

Molecular structure and magnetic properties of bis(μ -chloro)bis[7-amino-4-methyl-5-azahept-3-en-2-onato(1-)]dicopper(II)

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Abstract

The molecular structure and magnetic properties of the title compound along with some other solid-state and solution properties are reported. The complex formulated as $(\text{CuLCl})_2$ (L = singly deprotonated tridentate ligand 7-amino-4-methyl-5-azahept-3-en-2-one) is dimeric and consists of two identical CuLCl monomers wherein the copper center adopts a distorted square-pyramidal geometry. The monomers are bound together through two chloro bridges forming a four-membered planar central Cu_2Cl_2 ring. The complex is weakly antiferromagnetic ($2J = -5 \text{ cm}^{-1}$) and poorly fits to the previously reported empirical correlation linking J to the structural parameter Φ/R in this class of compounds. Crystallographic data: monoclinic, $P2_1/n$, $a = 6.018(1)$, $b = 12.648(4)$, $c = 12.877(5) \text{ \AA}$, $\beta = 101.39(2)^\circ$, $R = 3.2\%$.

Introduction

In 1952 Bleaney and Bowers [1] published a mathematical expression relating the magnetic susceptibility χ of dimeric copper(II) complexes with the temperature and the energy separation $2J$ between the singlet and triplet states of the two interacting copper ions. Since then there have been several attempts to rationalize the sign and the value of J in the light of structural data [2]. In some cases the empirical and semi-empirical correlations have been established between the magnetic and structural properties, and they constitute an important step towards the understanding of metal–metal interaction nature in dimeric molecules. For the bis-chloro-bridged copper(II) dimeric complexes, wherein the copper ions adopt square-pyramidal or trigonal-bipyramidal coordination geometry, Hodgson and co-workers [3] proposed an empirical correlation linking the value of J with the structural parameter Φ/R , where Φ is the Cu–Cl–Cu' bridging angle and R is the longer copper–chlorine distance in the bridge. Recently, we have shown this correlation is not true for the chloro-bridged dimer bis(μ -chloro)-bis[8-amino-4-methyl-5-azahept-3-en-2-onato(1-)]dicopper(II), characterized by the relatively

low Φ/R value of $29.52^\circ \text{ \AA}^{-1}$ [4]. For this value Hodgson's correlation predicts antiferromagnetic exchange with $2J$ of $c. -15 \text{ cm}^{-1}$; nonetheless the complex is ferromagnetic ($2J = +12 \text{ cm}^{-1}$). This unusual behavior prompted us to study the related dimeric chloro-bridged copper complexes of low Φ/R ratio (< 30) to see if the observed deviation from Hodgson's correlation is of more general nature. In this paper we report the synthesis, structure and magnetic data of a new chloro-bridged dimeric copper complex, bis(μ -chloro)bis[7-amino-4-methyl-5-azahept-4-en-2-onato(1-)]dicopper(II), together with some of its spectral and solution properties.

Experimental

Materials

The preparation of 7-amino-4-methyl-5-azahept-4-en-2-one, HL, and anhydrous copper(II) chloride was described elsewhere [4, 5]. All other chemicals were of reagent grade and were used without further purification.

Bis(μ -chloro)bis[7-amino-4-methyl-5-azahept-3-en-2-onato(1-)]dicopper(II), $(\text{CuLCl})_2$

A solution of HL (2.84 g, 0.02 mol) in 20 ml methanol was combined with 1.35 g (0.01 mol) an-

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hydrous copper(II) chloride in 20 ml methanol and the mixture was stirred for 1 h at room temperature. The precipitated copper complex was removed by filtration, washed with cold methanol, and recrystallized from acetonitrile to give the $(\text{CuLCl})_2$ complex as dark-green prisms (1.56 g). Melting point (m.p.) 175 °C (dec.). *Anal.* Found: C, 35.0; H, 5.5; N, 11.5. Calc. for $\text{C}_{14}\text{H}_{26}\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_2$: C, 35.0; H, 5.5; N, 11.6%.

