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Crystal Structure and Magnetic Properties of a Unique Copper(II) Compound, Octakis(μ-dichloroacetato-*O,O'*)bis(dichloroacetato-*O*)hexakis-[μ_3-(2-dimethylaminoethanolato)]di-μ_3-hydroxo-nonacopper(II)

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Abstract

The synthesis, characterization, X-ray structure, and magnetic properties are reported for the title compound $Cu_9(CHCl_2COO)_{10}(C_4H_{10}NO)_6(OH)_2$. The compound crystallizes in the monoclinic space group *P*2/*n*. Cell dimensions are $a = 14.835(3)$, $b = 14.205(4)$, $c = 20.887(5)$ Å, $\beta = 97.46(2)°$. The structure was solved by direct and Fourier methods and refined by least-squares techniques to a conventional *R* value of 0.059 for 3006 reflections. The crystal structure consists of discrete nonameric complex molecules which possess a twofold rotation axis passing through a copper atom. The nine copper atoms in the molecule are bridged together by carboxylate groups and triply bridging ethanolato oxygen and triply bridging hydroxo oxygen atoms. The aminoethanolato ligands chelate through the amino nitrogen (terminal) and the alcohol oxygen (triply bridging). One of the five independent carboxylato groups is unidentate; the other four bridge a pair of copper atoms each, and one of the four forms in addition a monoatomic unsymmetrical bridge to a third copper atom. The Cu1, Cu2, Cu3 and triply bridging hydroxo oxygen atoms form a trigonal pyramid with Cu–O bonds of 1.941, 1.964 and 2.149 Å. In a similar arrangement one of the three independent ethanolato oxygen bridges Cu2, Cu3 and Cu4 with Cu–O bonds of 1.996, 2.111 and 1.977 Å. The Cu–O distances of the other ethanolato oxygen atoms are 1.930, 2.645, 1.981 Å for Cu3, Cu4, Cu5 and 2.380, 1.963, 1.904 Å for Cu2, Cu4, Cu5. The copper coordination number is either five (Cu3 and Cu5) or six (Cu1, Cu2, Cu4), the coordination polyhedra being square-pyramidal or octahedral, respectively. The coordination sphere of the Cu1 atom lying on the twofold rotation axis is very unusual in that the equatorial Cu–O bonds (2.107 and 2.207 Å) are longer than the axial bonds (1.941 Å).

Introduction

The copper(II) ion plays a significant role in transition metal chemistry, impacting on such areas as catalysis, bioinorganic chemistry, magnetic interactions, electrical conductors in solids, etc. The ability of the copper(II) ion to form coordination complexes with a variety of ligands, and illustrating many stereochemistries has allowed the systematic study of the magnetostructural correlations [1–5].

Compounds of copper(II) ion with a variety of amine alcohols have been described [6–15]. Some of these have dinuclear structures, with the deprotonated alcohol oxygen acting as bridging groups and with other donor atoms completing square-planar coordination about the copper ions. One, or less commonly, two additional donor atoms are often weakly coordinated axially. These additional donor atoms are often the bridging oxygens of other groups to form tetranuclear clusters, or higher-order polymers.

We have previously reported the crystal structure of a copper(II) dichloroacetate compound with 2-dimethylaminoethanol, $[Cu_4(C_2HCl_2O_2)_4(C_4H_{10}NO)_4]$ [8]. The structure is composed of tetramers, in which the copper and bridging ethanolato oxygen atoms form cubane type Cu_4O_4 cores. In these cores the short Cu–O(ethanolato) bonds form eight-membered rings folded in a boat-like conformation with Cu–Cu distances of 3.124–3.935 Å.

Now we have succeeded in preparing a novel type of copper(II) dichloroacetate complex with 2-dimethylaminoethanol in which nine copper atoms are bridged together and the crystal structure and results of magnetic studies of this unusual complex are presented and discussed.

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Experimental

Preparation

The compound was prepared by adding 0.02 mol of copper(II) dichloroacetate to a solution of 0.03 mol of 2-dimethylaminoethanol in 200 ml of ethanol. The reaction mixture was refluxed for 1 h. After cooling of the solution to room temperature, crystallization was allowed to continue for four weeks. When most of the solvent was evaporated well-developed dark-green crystals were collected by filtration.

