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Synthesis, Structure and Magnetic Properties of a New Chloro-bridged Dimeric Copper Complex, Bis(μ-chloro)bis(8-amino-5-aza-4-methyl-3-octene-2-onato)-dicopper(II)

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Abstract

The synthesis, structure and important properties of the title compound are reported. The complex, formulated as $Cu_2L_2Cl_2$ (L = singly deprotonated 8-amino-5-aza-4-methyl-3-octene-2-one ligand), has a dimeric structure composed of two CuLCl subunits linked via bridging chlorine atoms. Each copper atom is five-coordinate in a distorted square-pyramidal coordination environment. The Cu_2Cl_2 structural core is characterized by an acute Cu–Cl–Cu′ angle of 82.9° and a short Cu–Cu′ separation of 3.418 Å. Crystallographic data: monoclinic space group $P2_1/c$ (No. 14), $a = 6.150(1)$, $b = 11.224(2)$, $c = 15.057(3)$ Å; $\beta = 99.08(1)°$; $R = 0.0222$, $R_w = 0.0291$. Magnetic susceptibility and magnetization measurements indicate ferromagnetic coupling of the copper(II) centers within the dimer, contrary to the predictions of a previously reported empirical correlation between the exchange energy, $2J$, and structural factors.

Introduction

Two interacting copper(II) centers yield a singlet and a triplet state separated by $2J$, where J is the isotropic exchange coupling parameter defined by $\mathcal{H} = -2JS_1S_2$. Correlation between the exchange energy, $2J$, and the structure of the dimeric molecules has received considerable attention from many researchers. One of the most elegant correlations was derived by Hatfield *et al.* [1], who showed that the magnitude of $2J$ in planar bis-hydroxy-bridged copper(II) dimers depends on the Cu–O–Cu′ bridging angle. For bis-chloro bridged dimers the correlation was found to be more complex, since apart from the bridging angle, bridging lengths and the coordination geometry of the copper centers have an effect on the magnitude of $2J$. Hodgson *et al.* [2] have shown that for bis-chloro-bridged Cu(II) dimers, wherein copper centers adopt a square-pyramidal or trigonal-bipyramidal geometry, an empirical correlation exists between the exchange energy and the ϕ/R ratio (where ϕ is the Cu–Cl–Cu′ bridging angle and R is the longer copper–chlorine distance in the bridge). This empirical correlation is based only on the limited number of structurally and magnetically characterized bis-chloro-bridged five-coordinated copper dimers that have been reported in the literature. To expand this data base we have been studying additional systems of this type. In this paper, we report the synthesis, structural and magnetic characterization, as well as some solution and spectral properties, of the new chloro-bridged dimer bis(μ-chloro)bis(8-amino-5-aza-4-methyl-3-octene-2-onato)-dicopper(II).

Experimental

Materials

Anhydrous copper(II) chloride was prepared by refluxing the hydrated salt (4 g) in freshly distilled thionyl chloride (20 ml) for 2 h and then evaporating the resulting mixture to dryness. The preparation of the ligand HL, 8-amino-5-aza-4-methyl-3-octene-2-one, was described elsewhere [3]. All other chemicals were of reagent grade and were used without further purification.

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Bis(μ-chloro)bis(8-amino-5-aza-4-methyl-3-octene-2-onato)dicopper(II), $Cu_2L_2Cl_2$

A solution of ligand HL (0.02 mol) in 20 ml methanol was added to 0.01 mol of anhydrous copper(II) chloride in 20 ml methanol and the mixture was stirred for 1 h. The resulting precipitate was removed by filtration and washed with cold methanol. Partial evaporation of the filtrate yielded another portion of the complex. The precipitates were combined and recrystallized from acetonitrile to give dark-green crystals of $Cu_2L_2Cl_2$ complex in 70% yield (relative to the amount of copper chloride used). Melting point (m.p.) 155 °C (dec.). *Anal.* Found: C, 37.9; H, 6.0; N, 11.0. Calc. for $Cu_2C_{16}H_{30}N_4O_2Cl_2$: C, 37.8; H, 6.0; N, 11.0%.