Physical measurements

Elemental analysis was performed on a Carlo Erba MOD 1106 elemental analyser. The diffuse reflectance spectrum was recorded on a Perkin-Elmer 402 spectrometer, IR spectra on a Perkin-Elmer 621 spectrometer using Nujol and hexachlorobutadiene mulls, and the EPR spectrum of the powdered complex on a Bruker 400X TE 102 spectrometer operating at X-band frequencies. Conductance measurements were made in 10^{-3} mol dm^{-3} methanol solution 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 using a Faraday magnetometer calibrated with mercury tetrakis-(thiocyanato)cobaltate [6]. Magnetic susceptibility was corrected for diamagnetism estimated as -105×10^{-6} cgsu per copper atom, and for TIP as 60×10^{-6} cgsu per copper atom.

X-ray crystallography of $(\text{CuLCl})_2$

A single crystal for X-ray study was selected from the material recrystallized from acetonitrile and mounted in a Siemens Nicolet R3m/V automatic four-circle diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) for characterization and data collection. Lattice parameters were derived from the setting angles of 50 reflections at $2\theta > 30^\circ$.

Crystal data

$\text{C}_{14}\text{H}_{26}\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_2$, $M = 480.4$, monoclinic, $P2_1/n$, $a = 6.018(1)$, $b = 12.648(4)$, $c = 12.877(5)$ Å, $\beta = 101.39(2)^\circ$, $V = 960.8(5)$ Å³, $D_{\text{calc}} = 1.66$ g cm^{-3} , $Z = 2$, $F(000) = 492$, $\mu = 2.5$ mm⁻¹.

Data collection

Data collection (ω - 2θ scans, scan speed variable from 3 to 15° min^{-1} in ω , scan range 1.20° in ω , $2\theta < 55^\circ$) yielded 1747 observed independent reflections with $F_o > 3\sigma(F_o)$. Two out of every 100 standard reflections were used for monitoring the stability of sample and instrument. They showed only random variations with the minimum and maximum drift corrections being 0.979 and 1.013, respectively.

TABLE 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $(\text{CuLCl})_2$

Atom	x	y	z	U_{eq}^a
Cu(1)	626(1)	1328(1)	4980(1)	34(1)
Cl(1)	1014(2)	127(1)	3672(1)	42(1)
O(1)	-2360(4)	1706(2)	4247(2)	45(1)
N(1)	1048(5)	2615(2)	5843(2)	37(1)
N(2)	3623(5)	895(3)	5843(3)	45(1)
C(1)	-3296(6)	2607(3)	4330(3)	40(1)
C(2)	-5569(6)	2760(3)	3601(3)	50(1)
C(3)	-2439(7)	3401(3)	5009(3)	47(1)
C(4)	-344(7)	3400(3)	5756(3)	45(1)
C(5)	183(10)	4382(3)	6440(4)	72(2)
C(6)	3240(6)	2630(3)	6600(3)	47(1)
C(7)	3932(6)	1497(3)	6847(3)	51(1)

^aEquivalent isotropic parameter U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

Refinement

The structure was solved using the heavy-atom method. Light atoms and finally most of the hydrogen atoms were found from the difference maps. The positions of the methyl H atoms were calculated based on tetrahedral geometry with C-H distance constrained to 0.96 Å. Hydrogen atoms parameters were included in subsequent least-squares calculations but not refined. Final refinement (quantity minimized: $\sum w\Delta F^2$) by a cascade-matrix procedure with anisotropic temperature factors for the non-hydrogen atoms converged with $R = 3.2\%$ (data to parameter ratio 17:1). A weighting scheme of the type $w = 1/\sigma^2(F)$, used during the refinement, did not improve the model. In the final cycle goodness-of-fit was 0.92 and the largest difference peak on the final ΔF map was 0.35 e Å⁻³. The program package used was SHELXTL PLUS (DIGITAL MicroVAX 3300 computer). Atomic coordinates along with isotropic displacement parameters are given in Table 1. See also 'Supplementary material'.

Results and discussion

The dark-green complex formed in the reaction between the HL ligand (Fig. 1) and anhydrous copper chloride in methanol can be formulated as $(\text{CuLCl})_n$ based on elemental analysis, i.e. the dispositive charge on each copper ion is neutralized by one uni-negative singly deprotonated ligand molecule L and a chloride anion. In the IR spectrum of this complex two N-H stretching bands are observed at 3315 and 3265 cm^{-1} . The C=O, C=C and C=N (of partially double character) stretching bands are found at 1603, 1575 and 1515 cm^{-1} , respectively. Their position is con-

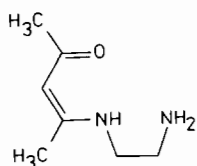


Fig. 1. Chemical structure of 7-amino-4-methyl-5-azahept-2-en-2-one, HL.