Characterization and Analysis

A ligand-field spectrum of the compound was recorded in the solid state, using a P.E. UV 330 instrument, with a diffuse reflectance attachment.

EPR powder spectra at X-band frequency were taken at 300 and 77 K using Varian E3 instrument, and at Q-band frequencies at 77 K using Varian E9.

Magnetic susceptibility measurements were performed on a Faraday balance in the region 80–300 K and on a PAR vibrating-sample magnetometer in the region 4–65 K, using $CoHg(SCN)_4$ as a calibrant. Chemical analyses were performed by commercial laboratories, and agree with the formula that results from the crystal structure determination.

Crystallographic Data Collection and Determination of the Structure

The X-ray structure was carried out at room temperature on a 0.3 X 0.4 X 0.3 mm crystal. Crystal data and relevant information about the data collection and refinement have been summarized in Table I. The data were corrected for Lorentz and polarization effects and absorption from Φ-scan data.

TABLE I. Crystal and Diffraction Data of $Cu_9(CHCl_2COO)_{10}(C_4H_{10}NO)_6(OH)_2$

M_r	2414.1
Space group	$P2/n$
Crystal system	monoclinic
a (Å)	14.835(3)
b (Å)	14.205(4)
c (Å)	20.887(5)
β (°)	97.46(2)
V (Å^3)	4364
Z	2 (nonamers)
D_{calc} (Mg m^{-3})	1.84
$F(000)$	2406
2θ, range (°)	4–48
Measured reflections	7456
Significant reflections ($I > 3\sigma(I)$)	3006
μ (cm^{-1})	29.1
Final R value ($\Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$)	0.059
Final R_w value ($[\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma wF_o{}^2]^{1/2}$)	0.049
Diffractometer	Nicolet P3
Monochromator	graphite
Radiation	Mo Kα

The structure was solved by direct and Fourier methods using MULTAN80 and XRAY76 program systems [16, 17]. Refinement with anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for hydrogen atom of the OH^- group gave $R = 0.059$ and $R_w = 0.049$, with $w = 1/\sigma^2(F_o)$. The other hydrogen atoms with $U = 0.09$ Å^2 were included at idealized positions (C–H = 1.0 Å) and held fixed. Scattering factors, including anomalous dispersion, were taken from the literature [18]. Atomic positions are listed in Table II. Listings of F_o and F_c values, hydrogen coordinates and anisotropic thermal parameters are available as Supplementary Material.

TABLE II. Fractional Atomic Coordinates (X 10^4) and Equivalent Isotropic Temperature Factors