Physical Measurements

Elemental analysis was performed on a Carlo Erba MOD 1106 Elemental Analyzer. Visible spectra were recorded on a Perkin-Elmer 402 spectrometer, IR spectra on a Perkin-Elmer 621 spectrometer using Nujol and hexachlorobutadiene mulls, and EPR spectra on a JES-ME-3X spectrometer at 9 GHz. Conductance measurements were made with a K-58 conducting bridge constructed at the Technical University of Warsaw. The magnetic susceptibility of a powdered sample of the copper complex was measured in the 4.2–290 K temperature range using a Faraday magnetometer calibrated with mercury tetrakis(thiocyanato)cobaltate [4]. The magnetic susceptibility data were corrected for diamagnetism, estimated as 119.3×10^{-6} cgsu per copper atom, and for TIP (60×10^{-6} cgsu per copper atom).

X-ray Crystallography of $Cu_2L_2Cl_2$

A suitable crystal of $Cu_2L_2Cl_2$ was isolated, mounted on a glass fiber with epoxy cement, and transferred to a Nicolet R3m four-circle diffractometer for characterization and data collection. Unit cell parameters were determined from the angular settings of 25 well-centered reflections ($21° < 2\theta < 44°$). Axial photographs, and a limited search through an octant of reciprocal space revealed systematic absences and symmetry consistent with the monoclinic space group $P2_1/c$.

$\theta/2\theta$ scans were collected with variable scan speeds ranging from 2.0 to 29.3°/min. One quadrant of data ($\pm h, +k, +l$) was collected with 2θ restricted to 3–45°. A total of 1504 reflections was measured, and corrected for Lorentz-polarization and absorption effects (the empirical absorption correction was based on 5 azimuthal reflections). The minimum and maximum drift corrections were 0.9918 and 1.0185, and the minimum and maximum transmission factors were 0.575 and 0.866, respectively. Data averaging yielded 1258 unique reflections of which 1074 had $F > 6\sigma(F)$ with $R_{int} = 0.0160$.

The structure was successfully solved and refined by full-matrix least squares in the monoclinic space group $P2_1/c$ (No. 14). A combination of direct methods (SHELXS with the TREF option) and Fourier techniques was used to locate the positions of the non-hydrogen atoms. Isotropic refinement of this model with unit weights converged to $R = 0.0852$ with uncorrected data. Anisotropic refinement of this model yielded $R = 0.0460$. Subsequent cycles of least-squares refinement included absorption corrected data, a weighting scheme based on $\sigma(F)$, and an empirical isotropic extinction parameter. Positional and isotropic temperature parameters for the hydrogen atoms were also included and refined. During the least-squares refinements, the N–H bonds were constrained to have a length of 0.87 Å. The final values for the refinement indices are given in Table 1 along with the crystal data and data collection parameters. Fractional atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms are assembled in Table 2. See also 'Supplementary Material'.

TABLE 1. Structure Determination Summary for $Cu_2L_2Cl_2$

Crystal data	
Molecular formula	$Cu_2C_{16}H_{30}N_4O_2Cl_2$
Color and habit	dark green prisms
Size	0.12 × 0.25 × 0.50 mm
Space group	$P2_1/c$ (No. 14).
Unit cell dimensions	$a = 6.150(1)$, $b = 11.224(2)$, $c = 15.057(3)$ Å $\beta = 99.08(1)°$
Volume	1026.4(3) $Å^3$
Z	2 molecules/cell
Molecular weight	508.44
Density (g/cm^3)	calc. 1.65, obs.[a] 1.63
$F(000)$	524 e^-
Data collection	
Diffractometer	Nicolet R3m
Radiation	Mo (0.71073)
Monochromator	highly oriented graphite crystal
Temperature	room temperature (294 K)
hkl limits	±9, +14, +18
2θ range	3–45°
Scan type	$\theta/2\theta$
Scan speed	variable, 2.0 to 29.3°/min
Scan range	0.8 below $K_{\alpha 1}$ to 0.8 above $K_{\alpha 2}$
Background measurement	stationary crystal and counter at beginning and end of scan; total background time to scan time ratio of 0.5
Standard reflections	3 measured every 37
Reflections collected	1504 total, 1258 independent
Reflections observed	1074; $F > 6\sigma(F)$
Absorption coefficient	23.16 cm^{-1}
No. psi scan reflections	5
Min./max. transmission	0.575/0.866

(continued)

TABLE 1. *(continued)*

Refinement	
System used	MicroVAX II; Nicolet SHELXS/ SHELXTL PLUS
Solution	Direct Methods (TREF)
Final residuals	$R = 0.0222, R_w = 0.0291^b$
Goodness-of-fit	$S = 1.16^c$
Largest |shift/e.s.d.|	0.001
No. variables	179
Data-to-parameter ratio	6.0:1
Largest difference peak	0.25 $e^- Å^{-3}$

[a] By flotation in 1,2-dibromoethane and 1,1,1-trichloroethane mixture. [b] $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$; $R_w = [\Sigma(w||F_o| - |F_c||^2)/\Sigma(w|F_o|^2)]^{1/2}$, $w = [\sigma^2(F) + |g|F^2]^{-1}$, $g = 0.000376$. [c] $S = [\Sigma(w||F_o| - |F_c||^2)/(M - N)]^{1/2}$ where M is the number of observed reflections, and N is the number of parameters refined.

