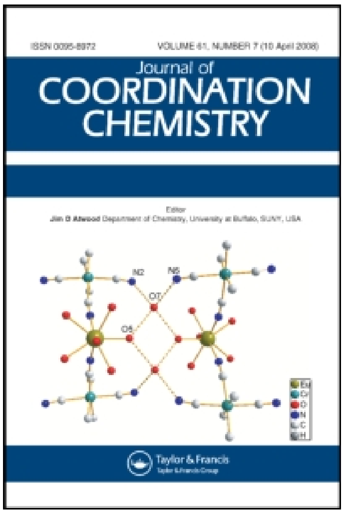

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Synthesis, structure, spectra and redox chemistry of mono- and dinuclear copper(II) complexes containing pyridyl groups

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Synthesis, structure, spectra and redox chemistry of mono- and dinuclear copper(II) complexes containing pyridyl groups

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Copper(II) complexes generalized as Cu_2N_6 and CuN_6 were prepared by using hexadentate ligands, and their spectral and electrochemical behavior was analysed. X-ray analysis of binuclear $[Cu_2L^2Cl_2]^{2+}$ reveals that one copper is trigonal bipyramidal and the other is square pyramidal. Electronic spectra used to determine their stereochemistry in solution indicate that dinuclear Cu_2N_6 has two visible bands that correspond to a typical five-coordinate copper(II) environment, whereas only one broad band was obtained for mononuclear CuN_6. When NaN_3 was added to the dinuclear compounds, their UV–visible spectra underwent significant changes and an isosbestic point at 650 nm was observed; however, no such feature was encountered for the mononuclear compounds.

Keywords: Dinuclear copper(II) complexes; Cu_2N_6, CuN_6 chromophores; Redox potentials

1. Introduction

Copper complexes with a wide variety of supporting ligands have been developed to model the active site structures and functions of copper proteins (enzymes) [1]. There has been considerable interest in the design of ligands and characterization of copper complexes as potential models for metalloproteins [2–6]. These model compounds not only provide a better understanding of biological systems but also assist in the development of new homogeneous catalysts for selective oxidation [2]. 2-Pyridylalkylamines have played important roles as ligands in copper-dioxygen model chemistry [4, 7]. The coordination chemistry of various elements with hexadentate ligands containing pyridyl groups has been studied extensively; for example, the following mononuclear compounds have been structurally examined: M(tpen) [tpen = N,N,N',N'-tetrakis(2-pyridylmethyl) ethylenediamine; M = Fe(II), Cu(II), Co(III), Mo(V), W(V)] [8–12]; M(tppn)

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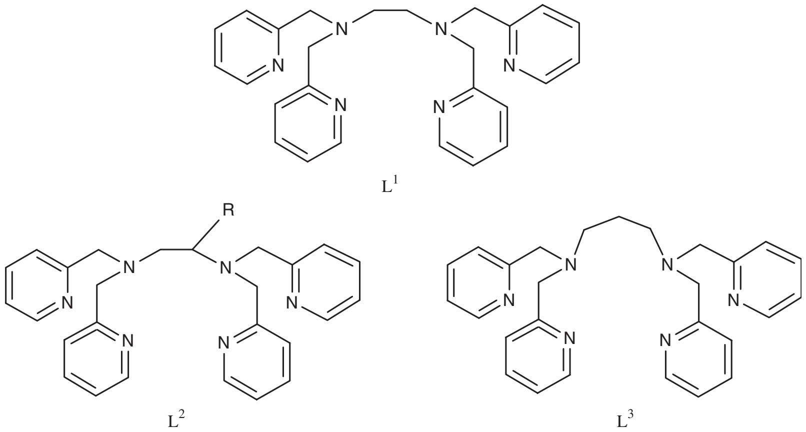

Scheme 1. Ligand structures.

[tppn = *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,2-diaminopropane; M = Fe(II), Co(III), Eu(III), Mo(V), W(V)] [8, 10, 12, 13]; M(tptn) [tptn = *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,3-diaminopropane; M = Fe(II), Co(III)] [8, 10, 12–15]; and M(bmped) [bmped = *N*,*N*′-bis(2-methylpyridyl)ethane-1,2-diamine; M = Mn(III, IV), Cu(II), Cr(III)] [16–19]. Other compounds reported are: M(dmped) [dmped = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)ethylenediamine; M = Cr(III), Cu(II), Mn(II, III, IV), Fe(III), Ru(III)] [20–29]; and M(dmpmed) [dmpmed = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-methylpyridyl)-1,3-propanediamine; M = Cr(III)] [30]. Recently, we reported nickel(II) complexes with tetra- and hexadentate ligands containing pyridyl groups [31].

Only a few binuclear complexes of *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)ethylenediamine with Fe(II, III), Mn(II, III) have been examined [24, 25, 28, 29]; notably, the dinuclear copper(II) complexes with these ligands have not been reported, even though these ligands have the ability to incorporate two metal centers in their coordination sphere. Furthermore, the dinuclear compounds encompass a variety of geometries and oxidation states and can display catalytic activity of biomolecules. Thus, in this article the copper coordination behavior with the title ligands (scheme 1) containing pyridyl groups is reported and spectral differences between mono- and dicopper compounds are established.