Atom^a	x	y	z	U_{eq} (Å^2)^b
Cu(1)	7500	3101(2)	2500	0.038
Cu(2)	7146(1)	1736(1)	3581(1)	0.045
Cu(3)	7372(1)	3758(1)	4130(1)	0.041
Cu(4)	7045(1)	1912(1)	5036(1)	0.053
Cu(5)	5254(1)	2725(1)	4319(1)	0.052
Cl(1)	10061(4)	−14(4)	2822(3)	0.168
Cl(2)	10472(3)	1831(5)	3345(3)	0.167
Cl(3)	8784(9)	−1332(9)	4963(6)	0.145
Cl(30)	9343(10)	−652(11)	4731(7)	0.187
Cl(4)	8246(7)	−1438(6)	3664(5)	0.266
Cl(5)	10534(3)	4394(6)	4118(2)	0.193
Cl(6)	9689(5)	5877(5)	3329(3)	0.194
Cl(7)	2611(3)	4387(4)	3472(2)	0.117
Cl(8)	3917(4)	5667(4)	3137(3)	0.166
Cl(9)	4185(6)	1705(7)	6454(4)	0.141
Cl(90)	4683(24)	2389(17)	6812(11)	0.165
Cl(10)	6103(5)	1832(6)	7116(2)	0.197
O(1)	6875(5)	3017(5)	3259(3)	0.043
O(2)	8396(5)	1996(6)	2975(4)	0.056
O(3)	8728(6)	1195(6)	2117(3)	0.059
O(4)	7664(6)	500(6)	3787(4)	0.071
O(5)	7540(7)	320(7)	4834(4)	0.079
O(6)	8581(5)	4069(6)	3944(3)	0.055
O(7)	8463(5)	4121(7)	2865(4)	0.062
O(8)	4432(5)	3752(7)	4040(4)	0.062
O(9)	4942(6)	3668(7)	3099(4)	0.075
O(10)	6348(6)	1608(7)	5724(4)	0.068
O(11)	5158(6)	2601(7)	5484(4)	0.081
O(12)	6335(5)	3523(5)	4579(4)	0.042
O(13)	7775(5)	2363(6)	4371(4)	0.043
O(14)	6063(5)	1683(5)	4328(4)	0.054
N(1)	7039(6)	5153(8)	4176(5)	0.053
N(2)	8145(7)	2258(8)	5679(5)	0.060
N(3)	4221(7)	1766(9)	4125(5)	0.071
C(1)	8832(8)	1423(9)	2688(5)	0.051
C(2)	9619(10)	954(11)	3148(6)	0.086
C(3)	7771(10)	66(10)	4322(7)	0.077
C(4)	8200(14)	−928(14)	4324(8)	0.148
C(5)	8862(8)	4222(10)	3411(5)	0.059
C(6)	9849(9)	4627(13)	3433(7)	0.098
C(7)	4416(8)	3929(10)	3462(5)	0.059
C(8)	3623(9)	4513(13)	3157(6)	0.097

(continued)

TABLE II. *(continued)*

Atom[a]	x	y	z	U_{eq} (Å^2)[b]
C(9)	5644(8)	2036(10)	5822(6)	0.068
C(10)	5301(11)	1802(18)	6483(6)	0.141
C(11)	6147(8)	5181(9)	4419(6)	0.061
C(12)	6148(7)	4358(9)	4891(5)	0.047
C(13)	7748(9)	5669(10)	4590(7)	0.084
C(14)	6935(10)	5587(11)	3529(6)	0.084
C(15)	8855(8)	2649(10)	5307(6)	0.068
C(16)	8721(7)	2240(9)	4636(5)	0.054
C(17)	7923(8)	2952(10)	6153(5)	0.070
C(18)	8519(9)	1408(10)	6029(6)	0.080
C(19)	4654(12)	890(11)	4415(7)	0.098
C(20)	5605(9)	805(10)	4272(6)	0.069
C(21)	3400(9)	1975(11)	4440(8)	0.097
C(22)	3953(11)	1641(12)	3447(6)	0.109

[a]Population parameters 0.5 for Cl(3), Cl(30), 0.75 for Cl(9) and 0.25 for Cl(90). [b]$U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*a_ia_j$.

Results and Discussion

Description of the Structure of the Title Compound

The crystal structure consists of discrete nonameric complex molecules, which are held in the crystal lattice by van der Waals forces. The molecules (depicted in Figs. 1–4) possess a twofold rotation axis passing through the central Cu1 atom. The nine copper atoms are bridged by ten carboxylate groups and six triply bridging ethanolato oxygen atoms and two triply bridging hydroxo oxygen atoms. One of the five independent carboxylate groups is unidentate; the other four bridge a pair of copper atoms each, and one of the four forms in addition a monoatomic unsymmetrical bridge to a third copper atom. The Cu1, Cu2, Cu3 and triply bridging oxygen atom of the OH$^-$ ion form a trigonal pyramid with Cu–O bonds of 1.941, 1.964 and 2.149 Å (Table III). In a similar arrangement one of the three independent ethanolato oxygen bridges Cu2, Cu3 and Cu4 with

