion

Binuclear complexes are synthesized by condensation between the terminal NH_2 group of [Cu(oxpn)] with acetyl-

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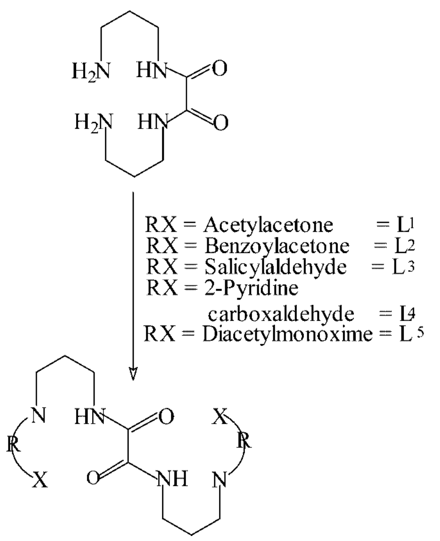
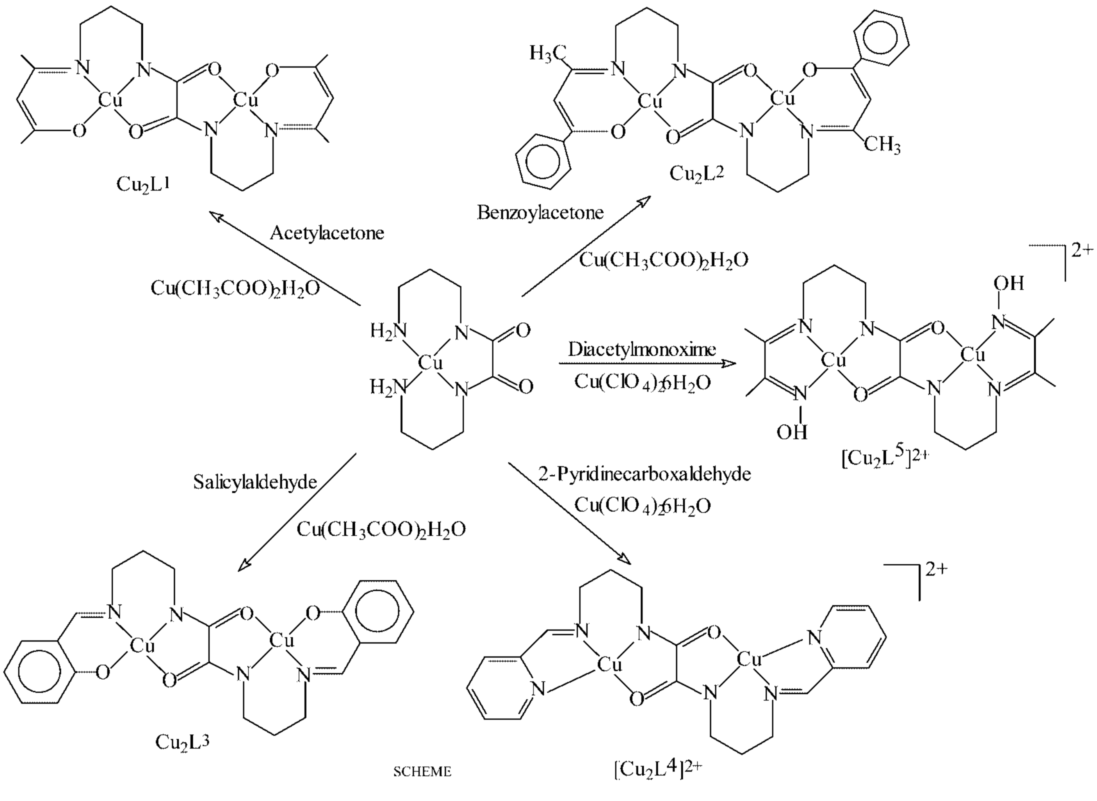


Figure 1. Schematic diagram of the ligand framework

acetone (L^1), benzoylacetone (L^2), salicylaldehyde (L^3), 2-pyridinecarboxaldehyde (L^4) or diacetyl monoxime (L^5) in the presence of copper(II) acetate (L^{1-3}) or copper(II) perchlorate ($L^{4,5}$). Complexes [Cu_2L^{1-3}] contain N_2O_2 coordination sites, whereas complexes [$Cu_2L^{4,5}$](ClO_4)$_2$ have N_3O coordinating sites. The synthetic pathway of the complexes is shown in Scheme 1.