2. Experimental

2.1. *Chemicals*

The following reagents were used as received: $Cu(ClO_4)_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, 2-chloromethylpyridine hydrochloride, tetra-*n*-hexylammonium perchlorate, sodium azide (Aldrich); potassium hydroxide (Baker).

2.2. *Physical measurements*

Elemental analyses were carried out on a Fisons Model EA 1108 CHNSO instrument. Diffuse reflectance and solution spectra in methanol were measured on a UV–Vis

Perkin-Elmer Lamda 2 spectrophotometer. ^{1}H NMR spectra were recorded at room temperature on a Varian (300 MHz) spectrometer using TMS as internal standard. GC-mass spectra were measured on a Joel JMS-Axsosha spectrometer. Cyclic voltammetry (EG&G PAR 263A potentiostat) at a platinum sphere electrode was performed at 25 ± 0.4°C and the temperature of the cell was maintained by a cryocirculator (Brabender T-150). The solutions were deoxygenated by bubbling research-grade nitrogen. A three-electrode cell configuration was used. The reference electrode was Ag(s)/($AgNO_3$) in methanol.

2.3. *Synthesis of ligands*

The ligands *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine (L^1), *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,2-diaminopropane (L^2) and *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,3-diaminopropane (L^3) were synthesized as reported elsewhere [32].

2.4. *Synthesis of complexes*

$CuL^1(ClO_4)_2 \cdot 2H_2O$ (1). Compound L^1 (0.424 g, 1.0 mmol) dissolved in methanol (10.0 mL) was added to a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.371 g, 1.0 mmol) in methanol (10.0 mL). The resulting solution was kept at room temperature. The blue compound obtained was collected, washed with methanol and dried over P_4O_{10} under vacuum. Anal. Calcd for $C_{26}H_{32}N_6Cl_2O_{10}Cu$ (%): C, 43.24; H, 4.47; N, 11.64. Found: C, 43.57; H, 4.47; N, 11.38.

$CuL^1Cl_2 \cdot H_2O$ (2). To a methanol solution of L^1 (0.424 g, 1.0 mmol) was added $CuCl_2 \cdot 2H_2O$ (0.170 g, 1.0 mmol) dissolved in methanol (10.0 mL). The resulting solution was allowed to evaporate slowly. The blue compound obtained was collected, washed with methanol and dried over P_4O_{10} under vacuum. Anal. Calcd for $C_{26}H_{30}N_6Cl_2OCu$ (%): C, 54.20; H, 5.25; N, 14.59. Found: C, 54.28; H, 4.99; N, 14.39.

The above procedure was used to prepare the mononuclear compounds by using L^2 and L^3 ligands with respective copper(II) salts: $CuL^2(ClO_4)_2 \cdot H_2O \cdot MeOH$ (**3**): Anal. Calcd for $C_{28}H_{36}N_6Cl_2O_{10}Cu$ (%): C, 44.82; H, 4.84; N, 11.20; Cu, 8.47. Found: C, 44.44; H, 5.00; N, 11.55; Cu, 8.23. $CuL^2Cl_2 \cdot 3H_2O$ (**4**): Anal. Calcd for $C_{27}H_{36}N_6Cl_2O_3Cu$ (%): C, 51.78; H, 5.79; N, 13.42; Cu, 10.15. Found: C, 51.69; H, 5.73; N, 13.27; Cu, 10.01. $CuL^3(ClO_4)_2 \cdot 2H_2O$ (**5**): Anal. Calcd for $C_{27}H_{34}N_6Cl_2O_{10}Cu$ (%): C, 44.05; H, 4.65; N, 11.42; Cu, 8.63. Found: C, 44.00; H, 4.33; N, 11.14; Cu, 8.47. $CuL^3Cl_2 \cdot 4H_2O$ (**6**): Anal. Calcd for $C_{27}H_{34}N_6Cl_2O_4Cu$ (%): C, 50.33; H, 5.94; N, 13.04; Cu, 9.86. Found: C, 50.57; H, 5.79; N, 13.00; Cu, 9.99.

$Cu_2L^1(ClO_4)_4 \cdot 4H_2O$ (7). To ligand L^1 (0.424 g, 1.0 mmol) dissolved in methanol (10.0 mL), a methanol solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.742 g, 2.0 mmol) was added. The resulting solution was kept at room temperature. The blue compound obtained was collected, washed with methanol and dried over P_4O_{10} under vacuum. Anal. Calcd for $C_{26}H_{36}N_6Cl_4O_{20}Cu_2$ (%): C, 30.62; H, 3.56; N, 8.24, Cu, 12.46. Found: C, 30.70; H, 3.33; N, 10.65; Cu, 12.17.

$[Cu_2L^1]Cl_4 \cdot 2H_2O$ (8). A methanol solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.742 g, 2.0 mmol) was added to ligand L^1 (0.424 g, 1.0 mmol) dissolved in methanol (10.0 mL). The resulting solution was kept at room temperature. The blue compound obtained was collected, washed with methanol and dried over P_4O_{10} under vacuum. Anal. Calcd for $C_{26}H_{32}N_6Cl_4O_2Cu_2$ (%): C, 42.90; H, 4.43; N, 11.55; Cu, 17.46. Found: C, 42.75; H, 4.60; N, 11.18; Cu, 17.67.