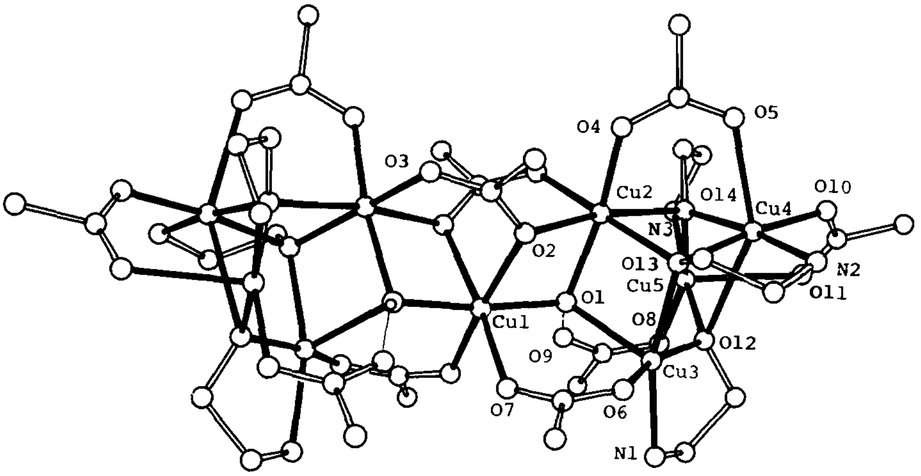

Fig. 1. View of the molecule $Cu_9(CHCl_2COO)_{10}(C_4H_{10}NO)_6(OH)_2$. The chlorine atoms and methyl carbon atoms of the ligands have been omitted for clarity.

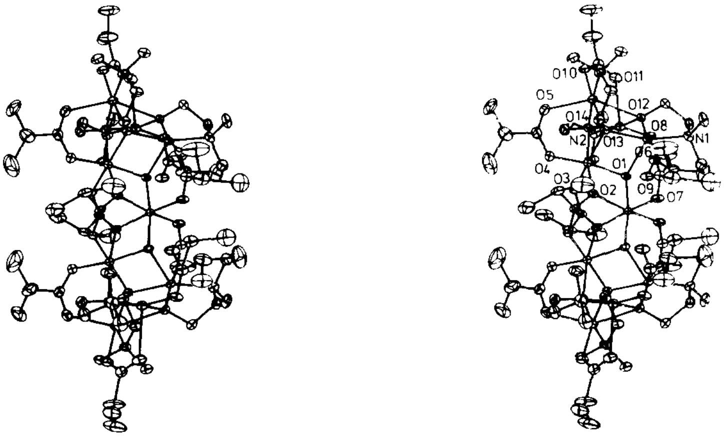

Fig. 2. Stereoview of the molecule.

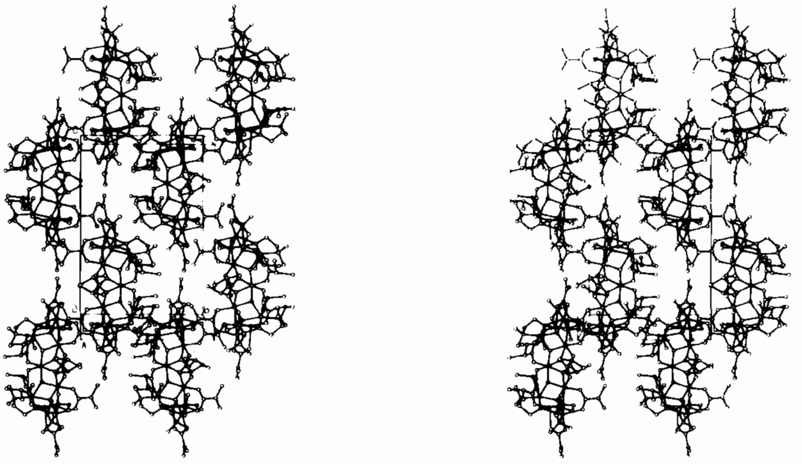

Fig. 3. Stereoview of the unit cell packing of the structure of the compound.