X-ray Structural Study of the Complex [Cu_2L^1]

[Cu_2L^1] crystallizes from a methanol/chloroform solution in the space group *Pbca*. The ORTEP view of the binuclear copper(II) complex, which consists of centrosymmetric binuclear copper(II) ions, along with the atomic labeling scheme, is given in Figure 2. Crystal data and structure refinement details are given in Table 1, with selected bond lengths (Å) and angles (°) in Table 2. Within the binuclear molecule, an oxamidate group in the *trans* conformation bridges crystallographically equivalent copper(II) ions. Each copper(II) ion is four-coordinate, with an N_2O_2 coordination environment in a distorted square-planar geometry. The oxamidato bridge is planar within experimental uncertainties and has a dihedral angle of 5.7° with the N_2O_2 coordination plane, so that the whole centrosymmetric molecule can be considered as planar. The bridging group N2−O1−C7−C7A−N1A−O1A is planar, with the copper atom being displaced by −0.0084(3) Å from this plane. The Cu1−Cu1A separation within the binuclear unit is 5.121 Å. One alkylamino nitrogen, one oxamidato nitrogen, one oxamidato oxygen and one acetonato oxygen atom are coordinated to each Cu ion with distances of Cu1−N2 = 1.954(2) Å, Cu1−N1 = 1.960(2) Å, Cu1−O1 = 2.008(2) Å and Cu1−O2 = 1.8871(19) Å, respectively. The Cu1−O1 distance is 0.1211 Å longer than the Cu1−O2 distance. Both the nitrogen atoms N1 and N2 are present at nearly the same distance from the Cu atom, within experimental error. The copper−amidic nitrogen (Cu−N2) distance is



Scheme 1

1.954 Å, which is close to those of several reported oxamidato complexes.[17,36] The copper−iminic nitrogen (Cu−N1) distance is 1.960 Å and the copper−oxamide oxygen (Cu−O1) bond length is 2.008 Å, which are comparable to those reported earlier.[17] The bond angles around the Cu atom show significant deviations from 90°, two of them – O1Cu1O2 [84.69°(9)] and N2Cu1O1 [82.98°(11)] – being narrower than the other two N1Cu1N2 [97.2°(11)] and N1Cu1O2 [95.41°(10)]. The sum of the angles around C7, O1and N2 is 360.0° indicating that these atoms are trigonal planar. This implies that Cu1−O−C−*N*−Cu1A is a delocalised unit as a result of conjugation of the electrons from the oxygen atoms and the lone pairs on the nitrogen atoms. This is further supported by the average O−C and C−N bond lengths [1.272(3) and 1.295(4) Å, respectively], which are shorter than expected for single O−C or C−N bonds (ca. 1.481 and 1.462 Å, respectively). From the molecular packing it is observed that there are no intermolecular contacts that are less than the sum of the corresponding van der Waals radii. This suggests that there are no forces other than van der Waals interactions stabilizing the structure.[30]

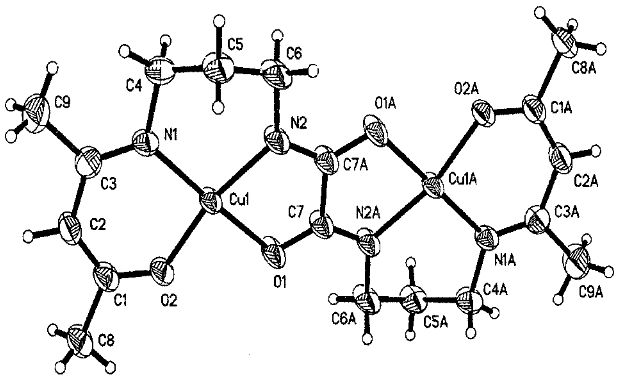


Figure 2. ORTEP diagram of complex [Cu_2L^1] with atom labels and numbering scheme; hydrogen atoms are omitted for clarity

Table 1. Crystal data and structure refinement for [Cu_2L^1]