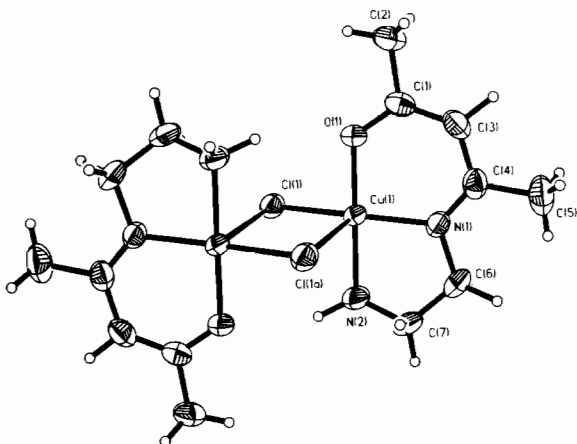


Fig. 2. ORTEP diagram of $(\text{CuLCl})_2$ projection and the atom numbering scheme.

sistent with the values reported for the related bis(μ -chloro)bis[8-amino-4-methyl-5-azahept-3-en-2-onato-(1-)]dicopper(II), $(\text{CuATCl})_2$ [4] and for [4,9-dimethyl-5,8-diazadodeca-3,9-dien-2,11-dionato(2-)]-copper(II), $\text{Cu}(\text{acac})_2\text{en}$ [7]. A broad d-d transition band is observed at 650 nm in the diffuse reflectance spectrum of the complex, within the range of 550–670 nm reported being indicative of square-pyramidal geometry around the copper center [8].

A single-crystal X-ray diffraction study reveals that the copper complex is dimeric and is best formulated as $(\text{CuLCl})_2$. An ORTEP view of the molecule including the atom numbering scheme is given in Fig. 2, while bond distances and angles are listed in Table 2. The dimeric molecule incorporates two identical monomeric subunits linked together by two chloro bridges to form a centrosymmetric structure with the inversion center (midway on the line joining copper atoms) coinciding with a crystallographic inversion center. The dimer is further stabilized by two weak hydrogen bonds occurring between the O(1) atom of one subunit and one of the hydrogen atoms on N(2) of the other, O(1)...H(2N) being 2.41 Å. The dimeric molecules are well separated from each other in the crystal lattice (Fig. 3).

Each monomeric subunit CuLCl incorporates a copper(II) ion coordinated by a tridentate singly-deprotonated ligand molecule and a chloride anion. The coordination geometry around each individual

TABLE 2. Bond distances (Å) and angles (°) for non-hydrogen atoms in $(\text{CuLCl})_2$

Cu(1)–Cl(1)	2.315(1)	N(1)–C(6)	1.477(4)
Cu(1)–Cl(1a)	2.837(1)	N(2)–C(7)	1.481(5)
Cu(1)–O(1)	1.918(2)	C(1)–C(2)	1.511(5)
Cu(1)–N(1)	1.959(3)	C(1)–C(3)	1.364(5)
Cu(1)–N(2)	1.999(3)	C(3)–C(4)	1.427(5)
O(1)–C(1)	1.285(5)	C(4)–C(5)	1.521(6)
N(1)–C(4)	1.290(5)	C(6)–C(7)	1.509(6)
Cl(1)–Cu(1)–O(1)	91.4(1)	Cu(1)–N(2)–C(7)	106.8(2)
Cl(1)–Cu(1)–N(1)	159.8(1)	O(1)–C(1)–C(2)	114.8(3)
O(1)–Cu(1)–N(1)	94.4(1)	O(1)–C(1)–C(3)	126.2(3)
Cl(1)–Cu(1)–N(2)	90.9(1)	C(2)–C(1)–C(3)	119.0(3)
O(1)–Cu(1)–N(2)	175.3(1)	C(1)–C(3)–C(4)	127.1(4)
N(1)–Cu(1)–N(2)	84.9(1)	N(1)–C(4)–C(3)	122.1(3)
Cu(1)–O(1)–C(1)	124.3(2)	N(1)–C(4)–C(5)	121.4(3)
Cu(1)–N(1)–C(4)	125.5(2)	C(3)–C(4)–C(5)	116.5(4)
Cu(1)–N(1)–C(6)	112.6(2)	N(1)–C(6)–C(7)	107.5(3)
C(4)–N(1)–C(6)	121.8(3)	N(2)–C(7)–C(6)	108.8(3)

