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THE CRYSTAL STRUCTURE AND MAGNETIC BEHAVIOR OF $[Cu_2(dien)_2Cl_2](ClO_4)_2$*

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Abstract The compound $[Cu_2(dien)_2Cl_2](ClO_4)_2$ crystallizes in the orthorhombic system, space group $Pbn2_1$, with unit cell dimensions: a = 7.637(1) Å, b = 13.549(3) Å, and c = 20.866(4) Å, with four molecules in the unit cell (Z = 4). The structure consists of dimeric $[Cu_2(dien)_2Cl_2]^{2+}$ units in which the coordination about copper(II) is highly distorted square-pyramidal. Magnetic susceptibility data shows a pair of exchanged coupled S = 1/2 ions and yields $J = +0.4(3)\text{cm}^{-1}$ when the EPR g-factor value of $\langle g \rangle = 2.104$ is used.

INTRODUCTION

Studies of magnetic properties of bis(μ-chloro) bimetallic copper (II) complexes[2-4] have shown that the copper ions in most of the complexes are antiferromagnetically exchange coupled with small singlet-triplet (ΔE_{ST}) splittings, although examples of triplet ground state, ferromagnetically coupled systems are known.[3] The singlet-triplet splittings in these chemically and structurally related compounds exhibit a strong correlation with the structural parameter ϕ/R, where ϕ is the Cu-Cl-Cu bridge angle and R is the longer bridge bond distance. The shorter Cu-Cl-Cu bond length is nearly constant (2.3Å) in these dimers. Similar correlations have been found for hydroxo-bridged, chloro-bridged, and sulfur-bridged copper (II) dimers.[13]

We have now found that the compound formulated as Cu(dien)Cl(ClO_4) (dien = diethylenetriamine) contains bis(μ-chloro)-bridged dimers with a small ΔE_{ST}. Here we describe the results of synthetic, structural, and magnetic studies on $[Cu_2(dien)_2Cl_2](ClO_4)_2$.

EXPERIMENTAL SECTION

Synthesis

Diethylenetriamine (1.0 g) was added with constant stirring to a solution of 1.7 g $CuCl_2 \cdot 2H_2O$ (10 mmole) in 40 ml water. Solid $NaClO_4$ (approx. 2g) was added to this deep blue solution and the solution was filtered to remove any solid particles. The filtrate was left at room temperature until deep blue crystals formed (24 hr). The crystals were collected by filtration, washed with ethanol and ether, and air dried. Yield 1.5g. Anal. Calcd. for $Cu_2(C_4H_{13}N_3)_2Cl_2(ClO_4)_2$: C, 15.93; H, 4.34; N, 13.93; Cl, 23.51. Found : C, 15.8; H, 4.4; N, 13.9; Cl, 23.4. UV-Vis spectrum: λ_{max} = 614 nm, ε = 158 l mole^{-1} cm^{-1}.

X-ray Data Collection and Reduction

The crystals were of low quality for X-ray study and selection of a suitable crystal was difficult. The crystal used for data collection had the approximate dimensions 0.05 x 0.07 x 0.1 mm. A total of 1072 independent reflections with $I \geq 2.5\sigma(I)$ were obtained giving a data-to-variables ratio of 4.3. The unit cell parameters were obtained at 295 K by least-squares refinements of the respective angular setting of 25 reflections. The cell constants and other crystallographic data are given in Table I. Intensity data were collected on a Syntex R3 diffractometer, and were corrected for Lorentz and polarization effects. An empirical absorption correction was also carried out.[5] The scattering factors for neutral atoms were corrected for both real and imaginary components of anomalous dispersion.

Solution and Refinement of Structure

The structure was solved via a three-dimensional Patterson synthesis which yielded the positions of the copper and chlorine atoms. Subsequent Fourier syntheses revealed the locations of all remaining non-hydrogen atoms. Refinements were carried out by using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms bound to carbon were included in the refinement in calculated, idealized positions with d(C-H) = 0.96 Å and regular tetrahedral geometry around the carbon atom and an isotropic temperature factor U. The function minimized during least-squares refinement was $(|F_o|-|F_c|)^2$ with final convergence to R = 0.044. The final positional parameters are given in Table II and relevant bond distances and angles are given in Table III.