Empirical formula	$C_{18}H_{26}Cu_2N_4O_4$
Molecular mass	489.51
Temperature	183(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	Pbca
Unit cell dimensions	a = 15.3679(5) Å b = 8.0448(3) Å c = 16.1903(6) Å
Volume	2001.63(12) Å^3
Z	4
Density (calculated)	1.718 g/cm^3
Absorption coefficient	2.160 mm^{-1}
F(000)	1072
Crystal size	0.50 × 0.46 × 0.10 mm
Theta range for data collection	2.65−28.26°
Index ranges	$-20 \le h \le 20$, $-10 \le k \le 10$, $-21 \le l \le 16$
Reflections collected	11341
Independent reflections	2461 [R(int) = 0.1099]
Completeness to theta	28.26° 99.0%
Absorption correction	empirical
Max. and min. transmission	0.8140 and 0.4133
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	2461/0/132
Goodness-of-fit on F^2	0.991
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0562, $wR2$ = 0.1426
R indices (all data)	$R1$ = 0.0738, $wR2$ = 0.1499
Extinction coefficient	0.0110(16)
Largest diff. peak and hole	0.800 and −1.078 e·Å^{-3}

Table 2. Selected bond lengths (Å) and angles (°) for complex [Cu_2L^1]

Cu1−O2	1.8871(19)	Cu1−N2	1.954(2)
Cu1−N1	1.960(2)	Cu1−O1	2.008(2)
O1−C7	1.272(3)	N2−C7	1.295(4)
C7−C7A	1.499(6)		
O2−Cu1−N1	95.41(10)	O2−Cu1−O1	84.69(9)
N2−Cu1−O1	82.98(11)	N2−Cu1−N1	97.20(11)
O2−Cu1−N2	166.73(11)	N1−Cu1−O1	176.50(12)
C7−O1−Cu1	110.88(18)	C1−O2−Cu1	125.8(2)
C6−N2−Cu1	128.0(2)	O1−C7−N2	128.0(3)
O1−C7−C7A	118.1(3)	N2−C7−C7A	113.9(3)

Spectral Studies

The IR spectra of all the complexes show sharp bands resulting from the C=N stretching vibration (1640 cm^{-1}) and the oximidato C=O stretching vibration (1590 cm^{-1}). The presence of an uncoordinated perchlorate anion in complexes Cu_2L^4 and Cu_2L^5 is inferred from a single broad band at 1100 cm^{-1} (ν_3 antisymmetric stretching), which is not split, and a medium band at 650 cm^{-1} (ν_4 antisymmetric bending). The absence of any band at 930 cm^{-1}(ν_2 symmetric stretching) indicates the lack of coordination of the perchlorate ion.[31−33] The UV/Vis spectrum of the mononuclear complex Cu(oxpn)[13] exhibits a d → d transition around 510 nm consistent with a tetracoordinate Cu atom in a nearly square-planar CuN_4 geometry. The binuclear complexes Cu_2L^{1-5} display a d-d band in the range 572−592 nm. The λ_{max} value of the binuclear complexes is higher than that of the mononuclear species; such a red shift implies that the conformation of the ligand is altered from *cis* to *trans*, which changes the environment of the Cu^{II} ions from N_4 to N_2O_2 and N_3O. This is consistent with a previously reported observation.[18] Besides the d → d transition, a moderately intense band in the range 300−400 nm is due to a ligand-to-metal charge transfer ($\pi \rightarrow d_\sigma$) transition and a band below 300 nm is assigned to an intraligand transition ($\pi \rightarrow \pi^*$). The absorptions around 570 nm are attributed to square-planar CuN_2O_2 and CuN_3O chromophores.[34] Therefore, it appears that there is a distorted square-planar geometry of the Cu centers in the copper(II) complexes. The solution X-band ESR spectrum of Cu_2L^1 is shown in Figure 3. The solution (10^{-3} M in DMF) ESR spectra of the complexes Cu_2L^{1-5} display one broad absorption at g = 2.10 centered at 3200 G at room temperature. The ESR spectra with no hyperfine splitting of the parallel component indicate that there is a strong antiferromagnetic interaction between the two copper(II) ions in the molecule.[16] Due to the favourable relative orientation of the magnetic orbitals a strong antiferromagnetic interaction is observed in spite of a Cu−Cu separation of about 5.121 Å. The fine structure of a triplet state for a Cu^{II} pair has two origins, namely the dipolar interaction and the combined effect of the local spin-orbit coupling and the exchange interaction, which leads to anisotropic and antisymmetric exchanges.[35] The above observation can be explained by earlier reports.[36,37]

