The Synthesis, Magnetic Properties, and Crystal Structure of Two Copper(II) Complexes Prepared from 2-Aminomethylpyridine

CHARLES J. O'CONNOR, ETIM E. EDUOK, JOHN W. OWENS, EDWIN D. STEVENS
The Department of Chemistry, University of New Orleans, New Orleans, La. 70148, U.S.A.
and CHERYL L. KLEIN
The Department of Chemistry, Xavier University of Louisiana, New Orleans, La. 70125, U.S.A.

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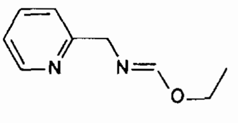
Abstract

The structures of $Cu(amp)_2(ClO_4)_2$ and $[CuLCl_2]_2$ (where $L = C_9H_{12}N_2O$) were determined by X-ray crystallographic techniques. $Cu(amp)_2(ClO_4)_2$ crystallized in space group $P1$ with $a = 7.630(2)$, $b = 7.980(1)$, $c = 7.972(5)$ Å, $\alpha = 106.67(3)$, $\beta = 108.75(3)$, $\gamma = 95.90(2)°$ and $Z = 1$. The structure was refined to $R = 0.025$ and $R_w = 0.037$ with 1146 reflections with $I > 3\sigma(I)$. $[CuLCl_2]_2$ crystallized in space group $P\bar{1}$ with $a = 7.093(1)$, $b = 9.412(1)$, $c = 9.541(2)$ Å, $\alpha = 94.25(1)$, $\beta = 103.69(2)$ and $\gamma = 108.32(1)°$. The structure was refined to $R = 0.040$ and $R_w = 0.051$ with 1265 reflections with $I > 3\sigma(I)$. $CuLCl_2$ forms a dimer through coordination of one of its chlorine atoms to the copper atom of an adjacent monomeric unit. $Cu(amp)_2(ClO_4)_2$ forms a monomer with an octahedral coordination sphere. The perchlorate groups are weakly coordinated to the copper atom. $Cu(amp)_2(ClO_4)_2$ exhibits Curie–Weiss behavior with $g = 2.11$ and $\theta = 0.16$ K. $[CuLCl_2]_2$ exhibits antiferromagnetic intra-dimer coupling with $g = 2.09$ and $2J = -3.50$ cm^{-1}.

Introduction

We have been synthesizing and investigating the structural and magnetic properties of complexes resulting from the coordination of copper(II) with 2-aminomethylpyridine and its derivatives. In an earlier report we described a linear chain complex of copper(II) chloride and 2-aminomethylpyridine [1]. Our previous reports of complexes that use 2-aminomethylpyridine as a building block also include the observation of binuclear [1, 2] species. In this report we describe some additional coordination chemistry of 2-aminomethylpyridine.

The coordination chemistry of 2-alkylpyridines with copper(II) has yielded a variety of interesting adducts. Hodgson and coworkers have reported ladder type linear chains with copper(II) bromides [3, 4], and similar complexes prepared from copper(II) chlorides have been reported by our laboratory [1]. The simple coordination salts of copper(II) halides with aminoalkylpyridine show a propensity for clustering with all reported examples being either dimers or polymers. In order to investigate the electron and molecular structure of some monomeric complexes of 2-aminomethyl pyridine, we prepared these complexes using a non-coordinating anion such as perchlorate. We also attempted to prepare a copper(II) chloride complex with this ligand in a nonaqueous environment by using triethylorthoformate as a dehydrating agent. However, a condensation reaction occurred between the aminomethylpyridine and one of the hydrolysis fragments of the triethylorthoformate (*vide infra*). The product of this condensation reaction (L) coordinates with Copper(II) chloride to produce a dimeric complex $[CuLCl_2]_2$. The dimer exhibits antiferromagnetic coupling propagated through the chlorine bridge. We report here on the synthesis, the room temperature crystal structure, and the variable temperature magnetic susceptibility over the 300 K temperature region for the two complexes, $Cu(amp)_2(ClO_4)_2$ and $(CuLCl_2)_2$, where amp = 2-aminomethylpyridine and $L = C_9H_{12}N_2O$.