$[Cu_2L^1]Cl_2 \cdot (ClO_4)_2 \cdot 3H_2O$ (9). Compound L^1 (0.424 g, 1.0 mmol) dissolved in methanol (10.0 mL) was added to a mixture of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.742 g, 2.0 mmol) and tetramethylammonium chloride (0.5 mmol) in methanol (10.0 mL). The resulting solution was allowed to evaporate slowly. The blue compound obtained was collected, washed with methanol and dried over P_4O_{10} under vacuum. Anal. Calcd for $C_{26}H_{34}N_6Cl_4O_{11}Cu_2$ (%): C, 35.73; H, 3.92; N, 9.62; Cu, 14.54. Found: C, 35.49; H, 4.22; N, 9.43; Cu, 14.82.

The above procedure was used to prepare the following compounds by using the ligands L^2 and L^3 with the respective copper(II) salts. $[Cu_2L^2 \cdot 2H_2O \cdot MeOH](ClO_4)_4$ (**10**): Anal. Calcd for $C_{28}H_{38}N_6Cl_4O_{19}Cu_2$ (%): C, 32.65; H, 3.72; N, 8.16; Cu, 12.34. Found: C, 32.39; H, 3.53; N, 8.01; Cu, 12.22. $[Cu_2L^2]Cl_4 \cdot 4H_2O$ (**11**): Anal. Calcd for $C_{27}H_{38}N_6Cl_4O_4Cu_2$ (%): C, 41.69; H, 4.92; N, 10.80; Cu, 16.34. Found: C, 41.39; H, 4.58; N, 10.61; Cu, 16.22. $[Cu_2L^2(H_2O)Cl_2](ClO_4)_2 \cdot H_2O$ (**12**): Anal. Calcd for $C_{27}H_{34}N_6Cl_4O_{10}Cu_2$ (%): C, 37.28; H, 3.94; N, 9.66; Cu, 14.61. Found: C, 36.97; H, 4.26; N, 9.38; Cu, 14.47. $[Cu_2L^3 \cdot 5H_2O](ClO_4)_4$ (**13**): Anal. Calcd for $C_{27}H_{40}N_6Cl_2O_5Cu_2$ (%): C, 30.54; H, 3.80; N, 7.92; Cu, 11.97. Found: C, 48.75; H, 4.60; N, 13.00; Cu, 19.82. $Cu_2L^3Cl_4 \cdot 4H_2O$ (**14**): Anal. Calcd for $C_{27}H_{38}N_6Cl_4O_4Cu_2$ (%): C, 41.69; H, 4.92; N, 10.80; Cu, 16.34. Found: C, 41.39; H, 4.53; N, 10.61; Cu, 16.24. $[Cu_2L^3Cl_2] \cdot 2H_2O(ClO_4)_2$ (**15**): Anal. Calcd for $C_{27}H_{34}N_6Cl_4O_{10}Cu_2$ (%): C, 37.28; H, 3.94; N, 9.66; Cu, 14.61. Found: C, 37.39; H, 3.53; N, 9.93; Cu, 14.35.

$[Cu_2L^2(H_2O)Cl_2](ClO_4)_2 \cdot H_2O$ (11). A solution of this complex (0.01 g) dissolved in methanol (10 mL) was allowed to slowly evaporate. The fine, light blue single crystals obtained were suitable for X-ray diffraction.

2.5. *Crystallographic data collection and structure analysis*

Details of the data collection and structure refinement for $[Cu_2L^2(H_2O)Cl_2](ClO_4)_2 \cdot H_2O$ are presented in table 1. The diffraction data were collected at 293 K on a Siemens P4/PC automatic diffractometer using graphite-monochromatized Mo–Kα radiation and the ω-scan mode at variable scan speed in ω (4 to $30^\circ\,\mathrm{min}^{-1}$) in the θ range of 1.50–25.03°. The measured intensities were corrected for variation of three check reflections monitored periodically and Lp effects, and were reduced to F_o^2. An absorption correction was applied using ψ-scans. Computations were performed with the SHELXTL [33] package on a PC and the scattering factors were taken from the *International Tables of Crystallography* [34]. The monoclinic structure was solved by direct methods followed by subsequent difference Fourier maps, and refined by full-matrix least-squares techniques.

Table 1. Crystal data for $[Cu_2L^2(H_2O)Cl_2](ClO_4)_2 \cdot H_2O$.