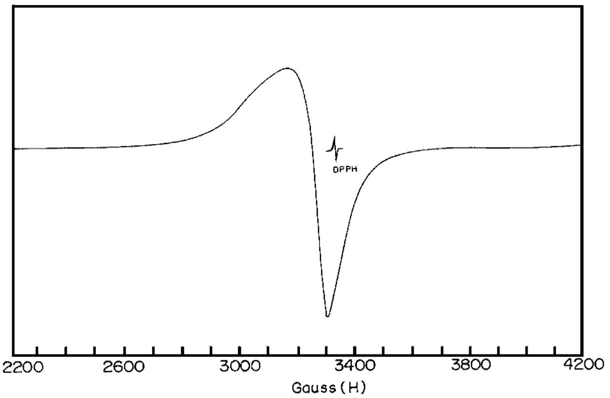


Figure 3. ESR spectrum of [Cu_2L^1]

Magnetic Susceptibility

The values of the magnetic moment for the binuclear copper(II) complexes measured at room temperature (298 K) are, at 1.14−1.24 μ_B, lower than the spin-only value and this clearly indicates that a strong antiferromagnetic exchange coupling is operating between the copper(II) ions. This behaviour shows a great similarity to that of binuclear Cu^{II} complexes involving bridging oxamido ligands and displaying a singlet−triplet energy gap of 500−600 cm^{-1}.[16,38−40] In order to determine the extent of magnetic interaction between the metal ions and to evaluate the singlet−triplet energy gap value $-2J$, magnetic susceptibilities at various temperatures (298−75 K) were measured. The temperature variation of $\chi_m T$ for the complexes [Cu_2L^1] and [Cu_2L^4](ClO_4)$_2$ are shown in Figure 4. The experimental magnetic susceptibility values corrected for diamagnetism were fitted with the theoretical values defined by the modified Bleaney−Bowers equation.[41]

$$\chi_m = (Ng^2\beta^2)/(3kT)[3 + \exp(-2J/kT)]^{-1}(1 - P) + (0.45P/T) + N_\alpha$$

where χ_m is the molar magnetic susceptibility of the complex, P is the percentage of monomeric impurities, N is Avogadro's number, β is the Boltzmann constant, g is the average gyromagnetic ratio, $-2J$ is the singlet−triplet separation, and N_α is the temperature-independent paramagnetism (120 × 10^{-6} $cm^3 \cdot mol^{-1}$). A nonlinear least-square fitting program was employed to calculate $-J$, g and P. From the best fit of the susceptibility data with this equation, a J value of −510 cm^{-1} was obtained with $g = 2.10$ and $P = 0.0012$ for [Cu_2L^1]. [Cu_2L^4] gave a J value of −497 cm^{-1} with $g = 2.12$ and $P = 0.0020$. Even though both complexes have the same bridging groups, [Cu_2L^4] has a lower J value than [Cu_2L^1] due to electronic effects. [Cu_2L^1], containing an N_2O_2 coordination environment, has an enriched electron density facilitating the exchange interaction, whereas in the case of [Cu_2L^4], the electron density at the N_3O site is lower than in [Cu_2L^1] and hence the exchange interaction is also less. Electronic effects in symmetrical ligands have little influence on the magnetic exchange between copper(II) ions.[42] Higher J values are observed for [Cu_2L^1] and [Cu_2L^4], in which the oxamide bridge has the *trans* configuration and the two copper atoms have the same environment so that the two copper atoms are equal in energy. The large J values reveal that the strong antiferromagnetic interaction between two bridged Cu^{II} ions in complexes [Cu_2L^1] and [Cu_2L^4] is mainly due to the enhanced in-plane overlap of the oxamidato bridge.[43] The J value reported in this case is consistent with earlier reports[44−47] for *trans*-oxamidate-bridged binuclear copper(II) complexes.