L

Experimental

Syntheses

Cu(amp)$_2$(ClO$_4$)$_2$

A solution of 200 mmol of 2-aminomethylpyridine in 100 ml of ethanol was reacted with a solution of 100 mmol of hydrated copper chloride also in ethanol. The reaction solution was heated for a few minutes, filtered and allowed to slowly evaporate yielding a blue crystal product suitable for X-ray and magnetic analysis.

$[CuLCl_2]_2$

A solution consisting of 100 mmol of 2-aminomethylpyridine was dissolved in 100 ml of ethanol with 5 ml of triethylorothoformate. This solution was added while hot to a solution of 100 mmol of copper(II) chloride in 100 ml ethanol also containing 5 ml of triethylorothoformate. The resulting mixture was heated for a few minutes and filtered. The filtered solution yielded small crystals of $Cu(L)Cl_2$ which were used for X-ray and magnetic analysis.

Magnetic Measurements

Polycrystalline samples of the complexes were measured on a model 905 Superconducting SQUID susceptometer purchased from SHE Corporation. The susceptometer is interface to an IBM 9000 computer system. Data were recorded over the 2–300 K temperature range. The general experimental technique used for data collection is described elsewhere.

Crystal Structure Determination

A single blue–green crystal of $[CuLCl_2]_2$ and a single violet crystal of $Cu(amp)_2(ClO_4)_2$ were mounted on an Enraf-Nonius CAD-4 diffractometer with graphite crystal monochromatized Mo Kα radiation.

Lattice constants for $Cu(amp)_2(ClO_4)_2$ were determined by a least-squares fit of 25 reflections with $20 \leqslant 2\theta \leqslant 30°$ resulting in $a = 7.630(2)$, $b = 7.980(1)$, $c = 7.972(5)$ Å, $\alpha = 106.67(3)$, $\beta = 108.75(3)$ and $\gamma = 95.90(2)°$. Unit cell dimensions and successful determination of the structure confirmed the space group as $P1$. Three dimensional intensity data were collected in the ω:2θ scan mode. A total of 1270 reflections were measured ($0 \leqslant 2\theta \leqslant 50°$) with 1146 considered observed ($I > 3\sigma(I)$). The data were corrected for absorbance as a function of psi (maximum absorbance, 18%). The structure was solved by placing Cu at the origin. All remaining atoms were located on successive Fourier maps. Subsequent full-matrix least-squares refinement on F of all atom positions and thermal parameters (except Cu positions) led to $R = 0.025$ and $R_w = 0.037$.

Lattice constants for $[CuLCl_2]_2$ were determined by a least-squares fit of 25 reflections with $18 \leqslant 2\theta \leqslant 37°$ resulting in $a = 7.093(1)$, $b = 9.412(1)$, $c = 9.541(2)$ Å, $\alpha = 94.25(1)$, $\beta = 103.69(2)$ and $\gamma = 108.32(1)°$. Unit cell dimensions and successful determination of the structure confirmed the space group as $P\bar{1}$. A total of 1521 reflections were measured ($0 \leqslant 2\theta \leqslant 44°$) with 1265 considered observed ($I > 3\sigma(I)$). The data were corrected for absorbance as a function of psi (maximum absorbance, 30%). The structure was solved using a Patterson function to locate the Cu atom. All other atoms were located on successive Fourier maps. Subsequent least-squares refinement of all atom positions and thermal parameters led to $R = 0.040$ and $R_w = 0.051$.

Results

The final fractional coordinates with estimated standard deviations (e.s.d.s) for each molecule are summarized for $[CuLCl_2]_2$ and $Cu(amp)_2(ClO_4)_2$ in Table I. Bond lengths and angles are shown in Tables II and III. Figure 1 shows a schematic drawing of one molecular unit of $Cu(amp)_2(ClO_4)_2$ and Fig. 2 shows a schematic drawing of one dimeric unit of $[CuLCl_2]_2$. The molecule dimerizes by coordination

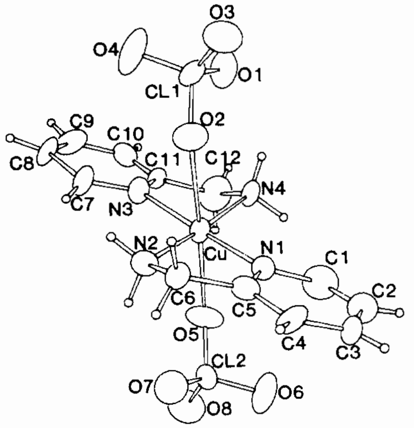


Fig. 1. ORTEP diagram of the formula unit of $Cu(amp)_2(ClO_4)_2$.