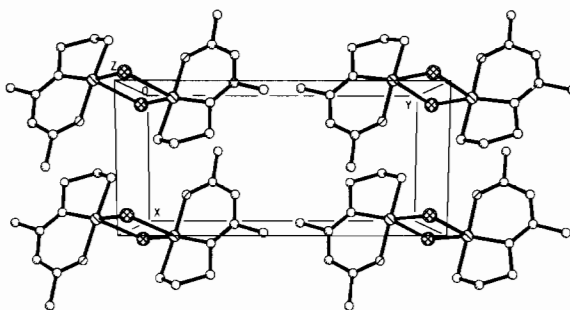


Fig. 3. Packing diagram in the unit cell of $(\text{CuLCl})_2$. Hydrogen atoms are omitted for clarity.

copper center can be best approximated as distorted square-pyramidal. The equatorial plane is defined by three donor atoms of the tridentate ligand O(1), N(1), N(2) and by the chlorine atom Cl(1), whilst the chlorine atom Cl(1a) of the adjacent monomer occupies the apex of the coordination pyramid. The deviation of four basal atoms from the least-squares plane vary from -0.24 Å for N(1) to $+0.22$ Å for N(2). As usual [10, 11], the copper atom is displaced by 0.14 Å above the base plane towards the apical chlorine Cl(1a). The Cl(1a)–Cu(1) line makes an angle of 174.4° with the normal to base plane and the tridentate ligand L is roughly perpendicular (95.1°) to the plane formed by the bridging Cu_2Cl_2 unit (Fig. 4). As a whole, the ligand L is essentially planar (no heavy atom deviating more than 0.01 Å from the mean plane apart from the C(7) atom displaced by 0.54 Å), and is inclined at an angle of 14.8° to the base plane through the four equatorial atoms. All distances and angles are comparable with the values reported for the number of related complexes [4, 12–16].

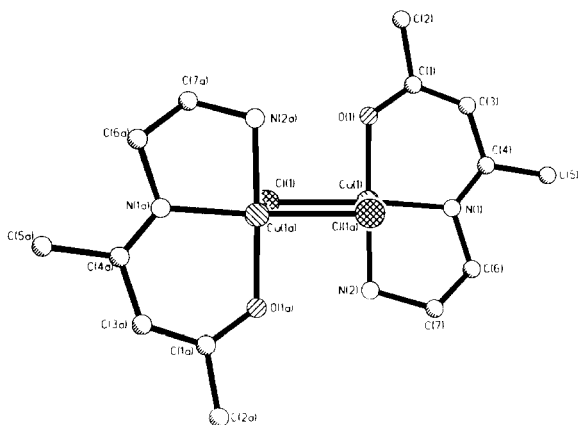


Fig. 4. A view of the $(\text{CuLCl})_2$ molecule showing positions of equatorial planes and apical sites in both the CuLCl subunits.

Two copper atoms and two bridging chlorine atoms form a centrosymmetric planar four-membered ring within the dimeric molecule. The long axial ($\text{Cu}(1)\text{--Cl}(1a)$, $2.837(1)$ Å) and short equatorial ($\text{Cu}(1)\text{--Cl}(1)$, $2.315(1)$ Å) copper–chlorine distances can be distinguished in this ring and the Cu--Cl--Cu angle is $83.3(1)^\circ$ (giving a value of $96.1(1)^\circ$ for the Cl--Cu--Cl angle). The $\text{Cu}\cdots\text{Cu}$ and $\text{Cl}\cdots\text{Cl}$ distances are $3.445(1)$ and $3.866(1)$ Å, respectively. Thus the Φ/R structural parameter for $(\text{CuLCl})_2$ is $29.36^\circ \text{Å}^{-1}$, close to $29.52^\circ \text{Å}^{-1}$ reported for the related ferromagnetic $(\text{CuATCl})_2$ [4]. For the value of Φ/R observed in $(\text{CuLCl})_2$ Hodgson's empirical correlation predicts antiferromagnetic exchange with $2J$ c. -16 cm^{-1} .