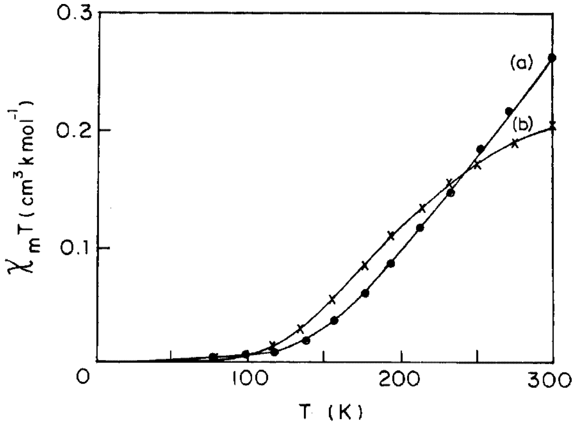


Figure 4. Temperature dependence of the magnetic properties for: (a) [Cu_2L^1], and (b) [Cu_2L^4](ClO_4)$_2$

Electrochemical Studies

The molar conductivity of freshly prepared solutions of the complexes [Cu_2L^{1-3}] in DMF falls in the range 10−15 Λ_m/S cm^2 mol^{-1}, indicating that the complexes are neutral. The molar conductance values of the complexes [$Cu_2L^{4,5}$] are in the range 107−110 Λ_m/S $cm^2 \cdot mol^{-1}$ indicating that the complexes are 1:2 electrolytes.[48]

Cyclic Voltammetric Studies

The cyclic voltammograms for the copper(II) complexes at negative potential were recorded in the potential range 0 to −1.5 V; the data are summarized in Table 3. The cyclic voltammograms obtained for the complexes [Cu_2L^1] and [Cu_2L^5](ClO_4)$_2$ in the cathodic region are shown in Figure 5. All the binuclear copper(II) complexes show two-step, one-electron, quasi-reversible reduction waves. Controlled potential electrolysis performed at a potential 100 mV more negative than the reduction wave indicates the consumption

Table 3. Electrochemical data[a] of copper(II) complexes (reduction at cathodic potential)

Complex	E^1_{pc} (V)	E^1_{pa} (V)	$E^1_{1/2}$ (V)	ΔE (mV)	E^2_{pc} (V)	E^2_{pa} (V)	$E^2_{1/2}$ (V)	ΔE (mV)	K_{con}
$[Cu_2L^1]$	−0.82	−0.68	−0.75	140	−1.08	−0.97	−1.02	110	3.7×10^4
$[Cu_2L^2]$	−1.02	−0.91	−0.96	110	−1.34	−1.24	−1.29	100	3.8×10^5
$[Cu_2L^3]$	−0.52	−0.42	−0.47	100	−0.89	−0.80	−0.85	90	2.7×10^6
$[Cu_2L^4](ClO_4)_2$	−0.48	−0.39	−0.44	90	−0.68	−0.62	−0.65	60	3.6×10^3
$[Cu_2L^5](ClO_4)_2$	−0.55	−0.30	−0.43	250	−0.88	−0.77	−0.83	110	5.9×10^6

[a] Measured by CV at 50 mV/s. E vs. Ag/AgCl. Conditions: GC working and Ag/AgCl reference electrode; supporting electrolyte TBAP; [complex] = 1×10^{-3} M, [TBAP] = 0.1 M.

of one electron per molecule for both the first and second reduction wave. Cyclic voltammograms for all the complexes are similar and involve two quasi-reversible redox processes. Even though in all the complexes both the metal ions have the same geometry and same environment, two reduction waves are obtained in the cathodic region corresponding to stepwise one-electron reductions through a Cu^ICu^{II} intermediate to give a binuclear Cu^I species. In spite of the ligands being symmetrical, their dicopper(II) complexes show two quasi-reversible reduction waves.[49] The two redox processes are represented as follows:

$$Cu^{II}Cu^{II} \rightleftarrows Cu^{II}Cu^{I} \rightleftarrows Cu^{I}Cu^{I}$$

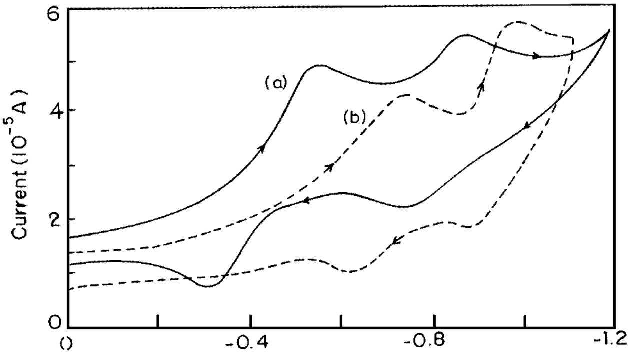


Figure 5. Cyclic voltammograms of: (a) $[Cu_2L^5](ClO_4)_2$, and (b) $[Cu_2L^1]$

The reason for the observation of two reduction waves may be due to electronic exchange between the metal ions: after the first one-electron reduction some of the electron density is transferred from the reduced metal ion to the other metal ion through the oxamidato bridge, and hence the second reduction appears at higher negative potential. The reduction waves are somewhat broad. This may be due to the equilibrium binding of solvent to the Cu^{II} center. The peak broadening diminishes as the scan rate increases.[50] The first reduction wave appears in the potential range −0.48 to −1.02 V. The second reduction wave occurs in the potential range −0.68 to −1.34 V. The potentials at the first reduction waves of the $[Cu_2L^{3-5}]$ are lower than for $[Cu_2L^{1,2}]$. This indicates that $[Cu_2L^{4,5}]$, with an N_3O coordination environment, are reduced more easily. Even though $[Cu_2L^3]$ possesses an N_2O_2 site like $[Cu_2L^{1,2}]$, the first reduction potential of $[Cu_2L^3]$ is lower than that of $[Cu_2L^{1,2}]$, possibly due to the combined effect of the phenoxide ion and unsaturation that reduce the electron density around the metal ion. The difference between the half-wave potentials of the two-redox processes is a measure of the relative stability of mixed-valence species. This approach used for symmetrical complexes with two metal ions in the same coordination environment. The stability of the mixed-valence species $Cu^{II}Cu^I$, can be related to their conproportionation constants, K_{con}. The conproportionation constant for the equilibrium was calculated using the relationship $\log K_{con} = \Delta E/0.0591$. A greater K_{con} value indicates greater stability for the mixed-valence species or that the exchange interaction is greater with respect to the isovalent species.[51] This indicates that the enhanced stability for the $Cu^{II}Cu^I$ intermediate species is probably due to the exchange interaction between the metal centers[52] through the oxamido bridge. The larger the separation between the potentials of the couple, the greater the stability of mixed-valence species with respect to conproportionation.[53,54] Among the copper(II) complexes, $[Cu_2L^4]$ has a lower separation between the potentials than the other complexes, and the lower K_{con} value of $[Cu_2L^4]$ suggests easier access to the $Cu^{II}Cu^I$ species. This is because the exchange interaction is less due to distortion of the geometry, and the stability of the mixed-valence species is lower than that of the rest of the complexes. $[Cu_2L^3]$ and $[Cu_2L^5]$ have higher K_{con} values due to a larger separation between the potentials, and there may be a greater exchange interaction between the metal ions in $[Cu_2L^3]$ and $[Cu_2L^5]$. The conproportionation constant was calculated by following the equilibrium:

$$Cu^{II}\,Cu^{II} \rightleftharpoons Cu^{II}\,Cu^{I} \rightleftharpoons Cu^{I}\,Cu^{I}$$

$$Cu^{II}\,Cu^{II} + Cu^{I}\,Cu^{I} \xrightleftharpoons{K_{con}} 2Cu^{II}\,Cu^{I}$$

Conclusion

A series of *N*,*N*′-bis(disubstituted) oxamidato-bridged binuclear copper(II) complexes has been synthesized. The spectral, electrochemical and magnetic properties of the complexes were studied. From these studies it can be seen that a small variation in the ligand environment imposes an influence on the spectral, magnetic and electrochemical properties of the complexes.