Formula	$C_{27}H_{35}Cl_4N_6Cu_2O_{10.50}$
M	880.49
T/K	293(2)
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	13.353(10)
b/Å	12.995(11)
c/Å	20.948(16)
α/°	90
β/°	96.22(4)
γ/°	90
V/Å^3	3614(5)
Z	4
μ (Mo–Kα)/mm^{-1}	0.869
No. of reflections collected/unique	6977
Independent reflections	6673
R (int)	0.1044
wR (F^2)	0.1758
$R1$ [$I > 2\sigma(I)$]	0.0936
Goodness of fit	1.052

3. Results and discussion

The ORTEP view of $[Cu_2L^2(H_2O)Cl_2]^{2+}$ (figure 1) shows that the ligand L^2† accommodates two copper(II) ions. The monoclinic unit cell (table 1) of the complex contains two cationic molecules (A and B) (see packing diagram, figure 2). Both structures A and B present similar characteristic properties but with small variations in the bond distances and angles. The relevant bond distances and angles are given in tables 2 and 3, respectively. The crystal structure reveals that one copper (Cu1) is positioned in a square-pyramidal configuration (1A) and another copper (Cu2) in trigonal-bipyramidal geometry (1B). In both geometries, one imine, two pyridyl nitrogens, one chlorine and water are involved in coordination with the metal ions. The equatorial distances for N(13), N(1), N(6) and Cl(1) with the metal ion are 1.91(2), 2.10(1), 2.01(5) and 2.273(7) Å, respectively. The equatorial Cu–N_{py} bond distances of the complex fall in the range of those reported for the copper(II) complexes of pyridyl-containing ligands [35–38]. The Cu–N_{py} bonds are shorter than Cu–N_{amine} because the nitrogen lone pair electrons are involved in the resonance of the pyridyl rings. It should be noted that the water molecule is located at the axial position in the Cu1 structure and the axial Cu(1)–O(1) distance is 2.31(2) Å. The maximum angle deviations from square-pyramidal geometry are: N(13)–Cu1–N(6) = 160.9(9), N(1)–Cu(1)–Cl(1) = 144.0°. The remaining angles subtended at the metal center by adjacent donors range from 81.4(9) to 111.9(9)° for donor atoms in the *cis* position and from 144.0(6) to 160.9(9)° for donor atoms in the *trans* position. Another Cu2 is placed in square-pyramidal geometry formed by an imine, two pyridyl nitrogens and one chlorine atom. The equatorial distances for N(27), N(20), N(4) and Cl(2) with the metal ion are 1.995(18), 2.00(2), 2.07(5) and 2.31(8) Å, respectively. The maximum

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†The Eu(II) complex of the same ligand L^2 exhibits a distorted dodecahedron coordination geometry with an R-configuration. In this complex cation Eu(III) is bound to all the six nitrogen donors of L^2 and two chloride ions.

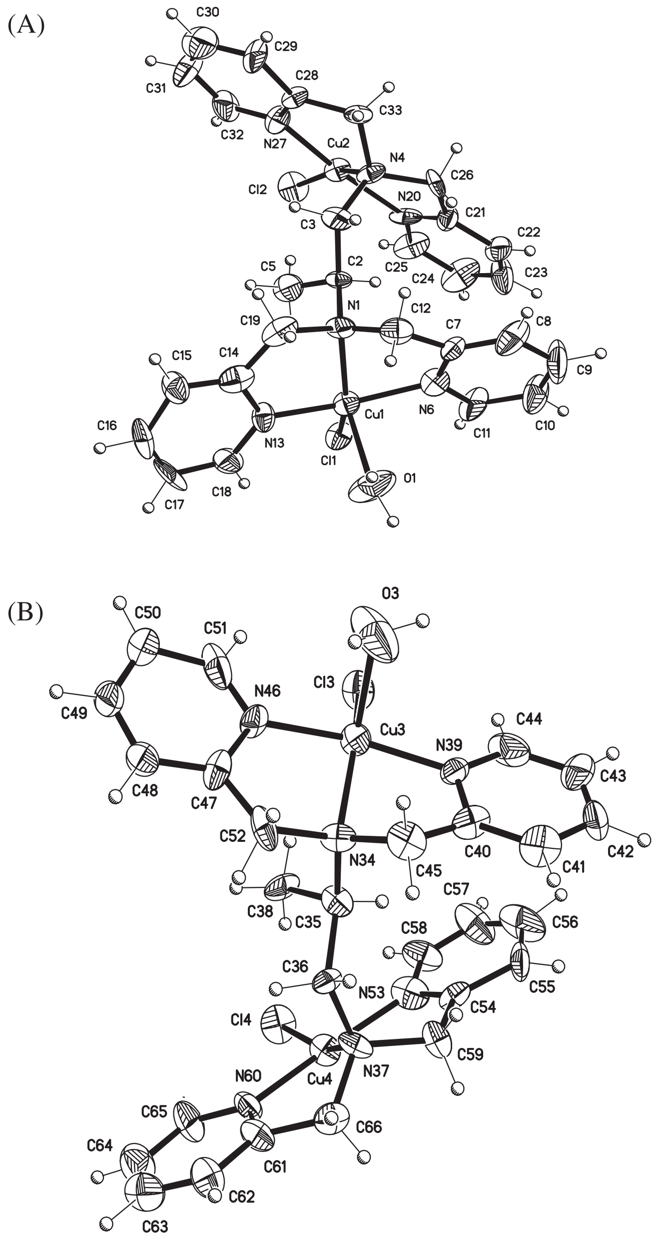


Figure 1. ORTEP drawing of the crystal structures (A and B) of $[Cu_2L^2(H_2O)(MeOH)Cl_2]^{2+}$ showing the atom numbering and the thermal motion ellipsoids (30% probability level).

angle deviations from ideal square-pyramidal geometry are N(27)–Cu2–N(20) = 164.1(9), N(4)–Cu(2)–Cl(2) = 164.0(6)°. The remaining angles subtended at the metal center by adjacent donor atoms range from 81.0(8) to 98.4(8)° for donor atoms in the *cis* position and from 144.0(6) to 160.9(9)° for donor atoms in the *trans* position. Structure B presents similar characteristics to structure A with small variation of bond distances and bond angles.