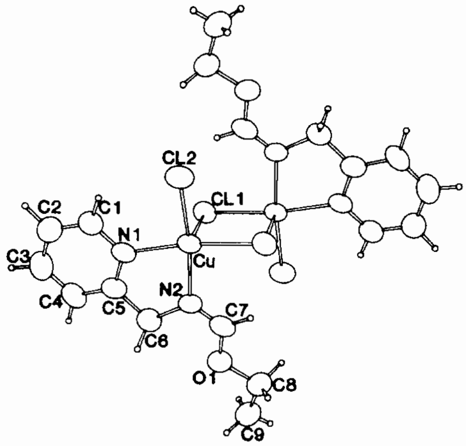


Fig. 2. ORTEP diagram of the binuclear unit of $[CuLCl_2]_2$.

TABLE I. Positional Parameters and their Estimated Standard Deviations

Atom	x	y	z	B (Å^2)[a]
For $[Cu(C_9H_{12}N_2O)Cl_2]_2$				
Cu	0.75106(8)	−0.52482(6)	0.56936(6)	3.85(1)
Cl1	0.6780(2)	−0.3392(1)	0.4495(1)	4.56(3)
Cl2	0.8567(2)	−0.3762(1)	0.7891(2)	5.33(3)
O1	0.5790(5)	−0.7469(4)	0.1402(4)	5.09(9)
N1	0.8265(5)	−0.6989(4)	0.6526(4)	3.83(9)
N2	0.7036(5)	−0.6592(4)	0.3839(4)	4.1(1)
C1	0.8912(8)	−0.7090(5)	0.7961(6)	4.9(1)
C2	0.9145(9)	−0.8364(6)	0.8429(6)	5.6(1)
C3	0.8703(8)	−0.9621(6)	0.7430(7)	5.6(2)
C4	0.8098(7)	−0.9529(5)	0.5965(7)	4.9(1)
C5	0.7896(6)	−0.8197(5)	0.5551(5)	4.1(1)
C6	0.7275(7)	−0.8052(5)	0.3983(6)	4.5(1)
C7	0.6340(7)	−0.6406(5)	0.2558(6)	4.9(1)
C8	0.4979(9)	−0.7105(6)	−0.0044(6)	5.8(2)
C9	0.4169(9)	−0.8527(7)	−0.1080(6)	6.2(2)
H1	0.920(6)	−0.618(5)	0.862(5)	5(1)*
H2	0.964(7)	−0.837(6)	0.953(6)	7(1)*
H3	0.905(7)	−1.040(6)	0.788(6)	7(1)*
H4	0.786(6)	−1.034(5)	0.524(5)	4(1)*
H5	0.597(5)	−0.887(4)	0.351(5)	4(1)*
H6	0.859(6)	−0.813(5)	0.361(5)	6(1)*
H7	0.596(6)	−0.560(5)	0.234(5)	5(1)*
H8	0.385(6)	−0.665(5)	−0.002(5)	5(1)*
H9	0.647(8)	−0.624(6)	−0.012(7)	8(2)*
H10	0.305(7)	−0.927(6)	−0.085(6)	8(2)*
H11	0.543(8)	−0.893(6)	−0.099(6)	7(1)*
H12	0.350(7)	−0.843(6)	−0.190(6)	7(1)*
For $Cu(amp)_2(ClO_4)_2$				
Cu	0.000	0.000	0.000	2.2
Cl1	0.3471(2)	0.7244(2)	0.0968(2)	2.58(3)
Cl2	0.6563(2)	0.2750(2)	0.9044(2)	2.52(3)
O1	0.1805(5)	0.5945(5)	0.0024(6)	4.1(1)
O2	0.3116(6)	0.8985(5)	0.1561(5)	3.6(1)
O3	0.4509(7)	0.6795(6)	0.2593(6)	5.3(1)
O4	0.4409(6)	0.7129(7)	−0.0347(6)	5.9(1)
O5	0.7043(6)	0.1031(5)	0.8364(6)	4.7(1)
O6	0.5649(6)	0.2694(7)	1.0283(6)	5.2(1)
O7	0.8365(5)	0.4075(6)	0.9983(6)	4.4(1)
O8	0.5318(6)	0.3038(6)	0.7502(6)	5.0(1)
N1	−0.0268(5)	0.1061(5)	0.2493(5)	1.93(9)
N2	0.1970(6)	0.2260(5)	0.1002(5)	2.5(1)
N3	0.0385(6)	−0.1061(6)	−0.2387(6)	2.9(1)
N4	−0.1855(5)	−0.2398(6)	−0.1001(5)	2.7(1)
C1	−0.1738(8)	0.0547(8)	0.2931(8)	3.3(1)
C2	−0.1854(7)	0.1288(7)	0.4552(7)	3.2(1)
C3	−0.0433(7)	0.2778(7)	0.5990(7)	2.9(1)
C4	0.1002(7)	0.3319(7)	0.5550(7)	2.8(1)
C5	0.1057(7)	0.2413(7)	0.3681(6)	2.4(1)
C6	0.2655(7)	0.3045(7)	0.3077(7)	2.8(1)
C7	0.1838(7)	−0.0547(8)	−0.2873(7)	3.1(1)
C8	0.1906(7)	−0.1459(7)	−0.4684(6)	3.6(1)
C9	0.0423(9)	−0.2781(8)	−0.5868(7)	3.7(1)
C10	−0.1094(7)	−0.3303(7)	−0.5371(7)	2.8(1)
C11	−0.1080(7)	−0.2485(6)	−0.3710(6)	2.0(1)
C12	−0.2618(7)	−0.2898(7)	−0.3091(7)	2.7(1)