Experimental Section

General: Elemental analysis was carried out on a Carlo Erba Model 1106 elemental analyzer. Electronic spectral studies were carried out on a Hitachi 320 model double beam spectrophotometer in the range 250−800 nm in DMF. IR spectra were recorded on a Hitachi 270−50 spectrophotometer as KBr disks in the range 4000−400 cm^{-1}. Cyclic voltammograms were obtained on a CH instruments electrochemical analyzer. The measurements were carried out at 50 mV/sec under oxygen-free conditions using a three-electrode cell with a glassy carbon electrode as the working electrode, a saturated Ag/AgCl electrode as the reference electrode and platinum wire as the auxiliary electrode. Tetra(*n*-butyl)ammonium perchlorate (TBAP) was used as the supporting electrolyte. The ferrocene/ferrocenium(1+) couple was used as an internal standard ($E_{1/2}$ of the Fc/Fc^+ couple under these experimental conditions is 470 mV in DMF and ΔE_p for Fc/Fc^+ is 70 mV at a 50 mV/sec scan rate). The conductivity measurements were carried out with an Elico digital conductivity bridge model CM-88 using freshly prepared 10^{-3} M solutions of the complexes in DMF. Room temperature magnetic moment and variable-temperature magnetic studies were performed on a PAR model 155 vibrating-sample magnetometer in the temperature range 77−300 K, and the instrument was calibrated using metallic nickel. All data were corrected for diamagnetism of the ligand estimated from Pascal's constants. X-band solution ESR spectra of the complexes (10^{-3} M in DMF) were recorded at 25 °C on a Varian EPR-E 112 spectrometer using diphenylpicrylhydrazine (DPPH) as the reference.

All the chemicals and solvents were of analytical grade and were used as received. The TBAP used as supporting electrolyte in electrochemical measurement was purchased from Fluka and recrystallised from hot methanol. (***Caution!*** *TBAP is potentially explosive, hence care should be taken in handling the compound*). DMF (HPLC) was obtained from Merck.

Preparation of [Cu(oxpn)]: The ligand H_2oxpn {*N*,*N*′-bis(3-aminopropyl) oxamide}[55] and its mononuclear copper(II) complex[18] were prepared following literature procedures.

Synthesis of [Cu_2L^1]: A methanolic solution (40 mL) of acetylacetone (0.40 mL, 3.8 mmol) and $Cu(CH_3COO)_2{\cdot}H_2O$ (0.38 g, 1.9 mmol) were added to a stirred suspension of Cu(oxpn) (0.5 g, 1.9 mmol) in methanol (20 mL). After stirring for an hour, the solution was heated to reflux for 20 min. The resulting solution was filtered and kept at room temperature. Green microcrystals were obtained on slow evaporation of the solution. Yield: 0.9 g (80%). Plate-shaped dark-green crystals suitable for XRD were obtained on recrystallisation from a methanol/chloroform mixture (1:1). $C_{18}H_{26}N_4Cu_2O_4$ (489.51): calcd. C 44.17, H 5.31, Cu 25.96, N 11.45; found C 44.15, H 5.28, Cu 25.43, N 11.42. Selected IR data (KBr): $\tilde{\nu}$ = 1618 (sh, I = 23.7%), 1598 (sh, 28.2%), 1552 (sh, 27.6%) cm^{-1} (sh = sharp, I = intensity). Conductance (Λ_m/S cm^2 mol^{-1}) in DMF 10. λ_{max} (nm) (ε/$M^{-1}{\cdot}cm^{-1}$) in DMF: 572 (200), 329 (18400), 263 (16500). $g = 2.10$; $\mu_{eff} = 1.15\ \mu_B$; $J = -510\ cm^{-1}$.

Synthesis of [Cu_2L^2]: This complex was synthesized by following the above procedure using benzoylacetone (0.61 g, 3.8 mmol) instead of acetylacetone. A dark-green crystalline compound was obtained. Yield: 0.75 g (67%). $C_{28}H_{30}Cu_2N_4O_4$ (613.66): calcd. C 54.81, H 4.89, Cu 20.71, N 9.13; found C 54.78, H 4.87, Cu 20.68, N 9.09. Selected IR data (KBr): $\tilde{\nu}$ = 1625 (sh, 7.6%), 1596 (sh, 20.5%), 1525 (sh, 17.6%) cm^{-1}. Conductance (Λ_m/S cm^2 mol^{-1}) in DMF: 14. λ_{max} (nm) (ε/$M^{-1}{\cdot}cm^{-1}$) in DMF: 581 (250), 344 (13600), 266 (11200). $g = 2.10$; $\mu_{eff} = 1.18\ \mu_B$

Synthesis of [Cu_2L^3]: This complex was synthesized by following the above procedure using salicylaldehyde (0.39 mL, 3.8 mmol) instead of acetylacetone. A pale-green compound was obtained. Yield: 0.83 g (79%). $C_{22}H_{22}Cu_2N_4O_4$ (533.53): calcd. C 49.53, H 4.12, Cu 23.82, N 10.50; found C 49.52, H 4.10, Cu 23.75, N 10.49. Selected IR data (KBr): $\tilde{\nu}$ = 1615 (sh, 9.1%), 1593 (sh, 41.6%), 1530 (sh, 46.3%) cm^{-1}. Conductance (Λ_m/S cm^2 mol^{-1}) in DMF: 15. λ_{max} (nm) (ε/$M^{-1}{\cdot}cm^{-1}$) in DMF: 599 (240), 366 (47200), 261 (46100). $g = 2.10$; $\mu_{eff} = 1.14\ \mu_B$