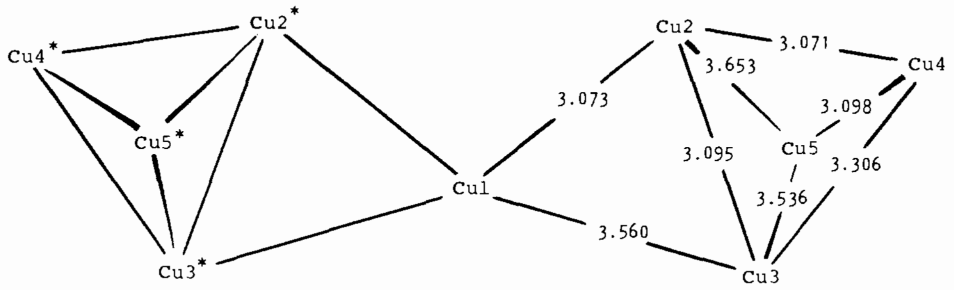

Fig. 4. The arrangement of the copper atoms with Cu–Cu distances (Å).

TABLE III. Interatomic Distances (Å) and Angles (°) Around the Copper Atoms[a]

Cu(1)–O(1)	1.941(7)	Cu(4)–O(10)	1.924(9)
Cu(1)–O(2)	2.207(8)	Cu(4)–O(13)	1.977(8)
Cu(1)–O(7)	2.107(9)	Cu(4)–O(14)	1.936(7)
		Cu(4)–N(2)	2.035(10)
Cu(2)–O(1)	1.964(8)	Cu(4)–O(5)	2.431(10)
Cu(2)–O(4)	1.943(9)	Cu(4)–O(12)	2.645(7)
Cu(2)–O(13)	1.966(7)		
Cu(2)–O(3^{i})	1.976(8)	Cu(5)–O(8)	1.943(9)
Cu(2)–O(2)	2.406(8)	Cu(5)–O(12)	1.981(7)
Cu(2)–O(14)	2.380(8)	Cu(5)–O(14)	1.904(9)
		Cu(5)–N(3)	2.051(11)
Cu(3)–O(1)	2.149(7)	Cu(5)–O(11)	2.463(9)
Cu(3)–O(6)	1.936(8)		
Cu(3)–O(12)	1.930(8)		
Cu(3)–O(13)	2.111(8)		
Cu(3)–N(1)	2.048(11)		

O(1)–Cu(1)–O(2)	85.0(3)	O(6)–Cu(3)–O(13)	91.2(3)
O(1)–Cu(1)–O(7)	96.9(3)	O(6)–Cu(3)–N(1)	91.4(4)
O(1)–Cu(1)–O(1^{i})	173.0(4)	O(6)–Cu(3)–O(12)	167.7(3)
O(1)–Cu(1)–O(2^{i})	90.0(3)	O(12)–Cu(3)–O(13)	86.6(3)
O(1)–Cu(1)–O(7^{i})	88.0(3)	O(13)–Cu(3)–N(1)	86.2(4)
O(2)–Cu(1)–O(7)	89.2(3)	O(13)–Cu(3)–N(1)	163.7(3)
O(2)–Cu(1)–O(2^{i})	89.4(3)		
O(2)–Cu(1)–O(7^{i})	172.8(3)	O(5)–Cu(4)–O(10)	97.2(4)

(continued)