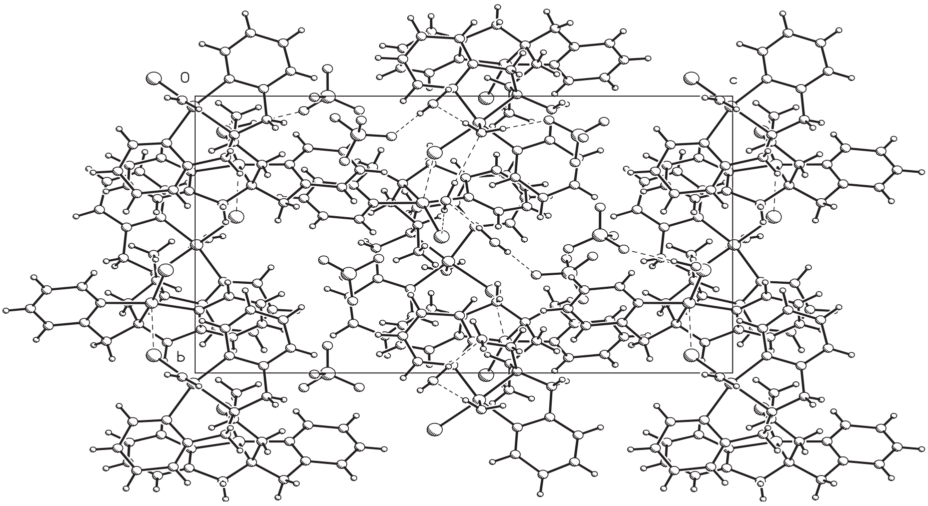


Figure 2. Perspective view of packing diagram of $[Cu_2L^2(H_2O)(MeOH)Cl_2]^{2+}$.

Table 2. Selected bond lengths (Å) for $[Cu_2L^2(H_2O)Cl_2](ClO_4)_2 \cdot H_2O$.

Cu(1)–N(13)	1.91(2)	Cu(1)–N(6)	2.01(2)
Cu(1)–N(1)	2.10(2)	Cu(1)–Cl(1)	2.273(7)
Cu(2)–N(27)	1.995(18)	Cu(2)–N(20)	2.00(2)
Cu(2)–Cl(2)	2.231(8)	Cu(2)–N(4)	2.07(2)
Cu(1)–O(1)	2.31(2)		
Cu(3)–N(39)	1.95(2)	Cu(3)–N(46)	1.96(2)
Cu(3)–N(34)	2.073(2)	Cu(3)–Cl(3)	2.312(7)
Cu(4)–N(60)	1.977(17)	Cu(4)–N(53)	2.05(2)
Cu(4)–Cl(4)	2.261(8)	Cu(4)–N(37)	2.051(2)
Cu(3)–O(3)	2.21(2)		

Table 3. Selected bond angles (°) for $[Cu_2L^2(H_2O)Cl_2](ClO_4)_2 \cdot H_2O$.

N(13)–Cu(1)–N(6)	160.9(9)	N(13)–Cu(1)–N(1)	84.4(8)
N(6)–Cu(1)–N(1)	81.4(9)	N(13)–Cu(1)–Cl(1)	99.5(6)
N(6)–Cu(1)–Cl(1)	99.5(6)	N(1)–Cu(1)–Cl(1)	144.0(4)
N(13)–Cu(1)–O(1)	85.3(10)	N(6)–Cu(1)–O(1)	88.3(10)
N(1)–Cu(1)–O(1)	111.9(9)	Cl(1)–Cu(1)–O(1)	104.1(8)
N(27)–Cu(2)–N(20)	164.1(9)	N(27)–Cu(2)–N(4)	83.3(8)
N(20)–Cu(2)–N(4)	81.0(8)	N(27)–Cu(2)–Cl(2)	98.4(7)
N(20)–Cu(2)–Cl(2)	97.4(7)	N(4)–Cu(2)–Cl(2)	164.0(6)
N(39)–Cu(3)–N(46)	162.7(8)	N(39)–Cu(3)–N(34)	82.8(8)
N(46)–Cu(3)–N(34)	82.7(8)	N(39)–Cu(3)–O(3)	92.9(11)
N(46)–Cu(3)–O(3)	84.3(10)	N(34)–Cu(3)–O(3)	113.3(11)
N(39)–Cu(3)–Cl(3)	98.6(6)	N(46)–Cu(3)–Cl(3)	98.7(6)
N(34)–Cu(3)–Cl(3)	146.3(5)	O(3)–Cu(3)–Cl(3)	100.3(11)
N(60)–Cu(4)–N(59)	165.0(9)	N(60)–Cu(4)–N(37)	81.5(8)
N(53)–Cu(4)–N(37)	83.5(9)	N(60)–Cu(4)–Cl(4)	98.2(7)
N(53)–Cu(4)–Cl(4)	96.1(8)	N(37)–Cu(4)–Cl(4)	161.6(7)