Synthesis of [Cu_2L^4] (ClO_4)$_2$: A methanolic solution (40 mL) of 2-pyridinecarboxaldehyde (0.36 mL, 3.8 mmol) and $Cu(ClO_4)_2{\cdot}6H_2O$ (0.7 g, 1.9 mmol) was added to a stirred suspension of Cu(oxpn) (0.5 g, 1.9 mmol) in methanol (20 mL). After stirring for an hour, the solution was heated to reflux for 20 min. The resulting solution was filtered and kept at room temperature. A brown crystalline compound was obtained on slow evaporation of the solution. Yield: 0.95 (71%). $C_{20}H_{22}Cl_2Cu_2N_6O_{10}$ (704.42): calcd. C 34.09, H 3.12, Cu 18.05, N 11.93; found C 34.02, H 3.15, Cu 17.92, N 11.89. Selected IR data (KBr): $\tilde{\nu}$ = 1624 (sh, 6.5%), 1590 (sh, 38.7%), 1098 (str, 4.3%), 650 (m, 24.2%) cm^{-1}. Conductance (Λ_m/S cm^2 mol^{-1}) in DMF: 110. λ_{max} (nm) (ε/$M^{-1}{\cdot}cm^{-1}$) in DMF: 592 (105), 345 (42400), 268 (47300). $g = 2.10$; $\mu_{eff} = 1.24\ \mu_B$, $J = -497\ cm^{-1}$.

Synthesis of [Cu_2L^5](ClO_4)$_2$: This complex was synthesized by following the above procedure using diacetyl monoxime (0.61 g, 3.8 mmol) instead of 2-pyridinecarboxaldehyde. A green compound was obtained. Yield: 1 g (86%). $C_{16}H_{26}Cl_2Cu_2N_6O_{12}$ (692.41): calcd. C 27.74, H 3.75, Cu 18.36, N 12.73; found C 27.69, H 3.71, Cu 18.25, N 12.69. Selected IR data (KBr): $\tilde{\nu}$ = 2750 (str, 42.6%), 1622 (sh, 10.2%), 1591 (sh, 43.3%), 1102 (str, 7.6%), 1230 (str, 44.7%), 648 (m, 31.7%) cm^{-1}. Conductance (Λ_m/S cm^2 mol^{-1}) in DMF: 107. λ_{max} (nm) (ε/$M^{-1}{\cdot}cm^{-1}$) in DMF: 572 (140), 334 (48400), 262 (43800). $g = 2.10$; $\mu_{eff} = 1.21\ \mu_B$

Crystal Structure Determinations: Accurate unit cell parameters and orientation matrices were obtained by a least-squares fit of high angle reflections with Mo-K_α radiation on a Siemens SMART CCD area detector in the ω-scan mode for [Cu_2L^1]. Cell refinement and data reduction were carried out using SAINT (Siemens, 1996). A total of 11341 reflections were collected, resulting in 2461 independent reflections of which 1805 had $I > 2\sigma(I)$ and these were considered as observed. The intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods as implemented in SHELXTL-97.[56] The positions of all non-hydrogen atoms were included in the full-matrix least-squares refinement using SHELXTL-97. The positions of all the hydrogen were geometrically fixed at calculated positions and they were allowed to ride on the corresponding non-hydrogen atoms. The final *R* factor was 0.0562, maximum and minimum values of the electron densities in the final electron density map were 0.800, −1.078 $e{\cdot}Å^{-3}$. A dark-green crystal of [Cu_2L^1] of dimension 0.50 × 0.46 × 0.10 mm^3 was used for indexing and intensity data collection on a Siemens Smart CCD diffractometer equipped with a fine focus, 3 kW sealed tube X-ray source and graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 183(2) K. Empirical absorption corrections were applied for compound by using SADABS (Sheldrick, 1996) program for the Siemens area detector.

CCDC-190328 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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