TABLE III. *(continued)*

O(7)–Cu(1)–O(7^{i})	93.1(3)	O(5)–Cu(4)–O(13)	88.5(3)
		O(5)–Cu(4)–O(14)	85.8(3)
O(1)–Cu(2)–O(2)	78.3(3)	O(5)–Cu(4)–N(2)	96.0(4)
O(1)–Cu(2)–O(4)	166.1(4)	O(5)–Cu(4)–O(12)	149.0(3)
O(1)–Cu(2)–O(13)	85.6(3)	O(10)–Cu(4)–O(12)	103.7(3)
O(1)–Cu(2)–O(14)	97.4(3)	O(10)–Cu(4)–O(14)	96.2(3)
O(1)–Cu(2)–O(3^{i})	91.3(3)	O(10)–Cu(4)–N(2)	91.4(3)
O(2)–Cu(2)–O(4)	86.8(4)	O(10)–Cu(4)–O(13)	173.7(4)
O(2)–Cu(2)–O(13)	93.2(3)	O(12)–Cu(4)–O(13)	72.2(3)
O(2)–Cu(2)–O(14)	168.9(3)	O(12)–Cu(4)–O(14)	69.5(3)
O(2)–Cu(2)–O(3^{i})	98.5(3)	O(12)–Cu(4)–N(2)	106.1(3)
O(4)–Cu(2)–O(13)	95.3(3)	O(13)–Cu(4)–O(14)	86.8(3)
O(4)–Cu(2)–O(14)	96.2(4)	O(13)–Cu(4)–N(2)	85.4(4)
O(4)–Cu(2)–O(3^{i})	90.8(4)	O(14)–Cu(4)–N(2)	171.9(4)
O(13)–Cu(2)–O(14)	75.9(3)		
O(13)–Cu(2)–O(3^{i})	167.1(3)	O(8)–Cu(5)–O(11)	103.6(3)
O(14)–Cu(2)–O(3^{i})	92.2(3)	O(8)–Cu(5)–O(12)	96.1(3)
		O(8)–Cu(5)–N(3)	90.8(3)
O(1)–Cu(3)–O(6)	99.5(3)	O(8)–Cu(5)–O(14)	163.2(3)
O(1)–Cu(3)–O(12)	96.8(3)	O(11)–Cu(5)–O(12)	85.4(3)
O(1)–Cu(3)–O(13)	78.3(3)	O(11)–Cu(5)–O(14)	93.0(3)
O(1)–Cu(3)–N(1)	117.1(3)	O(11)–Cu(5)–N(3)	90.6(4)
		O(12)–Cu(5)–O(14)	87.4(3)
		O(12)–Cu(5)–N(3)	172.6(4)
		O(14)–Cu(5)–N(3)	86.6(4)

[a] Symmetry code: $i = -x + \frac{3}{2}, -y, -z + \frac{1}{2}$.

Cu–O bonds of 1.996, 2.111 and 1.977 Å. The Cu–O distances of the other two ethanolato oxygens are 1.930, 2.645, 1.981 Å for Cu3, Cu4, Cu5 and 2.380, 1.963, 1.904 Å for Cu2, Cu4, Cu5.

The coordination number of copper atoms is five for Cu3 and Cu5 or six for the other Cu atoms, the coordination polyhedra being square-pyramidal or octahedral. A square-based pyramid description of the surroundings of the Cu3 places O12, O13, N1 belonging to aminoethanols and O6 of the carboxylic group in the basal plane and the oxygen atom O1 of the OH$^-$ ion in the apical position. Around Cu5 the basal plane is made of O8, O12, O14 and N3, and the apex is occupied by O11. The average deviations of the atoms in the basal planes with regard to the mean planes are 0.05 and 0.17 Å, respectively. The copper atoms Cu3 and Cu5 are displaced from the mean planes towards the apical sites by 0.29 and 0.11 Å, respectively. The apical bond lengths are Cu3–O1 = 2.149 and Cu5–O11 = 2.463 Å.

The Cu2 and Cu4 atoms are in a 4 + 2 surrounding. The four nearest neighbours of the Cu2 atom are the O1 of the OH$^-$ ion, O3 and O4 atoms of the carboxylic groups and O13 atom of the aminoethanolato with Cu–O distances of 1.943–1.976 Å. The two axial positions are occupied by the O2 atom of the carboxylic group and the O14 atom of the aminoethanolato with Cu–O distances of 2.406 and 2.380 Å, respectively. The Cu4 atom is surrounded by two ethanolato oxygen atoms, a carboxylic oxygen atom and an amino nitrogen atom with Cu–N and average Cu–O bonds of 2.035 and 1.946 Å. The axial sites are occupied by the carboxylic oxygen atom and the ethanolato oxygen atoms with Cu–O distances of 2.431 and 2.645 Å, respectively.

The coordination sphere of the Cu1 atom is interesting in that the equatorial Cu–O bonds are longer than the axial bonds, as shown in Fig. 5. The equatorial plane is made of carboxylic oxygen atoms O2 and O7, and the axial positions are occupied by the O1 atom of the OH$^-$ ions. Such a compressed octahedral CuO$_6$ chromophore appears to be very rare and has only been found earlier in the room temperature crystal structure of the diaquabis(methoxyacetato)copper(II) complex [19, 20]. Bond lengths of the ligands appear to be not usual (Table IV).