3.1. *Electronic spectra*

Electronic spectra were recorded in methanol and the band positions with molar absorption coefficients for the complexes are presented in table 4. The spectra of

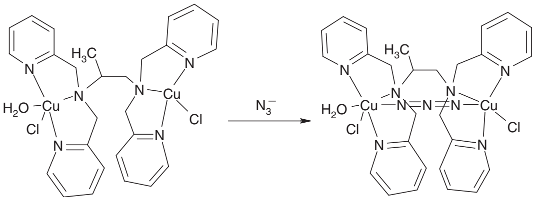
Table 4. Electronic absorption spectral data for copper(II) compounds: λ_{max} (nm), ε ($dm^3\,mol^{-1}\,cm^{-1}$) in parentheses.

Compound	d–d bands[a]	CT bands[b]
1	684 (150)	304 (716)
2	690 (175)	304 (716)
3	682 (135)	305 (720)
4	680 (135)	300 (720)
5	681 (138)	304 (718)
6	685 (146)	305 (740)
7	745 (286), 845 (279)	310 (750)
8	789 (293), 894 (286)	315 (935)
9	763 (284), 855 (280)	325 (915)
10	786 (293), 891 (286)	325 (910)
11	764 (280), 859 (275)	330 (930)
12	788 (300), 893 (294)	320 (900)
13	768 (275), 878 (270)	308 (910)
14	754 (290), 882 (280)	315 (925)
15	755 (285), 885 (280)	310 (920)

Concentrations: [a] $\approx 1.0 \times 10^{-2}$, [b] $\approx 1.0 \times 10^{-3}$ mol dm^{-3}.

the mononuclear compounds differ markedly from those of the dinuclear complexes. For the dinuclear compounds, two absorption maxima around 580 and 800 nm were obtained, indicating five-coordinated geometry around the copper(II) ion. The d–d band positions obtained for the dinuclear compounds indicate a square-pyramidal structure at copper(II) centers. Thus, for $[Cu_2L^2(H_2O)Cl_2]^{2+}$, two separate bands at 585 and 786 nm are observed. We suggest that this spectrum arises because of the presence of both square-pyramidal and trigonal-bipyramidal metal centers in the dinuclear complexes. However, a broad band (at around 680 nm) was observed for the mononuclear complexes, which may possess an octahedral structure. As expected, the center of the d–d envelope is found at higher energy for the mononuclear compounds than the dinuclear complexes, due to greater N(σ)–donor in-plane interaction with the copper ion than would be expected for other geometries such as trigonal bipyramidal or square pyramidal.

During NaN_3 addition to $[Cu_2L^2Cl_2]^{2+}$, two bands (572, 766 nm) were observed. The intensity of the 572 nm band decreased slowly and then disappeared whereas the intensity of the 766 nm band increased dramatically, indicating that N_3^- was coordinated to copper(II), leading to geometrical transformation; possibly the square-pyramidal and trigonal-bipyramidal structures are transformed to octahedral geometry. To estimate the azide affinity for the dinuclear complexes, we performed spectrophotometric N_3^- titrations against the complexes in methanol. The spectrum of the complexes underwent marked changes up to a ratio of $[N_3^-]:[Cu_2] \approx 1.2:1$ (figure 3) and we observed an isosbestic point at 650 nm. The possibility of bridging two Cu(II) ions by the azide is high as the N_3^- ion is a potential



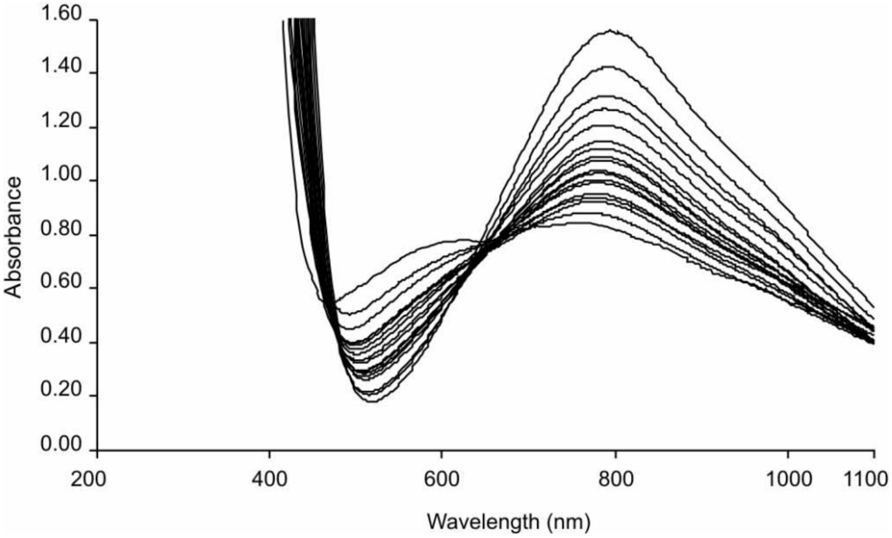


Figure 3. Electronic absorption spectra of $[Cu_2L^2(H_2O)(MeOH)Cl_2]^{2+}$ with sodium azide in methanol.