TABLE 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters[a] ($Å^2 \times 10^3$) for $Cu_2L_2Cl_2$

Atom	x	y	z	U_{eq}
Cu	9813.1(6)	1502.3(3)	5157.6(3)	30(1)
Cl	11711.2(13)	169.1(7)	6184.8(6)	37(1)
N(1)	7031(5)	1107(2)	5607(2)	32(1)
N(2)	8683(4)	3113(2)	4854(2)	31(1)
O	12277(3)	1709(2)	4526(2)	31(1)
C(1)	6592(7)	1835(4)	6381(3)	44(1)
C(2)	7569(6)	3065(3)	6352(3)	43(1)
C(3)	7177(6)	3626(3)	5428(3)	40(1)
C(4)	7743(7)	4776(3)	3812(3)	47(1)
C(5)	9027(5)	3677(3)	4132(2)	31(1)
C(6)	10616(6)	3280(3)	3607(2)	35(1)
C(7)	12112(5)	2379(3)	3819(2)	29(1)
C(8)	13748(7)	2110(4)	3208(3)	45(2)

[a] Equivalent isotropic parameter U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

The tridentate ligand HL, 8-amino-5-aza-4-methyl-3-octene-2-one (Fig. 1), was obtained by the reaction of pentane-2,4-dione with a three-fold excess of 1,3-diaminopropane, as reported recently [3]. The reaction of this ligand with anhydrous copper(II) chloride in methanol yields a dark-green copper complex, which can be formulated as $(CuLCl)_n$ based on elemental analysis data. The two-fold excess of ligand used in this preparation serves as a Brönsted base to consume the protons released from HL upon complexation.

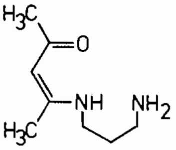

Fig. 1. Schematic representation of 8-amino-5-aza-4-methyl-3-octene-2-one (HL).

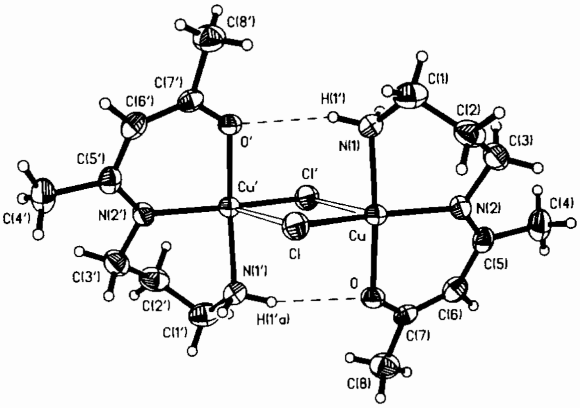

Fig. 2. A perspective view of the $Cu_2L_2Cl_2$ dimer including the atom numbering scheme.

TABLE 3. Bond Distances (Å) and Angles (°) for Non-hydrogen Atoms in $Cu_2L_2Cl_2$