(continued)

TABLE I. *(Continued)*

Atom	x	y	z	B (Å^2)[a]
H1	−0.254(9)	−0.007(9)	0.203(9)	7*
H2	−0.28(1)	0.086(9)	0.480(9)	7*
H3	−0.050(9)	0.322(9)	0.713(9)	7*
H4	0.183(9)	0.404(9)	0.615(9)	7*
H5	0.3807	0.2709	0.3621	7*
H6	0.3022	0.4395	0.3448	7*
H7	0.2960	0.2051	0.0587	7*
H8	0.1365	0.3123	0.0465	7*
H9	0.2674	0.0642	−0.2049	7*
H10	0.2943	−0.1273	−0.5016	7*
H11	0.0450	−0.3510	−0.7025	7*
H12	−0.2019	−0.4225	−0.6226	7*
H13	−0.3117	−0.4126	−0.3683	7*
H14	−0.3579	−0.2249	−0.3505	7*
H15	−0.1279	−0.3254	−0.0627	7*
H16	−0.2894	−0.2236	−0.0556	7*

[a] Starred atoms were refined isotropically; anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\cos(\gamma)B(1,2) + ac\cos(\beta)B(1,3) + bc\cos(\alpha)B(2,3)$.

TABLE II. Bond Distances[a] (Å)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
For $[Cu(C_9H_{12}N_2O)Cl_2]_2$								
Cu	Cl1	2.283(1)	N2	C7	1.252(6)	C6	H5	0.98(4)
Cu	Cl1	2.862(1)	C1	C2	1.354(7)	C6	H6	1.09(4)
Cu	Cl2	2.253(1)	C1	H1	0.96(5)	C7	H7	0.90(5)
Cu	N1	2.036(3)	C2	C3	1.366(7)	C8	C9	1.466(8)
Cu	N2	1.991(3)	C2	H2	1.02(5)	C8	H8	1.02(4)
O1	C7	1.326(5)	C3	C4	1.379(7)	C8	H9	1.14(6)
O1	C8	1.473(6)	C3	H3	0.95(5)	C9	H10	0.96(6)
N1	C1	1.358(6)	C4	C5	1.382(6)	C9	H11	1.06(5)
N1	C5	1.329(5)	C4	H4	0.94(4)	C9	H12	0.84(6)
N2	C6	1.449(5)	C5	C6	1.485(6)			
For $Cu(amp)_2(ClO_4)_2$								
Cu	O2	2.632(8)	Cl2	O5	1.454(9)	C1	C2	1.294(14)
Cu	O5	2.564(9)	Cl2	O6	1.388(7)	C2	C3	1.435(15)
Cu	N1	2.010(7)	Cl2	O7	1.468(8)	C3	C4	1.321(13)
Cu	N2	1.999(7)	Cl2	O8	1.386(7)	C4	C5	1.474(12)
Cu	N3	1.977(8)	N1	C1	1.337(12)	C5	C6	1.537(11)
Cu	N4	2.035(8)	N1	C5	1.288(13)	C7	C8	1.439(13)
Cl1	O1	1.387(7)	N2	C6	1.478(11)	C8	C9	1.33(2)
Cl1	O2	1.418(8)	N3	C7	1.350(11)	C9	C10	1.401(14)
Cl1	O3	1.449(8)	N3	C11	1.395(12)	C10	C11	1.293(13)
Cl1	O4	1.435(8)	N4	C12	1.491(11)	C11	C12	1.454(12)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