Magnetic properties of powdered $(\text{CuLCl})_2$ have been studied over the temperature range 4.6–300 K. Plots of the inverse of magnetic susceptibility χ_{Cu}^{-1} and of the effective magnetic moment μ_{eff} per copper atom as a function of temperature are shown in Fig. 5. The effective magnetic moment decreases from 1.77 at 300.85 to 1.30 at 4.63 K displaying the behavior typical for antiferromagnetic exchange. The value of $2J$, i.e. the energy separation between the ground singlet and the excited triplet states for two interacting copper(II) ions can be obtained from the Bleaney–Bowers equation [1]

$$\chi_{\text{Cu}} = Ng^2\beta^2\{kT[3 + \exp(-2J/kT)]\}^{-1} \quad (1)$$

A least-squares fit of the magnetic data to this equation yields $g=2.08$ and $2J = -5.0(\pm 0.5) \text{ cm}^{-1}$. The calculated curves based on the optimized parameters and eqn. (1) are in a good agreement with the experimental data and are shown as solid lines in Fig. 5. The value of the optimized parameter g is reasonably close to the average g value of 2.11 obtained from the EPR spectrum (*vide infra*). The

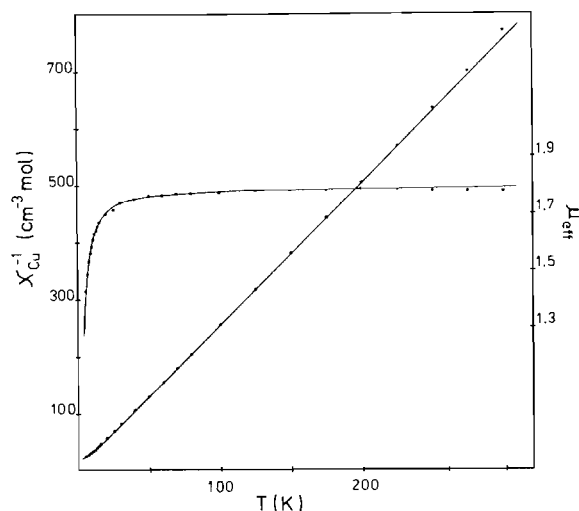


Fig. 5. Temperature dependence of the inverse of magnetic susceptibility, χ_{Cu}^{-1} , and of the effective magnetic moment, μ_{eff} , per copper atom for $(\text{CuLCl})_2$. The solid lines represent the best fit with parameters $g=2.08$ and $2J = -5.0(\pm 0.5) \text{ cm}^{-1}$ (see text).

optimized $2J$ parameter for the $(\text{CuLCl})_2$ complex (-5 cm^{-1}) is significantly different from the value predicted by the empirical Hodgson's correlation (-16 cm^{-1}) for this type of dimeric copper complex.

The powdered $(\text{CuLCl})_2$ complex shows a rhombic EPR spectrum at room temperature with $g_1=2.047$, $g_2=2.116$, and $g_3=2.181$, except for an additional weak inflection occurring between g_1 and g_2 at $g=2.081$. No fine structure related to the zero-field splitting, expected in dimeric copper(II) complexes, is observed. Apparently, the zero-field splitting parameter is incidentally very small, probably due to the particular orientation of copper(II) magnetic moment versus the Cu--Cu vector (angle close to 54.7°) and/or small $2J$ value, and thus the splitting of EPR lines is not observed. The position of the high-field signal at $g>2.04$ is consistent with a $d_{x^2-y^2}$ ground state, though the observed very non-axial spectrum reflects the appreciable distortion from the idealized square-pyramidal arrangement.

The $(\text{CuLCl})_2$ complex is moderately soluble in polar organic solvents and decomposes in aqueous solution. The conductance measurements made in $10^{-3} \text{ mol dm}^{-3}$ methanol solution give the molar conductivity of $\lambda_{M/2} = 85 \text{ Ω}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ which is in the range of $80\text{--}115 \text{ Ω}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ usually observed for 1:1 electrolytes at this concentration in methanol [17]. This is consistent with the dissociation of the dimer in solution to form $[\text{CuL}(\text{CH}_3\text{OH})_n]^+$ and Cl^- ionic species.

Supplementary material

Tables of anisotropic displacement parameters (Table 3), hydrogen atom coordinates (Table 4), and observed and calculated structure factors (Table 5) are available upon request from author G.B.

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