Cu–Cl	2.329(1)	O–C(7)	1.294(4)
Cu–Cl'	2.808(1)	C(1)–C(2)	1.509(5)
Cu–N(1)	1.987(3)	C(2)–C(3)	1.511(6)
Cu–N(2)	1.965(2)	C(4)–C(5)	1.503(4)
Cu–O	1.926(2)	C(5)–C(6)	1.422(5)
N(1)–C(1)	1.483(5)	C(6)–C(7)	1.370(4)
N(2)–C(3)	1.480(4)	C(7)–C(8)	1.497(5)
N(2)–C(5)	1.304(4)		
N(1)–Cu–Cl	89.9(1)	C(5)–N(2)–C(3)	119.9(3)
N(2)–Cu–Cl	150.2(1)	C(7)–O–Cu	120.7(2)
Cl'–Cu–Cl	97.1(1)	C(2)–C(1)–N(1)	111.1(3)
N(1)–Cu–Cl'	83.6(1)	C(3)–C(2)–C(1)	113.7(3)
N(2)–Cu–Cl'	112.4(1)	C(2)–C(3)–N(2)	110.7(3)
O–Cu–Cl'	85.7(1)	C(4)–C(5)–N(2)	121.3(3)
N(2)–Cu–N(1)	89.6(1)	C(6)–C(5)–N(2)	121.8(3)
O–Cu–Cl	93.1(1)	C(6)–C(5)–C(4)	116.9(3)
O–Cu–N(1)	169.1(1)	C(7)–C(6)–C(5)	126.7(3)
O–Cu–N(2)	92.9(1)	C(6)–C(7)–O	125.6(3)
C(1)–N(1)–Cu	114.7(2)	C(8)–C(7)–O	114.5(3)
C(3)–N(2)–Cu	116.9(2)	C(8)–C(7)–C(6)	119.9(3)
C(5)–N(2)–Cu	122.8(2)		

Symmetry code for Cl' = $(2 - x, -y, 1 - z)$.

A single-crystal X-ray diffraction study on the complex reveals that it is dimeric in nature and is best formulated as $Cu_2L_2Cl_2$. A perspective view of the centrosymmetric dimeric $Cu_2L_2Cl_2$ molecule with its associated atom numbering scheme is depicted in Fig. 2, while the final bond distances and angles are presented in Table 3. The complex consists of two identical monomeric CuLCl subunits, wherein the copper atom is bound to a singly deprotonated ligand molecule and a chloride anion. The subunits are held together principally through their bridging chloride ligands. The dimeric structure of $Cu_2L_2Cl_2$ is further stabilized by the presence of two intramolecular hydrogen bonds, each of them formed between one of the primary amino hydrogen atoms of one subunit and the carbonyl oxygen atom of the other. The dimeric $Cu_2L_2Cl_2$ molecules are rather well separated in the crystal lattice and interact with each other only by interdimer hydrogen bonding in which the remaining amino hydrogen atoms are involved (Fig. 3).

Each copper atom is five-coordinated, and the bond angles at the copper center (Table 3) indicate that it adopts a distorted square-pyramidal rather than a trigonal-bipyramidal geometry. Three donor atoms from the ligand L and a chlorine atom (Cl) form the square base. The other chlorine atom (Cl′) occupies the fifth apical position. The four basal atoms N(1), N(2), O, and Cl deviate markedly from coplanarity (−0.369, 0.400, −0.358 and 0.327 Å, respectively, from the least-squares basal plane). As usual in square-pyramidal copper complexes, the copper atom is displaced 0.178 Å towards the apical chlorine atom (Cl′). The Cu–N and Cu–O distances are not unusual and are comparable to those reported for similar systems [3, 5, 6]. Two six-membered chelate rings are present within each monomeric CuLCl subunit. One of them, incorporating the pentane-2,4-dione core, is planar and the bond distances within this ring indicate that the ligand L is coordinated in its imino-enolic tautomeric form, as was reported for a related $[(CuL)_3(OH)](ClO_4)_2$ compound [3]. The second ring, defined by the 1,3-diaminopropane moiety, assumes a half-boat conformation with the N(1)–Cu–N(2) angle equal to 89.6°.

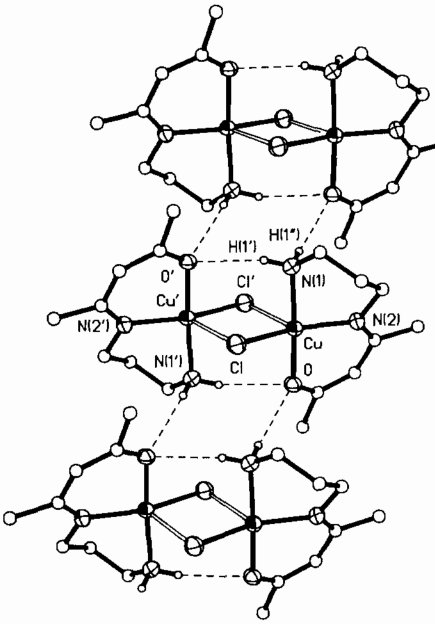

Fig. 3. An illustration of the hydrogen-bonding interactions between the $Cu_2L_2Cl_2$ molecules.