of Cl1 to the Cu atom of an adjacent monomeric unit (Cu → Cl1, 2.862(1) Å). The coordination sphere about the metal atom is distorted square pyramid (4 + 1) resulting from the formation of two single chlorine atom bridges between metal atoms forming a dimer related by an inversion center. The Cu–Cu distance is 3.683(1) Å. The distortion of the coordination plane is primarily due to constraints imposed by the bidentate ligand resulting in the formation of a five membered ring at the copper atom. Although

TABLE III. Bond Angles[a] (°)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
For $[Cu(C_9H_{12}N_2O)Cl_2]_2$											
Cl1	Cu	Cl1	89.30(3)	C1	C2	H2	120.0(3)	O1	C7	N2	123.4(4)
Cl1	Cu	Cl2	92.43(4)	C3	C2	H2	121.0(3)	O1	C7	H7	112.0(3)
Cl1	Cu	N1	172.45(9)	C2	C3	C4	118.4(5)	N2	C7	H7	124.0(3)
Cl1	Cu	N2	92.8(1)	C2	C3	H3	112.0(3)	O1	C8	C9	106.7(4)
Cl1	Cu	Cl2	99.36(4)	C4	C3	H3	129.0(3)	O1	C8	H8	110.0(3)
Cl1	Cu	N1	93.73(9)	C3	C4	C5	119.6(4)	O1	C8	H9	98.0(3)
Cl1	Cu	N2	88.6(1)	C3	C4	H4	121.0(3)	C9	C8	H8	111.0(2)
Cl2	Cu	N1	93.9(1)	C5	C4	H4	119.0(3)	C9	C8	H9	117.0(3)
Cl2	Cu	N2	170.6(1)	N1	C5	C4	121.9(4)	H8	C8	H9	113.0(3)
N1	Cu	N2	80.4(1)	N1	C5	C6	117.1(4)	C8	C9	H10	112.0(3)
C7	O1	C8	117.9(4)	C4	C5	C6	121.0(4)	C8	C9	H11	105.0(3)
C1	N1	C5	117.6(4)	N2	C6	C5	110.3(3)	C8	C9	H12	112.0(4)
C6	N2	C7	115.4(4)	N2	C6	H5	110.0(2)	H10	C9	H11	109.0(4)
N1	C1	C2	123.0(4)	N2	C6	H6	111.0(2)	H10	C9	H12	97.0(5)
N1	C1	H1	115.0(3)	C5	C6	H5	108.0(2)	H11	C9	H12	121.0(5)
C2	C1	H1	122.0(3)	C5	C6	H6	102.0(2)				
C1	C2	C3	119.5(5)	H5	C6	H6	114.0(3)				
For $Cu(amp)_2(ClO_4)_2$											
O2	Cu	O5	177.0(4)	O1	Cl1	O2	111.8(5)	C1	C2	C3	121.9(8)
O2	Cu	N1	92.2(3)	O1	Cl1	O3	105.7(5)	C2	C3	C4	119.4(9)
O2	Cu	N2	77.7(3)	O1	Cl1	O4	106.0(6)	C3	C4	C5	120.1(8)
O2	Cu	N3	85.1(3)	O2	Cl1	O3	109.9(5)	N1	C5	C4	120.0(8)
O2	Cu	N4	98.4(3)	O2	Cl1	O4	109.9(6)	N1	C5	C6	118.0(9)
O5	Cu	N1	90.2(3)	O3	Cl1	O4	113.5(6)	C4	C5	C6	121.9(8)
O5	Cu	N2	100.8(3)	O5	Cl2	O6	109.7(6)	N2	C6	C5	107.1(7)
O5	Cu	N3	92.5(3)	O5	Cl2	O7	106.0(5)	N3	C7	C8	121.0(1)
O5	Cu	N4	83.0(3)	O5	Cl2	O8	107.6(6)	C7	C8	C9	116.3(8)
N1	Cu	N2	81.6(3)	O6	Cl2	O7	111.4(6)	C8	C9	C10	122.4(9)
N1	Cu	N3	177.2(5)	O6	Cl2	O8	108.3(6)	C9	C10	C11	119.5(9)
N1	Cu	N4	99.8(3)	O7	Cl2	O8	113.7(5)	N3	C11	C10	122.4(9)
N2	Cu	N3	97.4(3)	C1	N1	C5	119.5(8)	N3	C11	C12	114.2(8)
N2	Cu	N4	175.9(4)	C7	N3	C11	118.0(9)	C10	C11	C12	123.4(8)
N3	Cu	N4	81.0(3)	N1	C1	C2	123.0(9)	N4	C12	C11	109.2(7)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