Spectroscopic and Magnetic Data

The interesting structure prompted us to investigate the spectroscopic and magnetic properties, using UV–Vis, EPR and susceptibility. The magnetic susceptibility data in the 80–300 K region indicate a weak antiferromagnetic behaviour (μ_{eff}/Cu $\approx$ 1.8 BM) with a θ value of -20 ± 1 K. On the other hand, in the temperature area 4–65 K, the compound shows (Fig. 7) a weak ferromagnetic pattern, with μ_{eff} slowly increasing from 1.6 BM (65 K) to 1.9 BM (4 K). The θ value in the 20–60 K area amounts to +6 K. Because of the complicated exchange pathways

TABLE IV. Bond Lengths (Å) and Angles (°)

O(2)–C(1)	1.24(2)	O(10)–C(9)	1.25(2)
O(3)–C(1)	1.23(1)	O(11)–C(9)	1.24(2)
C(1)–C(2)	1.56(2)	C(9)–C(10)	1.57(2)
C(2)–Cl(1)	1.70(2)	C(10)–Cl(9)	1.66(2)
C(2)–Cl(2)	1.78(2)	C(10)–Cl(10)	1.66(2)
O(4)–C(3)	1.27(2)	O(12)–C(12)	1.40(2)
O(5)–C(3)	1.22(2)	C(12)–C(11)	1.53(2)
C(3)–C(4)	1.55(3)	C(11)–N(1)	1.48(2)
C(4)–Cl(3)	1.60(2)	N(1)–C(13)	1.47(2)
C(4)–Cl(4)	1.57(2)	N(1)–C(14)	1.47(2)
O(6)–C(5)	1.26(2)	O(13)–C(16)	1.45(1)
O(7)–C(5)	1.22(1)	C(16)–C(15)	1.50(2)
C(5)–C(6)	1.57(2)	C(15)–N(2)	1.49(2)
C(6)–Cl(5)	1.68(2)	N(2)–C(17)	1.46(2)
C(6)–Cl(6)	1.80(2)	N(2)–C(18)	1.48(2)
O(8)–C(7)	1.23(1)	O(14)–C(20)	1.42(2)
O(9)–C(7)	1.21(3)	C(20)–C(19)	1.48(2)
C(7)–C(8)	1.51(2)	C(19)–N(3)	1.49(2)
C(8)–Cl(7)	1.73(2)	N(2)–C(21)	1.49(2)
C(8)–Cl(8)	1.70(2)	N(2)–C(22)	1.43(2)
O(2)–C(1)–O(3)	129(1)	O(10)–C(9)–O(11)	131(1)
O(2)–C(1)–C(2)	112(1)	O(10)–C(9)–C(10)	115(1)
O(3)–C(1)–C(2)	118(1)	O(11)–C(9)–C(10)	114(1)
C(1)–C(2)–Cl(1)	107(1)	C(9)–C(10)–Cl(9)	115(1)
C(1)–C(2)–Cl(2)	113(1)	C(9)–C(10)–Cl(10)	115(1)
Cl(1)–C(2)–Cl(2)	111(1)	Cl(9)–C(10)–Cl(10)	130(1)
O(4)–C(3)–O(5)	128(1)	O(12)–C(12)–C(11)	109(1)
O(4)–C(3)–C(4)	117(1)	C(12)–C(11)–N(1)	106(1)
O(5)–C(3)–C(5)	115(1)	C(11)–N(1)–C(13)	113(1)
C(3)–C(4)–Cl(3)	120(1)	C(11)–N(1)–C(14)	108(1)
C(3)–C(4)–Cl(4)	119(1)	C(13)–N(1)–C(14)	108(1)
Cl(3)–C(4)–Cl(4)	119(1)		
O(6)–C(5)–O(7)	129(1)	O(13)–C(16)–C(15)	108(1)
O(6)–C(5)–C(6)	117(1)	C(16)–C(15)–N(2)	109(1)
O(7)–C(5)–C(6)	114(1)	C(15)–N(2)–C(17)	110(1)
C(5)–C(6)–Cl(5)	114(1)	C(15)–N(2)–C(18)	108(1)
C(5)–C(6)–Cl(6)	104(1)	C(17)–N(2)–C(18)	109(1)
Cl(5)–C(6)–Cl(6)	111(1)		
O(8)–C(7)–O(9)	128(1)	O(14)–C(20)–C(19)	112(1)
O(8)–C(7)–C(8)	116(1)	C(20)–C(19)–N(3)	111(1)
O(9)–C(7)–C(8)	115(1)	C(19)–N(3)–C(21)	109(1)
C(7)–C(8)–Cl(7)	117(1)	C(19)–N(3)–C(22)	110(1)
C(7)–C(8)–Cl(8)	111(1)	C(21)–N(3)–C(22)	109(1)
Cl(7)–C(8)–Cl(8)	110(1)		