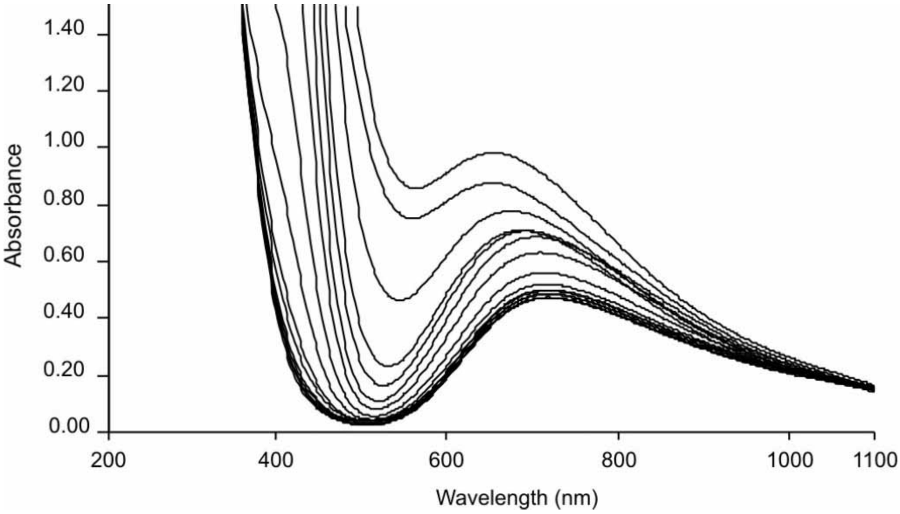


Figure 4. Electronic absorption spectra of $[CuL^2]^{2+}$ with sodium azide in methanol.

bridging anion. We tried unsuccessfully to isolate an azide-bridged dinuclear molecule for structural analysis. After reaching this ratio, the intensity of the band decreased and no further effects on the bands were observed. By contrast, when NaN_3 was added to the mononuclear compounds, only one band at around 715 nm was observed, the intensity of the band is steadily increased up to $[N_3^-]:[Cu] \approx 0.9:1$, then it decreases and no isosbestic point was encountered. The band position was moved towards the high-energy side (blue shift) in the visible band (figure 4) because of the solvation of the azide moiety as the polarity of the environment increases during N_3^- addition.

Table 5. Electrochemical data[a] for Cu(II) complexes at 25°C.

Compound	Epc I	Epa I	Epc II	Epa II	Epc III	Epa III	Epc IV	Epa VI	$E_{1/2}$
1	–	–	–	–	–0.80	–0.62	–	–	–0.72
3	–	–	–	–	–0.78	–0.62	–	–	–0.70
5	–	–	–	–	–0.76	–0.62	–	–	–0.68
8	–	–	0.04	–	–0.69	–0.07	–0.92	–0.50	–
11	0.24	–	0.05	–	–0.63	–0.05	–0.89	–0.52	–
12	–	–	0.03	–	–0.69	–0.07	–0.95	–0.53	–

[a] Measured *vs.* nonaqueous silver reference electrode; add 544 mV to convert into normal hydrogen electrode (NHE); scan rate 50 mV s^{-1}, supporting electrolyte tetra-*n*-hexylammonium perchlorate (0.1 mol dm^{-3}); complex concentration 1.0 mM dm^{-3}.

3.2. *Redox chemistry*

The redox behavior of the Cu(II) complexes was studied by cyclic voltammetry (CV) on a stationary platinum electrode. The electrochemical data for the complexes are presented in table 5. During the experiment, the cathodic shift in the reduction peak and the anodic shift in the oxidation wave increased when the scan rate was raised. This may be due to the non-Nernstian behaviors of heterogeneous electron-transfer kinetics [39]. All the mononuclear compounds exhibit quasi-reversible redox properties while for dinuclear compounds, irreversible redox behavior was detected, suggesting that the electrochemistry of the dinuclear compounds differs from that of the mononuclear compounds, as was seen in the electronic spectra. For instance, a redox potential ($E_{1/2}$) of −0.68 to −0.72 V, with $\Delta E = 138$–142, corresponding to Cu(II) → Cu(I), was obtained for the mononuclear complexes. For the dinuclear compounds, two reduction wave potentials were obtained (the first reduction wave at around −0.63 to −0.69 V and the second wave at around −0.89 to −0.95 V); these observations can be represented by $\mathrm{Cu^{II}Cu^{II}} \leftrightarrow \mathrm{Cu^{II}Cu^{I}} \leftrightarrow \mathrm{Cu^{I}Cu^{I}}$. Thus, $[\mathrm{Cu_2L^2Cl_2}]^{2+}$ undergoes four cathodic reduction potentials, 0.24 V (Epc I), 0.05 V (Epc II), −0.63 V (Epc III) and −0.89 V (Epc IV) (figure 5), but only two anodic peaks (see table 5) were noted. The four cathodic peaks can be explained in terms of the following equations,