the ligand has three possible coordination sites, only two (N1 and N2) are actually coordinated to the copper atoms.

$Cu(amp)_2(ClO_4)_2$ has a pseudo inversion center at the copper position. However, the copper atom sits slightly above (0.505 Å) the coordination plane (N1, N2, N3 and N4).

The coordination sphere about the copper atom is a distorted octahedron with two perchlorate groups weakly coordinated axially to the copper atom through O2 and O5, 2.632(8) and 2.564(9) respectively. Additional distortion results from the formation of two five membered rings upon coordination of the copper atom to N1 and N2, and N3 and N4. There appear to be no significant intermolecular interactions.

The magnetic susceptibility data for the complexes are plotted in Figs. 3 and 4. The data for the monomeric complex $Cu(amp)_2(ClO_4)_2$ is shown in Fig. 3 as the inverse magnetic susceptibility plotted as a function of temperature. The data show a straight line dependence that is consistent with the simple Curie–Weiss law.

$$\chi = \frac{Ng^2\mu_B^2S(S+1)}{3k(T-\theta)}$$

where all the parameters have their usual meaning and $S = 1/2$ for copper(II). The magnetic data were fitted to this equation with the parameters listed in Table IV.

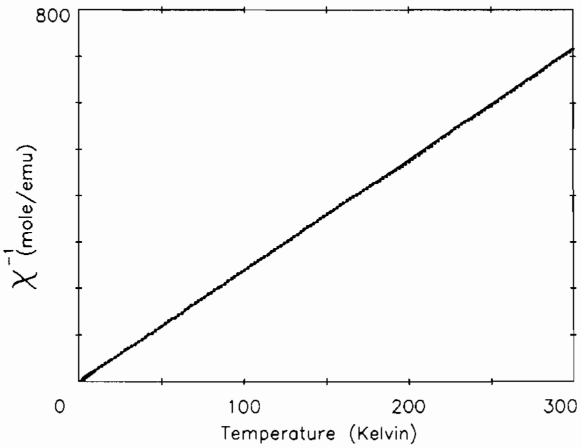


Fig. 3. The inverse magnetic susceptibility of $Cu(amp)_2(ClO_4)_2$ plotted as a function of temperature. The line drawn through the points is the best fit of the data to the Curie–Weiss law as described in the text.