and the chemical differences for each of the Cu ions, no attempts were undertaken to fit the data in an exchange model. EPR spectra at 300 and 77 K show no unusual phenomena at X-band frequencies (asymmetric signal with g_{max} = 2.08 (77 K) or 2.09 (300 K)). At Q-band frequencies (70 K) the spectrum shows a small resolution at $g_{\parallel}$ (2.38), with $g_{\perp}$ = 2.10. The diffuse reflectance spectra (Fig. 6) just shows a broad band at 14300 cm^{-1}, which would agree [20, 21] with copper geometries/chromophores CuO_6, CuO_3NO, CuO_5N.

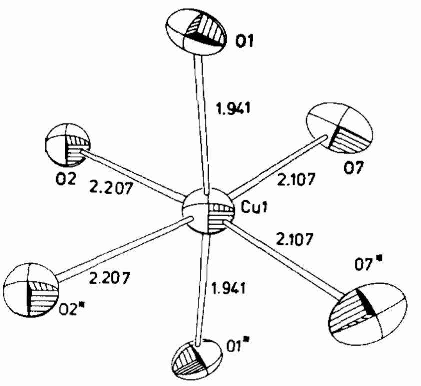

Fig. 5. View of the CuO_6 chromophore with the compressed octahedral coordination geometry.

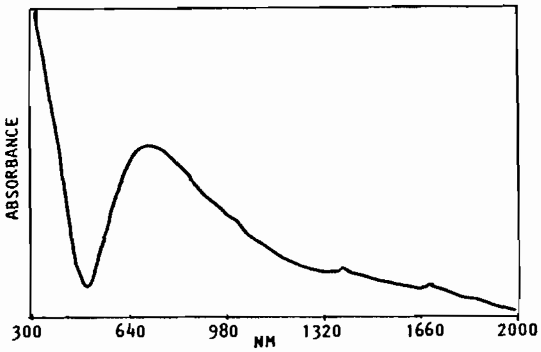

Fig. 6. The ligand-field spectrum of the nonameric compound.

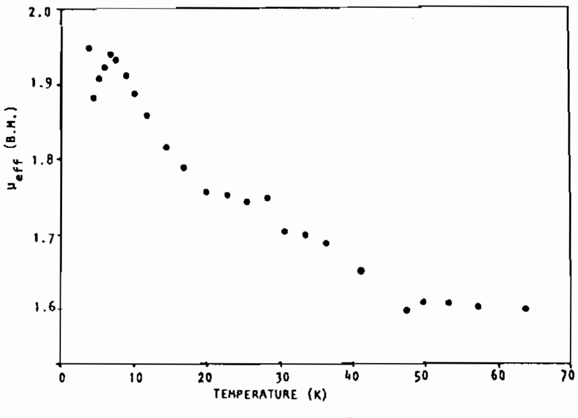

Fig. 7. Temperature dependence of the effective magnetic moment of the compound.

Supplementary Material

Listings of F_o and F_c values, hydrogen coordinates and anisotropic thermal parameters are available on request.

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