$$\begin{tikzcd}
{[\mathrm{Cu_2L^2Cl_2}]^{2+}} \arrow[r, shift left, "-\mathrm{Cl}^-"] & {[\mathrm{Cu_2L^2Cl}]^{3+}} \arrow[l, shift left] \arrow[r, shift left, "-\mathrm{Cl}^-"] & {[\mathrm{Cu_2L^2}]^{4+}} \arrow[l, shift left] \arrow[r, shift left, "+\mathrm{e}^-"] & {[\mathrm{Cu_2L^2}]^{3+}} \arrow[l, shift left, "-\mathrm{e}^-"] \arrow[d, shift left, "+\mathrm{e}^-"] \\
{[\mathrm{Cu_2L^2(sol)_2}]^{2+}} \arrow[r, shift left, "\text{solvent} +"] & {[\mathrm{Cu_2L^2(sol)}]^{2+}} \arrow[l, shift left] \arrow[r, shift left, "\text{solvent} +"] & {} & {[\mathrm{Cu_2L^2}]^{2+}} \arrow[u, shift left, "-\mathrm{e}^-"] \arrow[ll, shift left]
\end{tikzcd}$$

For the oxidation process:

$$[\mathrm{Cu_2L^2(sol)_2}]^{2+} \underset{+\mathrm{e}^-}{\overset{-\mathrm{e}^-}{\rightleftharpoons}} [\mathrm{Cu_2L^2(sol)_2}]^{3+} \underset{+\mathrm{e}^-}{\overset{-\mathrm{e}^-}{\rightleftharpoons}} [\mathrm{Cu_2L^2(sol)_2}]^{4+}$$

4. Conclusion

Mononuclear copper(II) complexes differ spectrally from dinuclear copper complexes. In the electronic spectra, the dinuclear $\mathrm{Cu_2N_6}$ chromophore, where two types

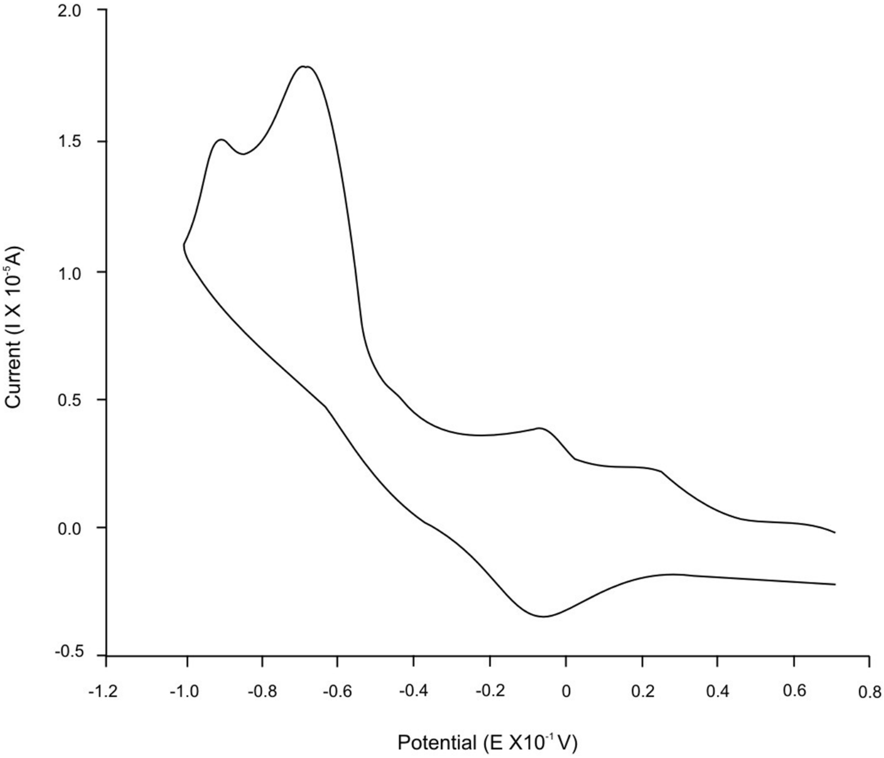


Figure 5. Cyclic voltammogram of $[Cu_2L^2(H_2O)(MeOH)Cl_2]^{2+}$ (1.0 mmol dm^{-3}) in methanol at 25°C. Supporting electrolyte: 0.1 mol dm^{-3} *tetra-n*-hexylammonium perchlorate.

of geometrical centers were identified by X-ray analysis, exhibits two visible bands corresponding to five-coordinate copper(II) geometry; by contrast, a broad band resulted for mononuclear CuN_6. When NaN_3 was added to the dinuclear compounds, changes in the spectral bands were observed, including an isosbestic point at 650 nm, suggesting that a geometrical transformation occurred during the N_3^- addition. However, no such structural change was observed for the mononuclear compounds.

Supplementary material

Crystallographic data (CCDC No. 273914) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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