The copper and chlorine atoms form a planar centrosymmetric four-membered ring within the dimeric $Cu_2L_2Cl_2$ molecule, with Cu–Cl and Cu–Cl′ distances of 2.329 and 2.808 Å, respectively, and a Cu–Cl–Cu′ angle of 82.9°. Both copper–chlorine distances are within the range typically observed for chloro-bridged copper dimers (2.24 to 2.70 Å for Cu–Cl [7] and 2.45 [8] to 3.36 [9, 10] Å for Cu–Cl′). The bridging Cu–Cl–Cu′ angle in $Cu_2L_2Cl_2$ is markedly smaller than in related chloro-bridged copper(II) dimers, and thus the Cu–Cu′ distance of 3.418 Å is close to the shortest Cu–Cu′ separation in this class of compounds, *viz.* 3.416 Å for the Cu_2[1-(2-pyridylazo)-2-naphtholate$]_2Cl_2$ complex [11]. The value of ϕ/R, where ϕ is the Cu–Cl–Cu′ angle (°) and R is the longer Cu–Cl′ distance (Å), is 29.52 for $Cu_2L_2Cl_2$, and is comparable to the values of 29.30 and 29.91 reported for the antiferromagnetically coupled dimers Cu_2(tetramethylenesulfoxide$)_4Cl_4$ and Cu_2(2-methylpyridine$)_4Cl_4$, respectively [2]. For this ϕ/R value Hodgson's empirical correlation [2] predicts antiferromagnetic exchange in $Cu_2L_2Cl_2$ with an exchange energy, $2J$, of *ca.* -15 cm^{-1}.

Magnetic data for a powdered sample of $Cu_2L_2Cl_2$ were collected over the temperature range 4.2–290 K. Plots of inverse magnetic susceptibility χ_{Cu}^{-1} and effective magnetic moment μ_{eff} (per copper atom) as a function of temperature are shown in Fig. 4. Analysis of the data within the Curie–Weiss law leads to a positive value for the Weiss constant. The effective magnetic moment of $Cu_2L_2Cl_2$ increases with decreasing temperature within the 290–10 K region, reaches a maximum at around 10 K,

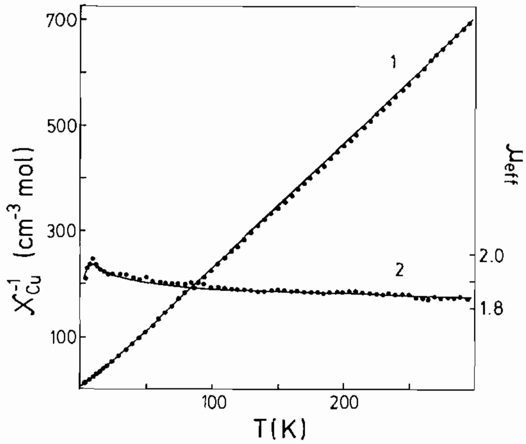

Fig. 4. Temperature dependence of the inverse magnetic susceptibilities χ_{Cu}^{-1} (trace 1) and the magnetic moment μ_{eff} per copper atom (trace 2) for $Cu_2L_2Cl_2$. The solid lines are theoretical fits based on eqn. (1) with $g = 2.11$, $2J = 12$ cm^{-1} and $\theta = -0.9$ K.

and then drops sharply at lower temperatures. The behavior down to 10 K is typical for ferromagnetic interaction with a triplet ground state. The energy separation, $2J$, between the ground triplet and excited singlet states for two interacting copper(II) ions can be derived from the following equation [12]

$$\chi_{Cu} = \frac{Ng^2\beta^2}{k(T-\theta)}[3 + e^{-2J/kT}]^{-1} \tag{1}$$

where the correction factor θ accounts for both interdimer effects and zero-field splitting. A least-squares fit of the data to this equation yields the values $g = 2.11$, $2J = 12$ cm^{-1} and $\theta = -0.9$ K. The calculated curves based on these optimized parameters and eqn. (1) are in good agreement with the experimental data, and are shown as solid lines in Fig. 4. Below 10 K the magnetic moment of $Cu_2L_2Cl_2$ decreases upon cooling, most likely due to weak antiferromagnetic interaction between the dimeric units within the crystal lattice.