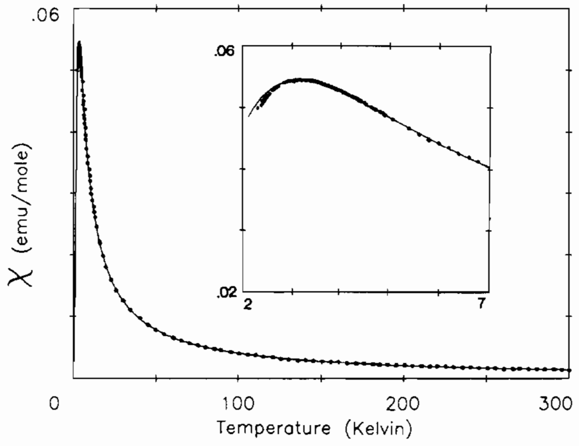


Fig. 4. The magnetic susceptibility of $(CuLCl_2)_2$ plotted as a function of temperature. The curve drawn through the points is the best fit of the data to the dimer equation as described in the text.

TABLE IV. Magnetic Parameters for the Complexes $Cu(amp)_2(ClO_4)_2\cdot 2H_2O$ and $(CuLCl_2)_2$ as Described in Text

	$Cu(amp)(ClO_4)_2\cdot 2H_2O$	$[CuLCl]_2$
g	2.11	2.09
θ	0.16 K	
$2J$		$-3.50\ cm^{-1}$

Magnetic susceptibility data for the dimeric complex $[CuLCl_2]_2$ are plotted in Fig. 4 as a function of temperature over the 2–300 K temperature range. The data exhibit a maximum in the magnetic susceptibility at about 3 K. This behavior is consistent with an antiferromagnetic interaction between the two copper(II) ions.

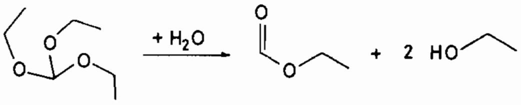
The equation that describes the behavior of the magnetic susceptibility of the spin-coupled copper(II) dimer may be written as follows:

$$\chi = \frac{2Ng^2\mu_B^2}{kT}\ \frac{e^x}{1+3e^x}$$

where $X = 2J/kT$ and $2J$ is the splitting between the singlet and the triplet with a negative J having a ground singlet. The magnetic data for the binuclear complex were fit to this equation but with a correction for a temperature independent paramagnetism of 120×10^{-6} emu/(mol Cu) for the two copper(II) ions and a small amount of paramagnetic (monomeric) impurity. The best fitted values are listed in Table IV.

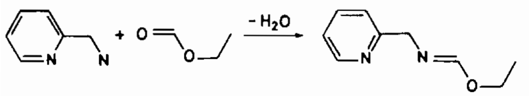
Discussion

The preparation of the dimeric complex $[CuLCl_2]_2$ was somewhat surprising because the sequence of reactions was not expected. The solvent triethylorthoformate $[HC(OCH_2CH_3)_3]$ is an excellent drying agent that may be used in reactions in which water must be removed. In the presence of water, the triethylorthoformate follows eqn. (1).



(1)

The ethylformate ester will then react with 2-aminomethylpyridine following eqn. (2).



(2)

The ligand L has a *trans* configuration about the immine bond and coordinates as a bidentate ligand to the copper(II) ion through the two nitrogen atoms. The $CuLCl_2$ units then dimerize through the bridging chlorines.

The study of magneto-structural relationships in exchanged coupled systems continues to be an area of active research by many laboratories [5–10], much of this research concerns copper(II) magnetic interaction. Many theories have been proposed to describe and predict the magnetic behavior of exchange coupled systems [11–20].

The bridging center geometry between 4, 5 and 6 coordinate doubly bridged metal ions is often divided into two categories. These categories are illustrated by parallel plane bridging (I) in which the bridging ligands are equatorially bound to both metal ions and perpendicular plane (II) bridging in which the bridging ligands are axially bound to one metal ion and equatorial bound to the other. The binuclear complex $[CuLCl_2]_2$ has bridging of the perpendicular plane type (II). Initial successes predicting magnetic properties from structural parameters were realized from an empirical correlation of the magneto-structural parameters of hydroxide bridged complexes of type I by Hatfield and Hodgson [21] and verified by several other laboratories. Many chlorine bridged binuclear and polymeric complexes have been synthesized [22–28] but attempts to correlate the magneto-structural properties have met with only limited success. The situation for chlorine bridge complexes is much more complicated due to the low lying d-orbitals that are involved in the magnetic exchange overlap pathways.

Supplementary Material

Molar magnetic susceptibility data corrected for diamagnetism with Pascal constants are available from the authors on request.

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