Magnetization data for the $Cu_2L_2Cl_2$ complex are shown in Fig. 5. They were fitted with the following Brillouin function [13]

$$\langle\mu\rangle = g\beta S'\left[\frac{2S'+1}{2S'}\coth\left(\frac{2S'+1}{2S'}x\right) - \frac{1}{2S'}\coth\frac{x}{2S'}\right] \tag{2}$$

where x is the ratio of magnetic and thermal energies defined as $g\beta S'H/kT$, and S' is the effective spin. The fit obtained with $S' = 1$ was much better than that resulting from a similar analysis based on two uncoupled doublet states with $S' = 1/2$ (Fig. 5). This is consistent with the existence of a weak paramagnetic interaction within the $Cu_2L_2Cl_2$ dimer resulting in an effective spin $S' = 1$, since the complex is more easy to magnetize than are two uncoupled doublet states of $S' = 1/2$.

The powdered $Cu_2L_2Cl_2$ complex shows a typical rhombic EPR spectrum in the 150–300 K temperature range with $g_1 = 2.03$, $g_2 = 2.10$ and $g_3 = 2.20$.

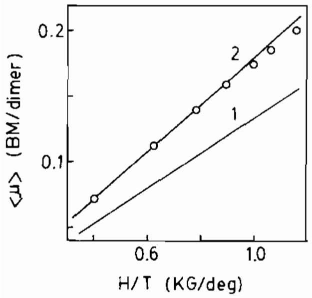

Fig. 5. Magnetization $\langle\mu\rangle$ data for $Cu_2L_2Cl_2$ (circles). The solid lines are the plots of Brillouin functions calculated for two uncoupled doublet states with $S' = 1/2$ (trace 1), and for a triplet state with $S' = 1$ (trace 2).

The average value of $g = 2.11$ from the EPR spectrum is equal to the optimized g parameter derived from eqn. (1). In the IR spectrum of $Cu_2L_2Cl_2$ three bands above 3000 cm^{-1} are observed at 3250, 3210 and 3115 cm^{-1}. Since the elemental analysis and structural data rule out the presence of water or hydroxy groups, these bands presumably arise from the N–H stretching vibrations of the coordinated primary amino groups. The presence of three bands indicate that either the symmetric or antisymmetric vibration is split into two components. Figure 2 shows that whereas one amino hydrogen atom is involved in intradimer hydrogen bonding, the other one takes part in interdimer interactions. Thus, these two hydrogen atoms are in slightly different local environments in the solid state and form hydrogen bonds of slightly different strengths leading to the observed splitting. The C=O and C=C stretching bands are found at 1590 and 1575 cm^{-1}, respectively, and the band corresponding to the vibration of the C–N moiety with partial double bond character is found at 1512 cm^{-1}.

The $Cu_2L_2Cl_2$ complex is moderately soluble in polar solvents. Its molar conductivity (per monomer unit) in 10^{-3} M methanol solution is $\lambda_M/2 = 84$ Ω^{-1} cm^2 mol^{-1}, and is within the range (80–115 Ω^{-1} cm^2 mol^{-1}) typically observed for 1:1 electrolytes at this concentration in methanol [14]. The visible spectrum of $Cu_2L_2Cl_2$ in methanol exhibits an absorption band at 630 nm ($\epsilon = 150$) and a shoulder at *ca.* 440 nm. The positions of these bands are consistent with the observed distorted square-pyramidal geometry around the copper centers.

Conclusions

The bis-chloro-bridged dimer $Cu_2L_2Cl_2$ has been synthesized, structurally characterized, and found to contain the most acute Cu–Cl–Cu′ bridging angle ($\phi = 82.9°$) observed to date in chloro-bridged dimeric copper(II) complexes wherein copper centers adopt square-pyramidal or trigonal-bipyramidal geometry. The acuteness of this angle, together with the typical length of the out-of-plane Cu–Cl′ distance ($R = 2.808$ Å) results in the low value of ϕ/R ratio equal to 29.52. For this ϕ/R value antiferromagnetic interactions between the copper centers are expected. However, contrary to expectations, the $Cu_2L_2Cl_2$ complex is found to be ferromagnetic, and does not obey the empirical correlation between $2J$ and ϕ/R described by Hodgson *et al.* [2] for this class of compounds.

Supplementary Material

Tables of anisotropic temperature parameters for non-hydrogen atoms (Table 4), hydrogen atom coordinates and their isotropic displacement parameters (Table 5), bond distances and angles involving hydrogen atoms (Tables 6 and 7), non-bonding and hydrogen-bonding interactions (Table 8), least-squares planes (Table 9), and observed *versus* calculated structure factors (Table 10), as well as a stereoview of the $Cu_2L_2Cl_2$ dimer (Fig. 6) are available upon request from author D.M.H.

Acknowledgements

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