Magnetic Susceptibility

Magnetic susceptibility data were collected in the

TABLE I Crystal Data and Intensity Collection for $[Cu_2(dien)_2Cl_2](ClO_4)_2$

a,Å	7.637(1)	Z = 4
b,Å	13.549(3)	space group $Pbn2_1$ (C^9_{2v})
c,Å	20.866(4)	mol. form. $[Cu_2C_8H_{26}N_6Cl_4O_8]$
V,Å^3	2159	form. weight 603.2
μ(MoKα), cm^{-1}		25.2
radiation		MoKα (λ = 0.7107 Å)
data collcn.		θ - 2θ mode; 2θ range 3-60
std. reflcn.		2 every 100 reflections
obs. data		1072 ($I \geq 2.5\sigma(I)$)

temperature range 2-60 K on a powdered sample by using a PAR Model 155 vibrating-sample magnetometer which was operated at 10 kG. The magnetometer was calibrated with $HgCo(NCS)_4$.[8,9] A calibrated GaAs diode was used to monitor the sample temperature. The data were corrected for diamagnetism of constituent atoms and for temperature-independent paramagnetism of the copper(II) ion (60 x 10^{-6} cgsu).

DESCRIPTION OF THE STRUCTURE

The crystal structure consists of the binuclear cations $[Cu_2(dien)_2Cl_2]^{2+}$ and essentially uncoordinated perchlorate ions. The nearest distances between oxygens of perchlorate ions and copper ions are Cu1-O2 (3.03 Å) and Cu2-O7 (3.15 Å). These distances are considerably longer than those found for the perchlorate ions coordinated to Cu(II).[8,9] The overall dimer geometry, as shown in Figure 1, may be described as two distorted square-pyramids which

TABLE II Positional Parameters ($\times 10^4$) for $[Cu_2(dien)_2Cl_2](ClO_4)_2$

atom	x	y	z
Cu 1	810(2)	-2002(1)	0000
Cu 2	9252(2)	581(1)	1368(1)
Cl 1	1378(6)	242(3)	642(2)
Cl 2	6336(6)	-2668(3)	753(2)
Cl 3	5874(7)	- 603(3)	9111(2)
Cl 4	824(7)	-1894(3)	2202(2)
N 11	5840(16)	-3548(8)	9337(5)
N 12	2305(14)	-3424(8)	9414(5)
N 13	2395(20)	-2141(15)	465(11)
N 21	-2544(14)	- 321(15)	1015(7)
N 22	-2648(17)	903(8)	2019(6)
N 23	923(20)	1087(10)	2037(6)
C 11	223(24)	867(11)	8922(8)
C 12	8170(36)	1032(18)	2648(11)
C 13	4064(28)	2417(14)	9421(9)
C 14	4331(23)	2653(13)	95(9)
C 21	4223(31)	103(12)	1266(10)
C 22	4029(21)	203(12)	1981(7)
C 23	2004(28)	1374(16)	8768(11)
C 24	- 171(25)	1607(15)	2541(8)
O 1	5985(20)	- 126(10)	8526(5)
O 2	4310(20)	-1154(12)	9179(8)
O 3	7320(20)	-1279(11)	9109(8)
O 4	5982(20)	104(8)	9611(6)
O 5	4223(24)	2422(10)	1690(6)
O 6	4035(20)	2571(9)	2766(5)
O 7	5690(24)	3651(15)	2210(9)
O 8	2657(21)	3648(13)	2080(7)

share a common base-to-apex edge via the μ-chloro bridges. The copper ions are five-coordinated. The basal plane is formed by a tridentate diethylenetriamine ligand and one bridging chloride ion. The individual complex geometry is strongly distorted from a regular tetragonal pyramid. The dimeric unit has unsymmetrical Cu-Cl bridging distances of 2.770(5) Å, 2.735(5) Å, 2.313(5) Å, and 2.266(5) Å, a Cu-Cu separation of 3.643(2) Å and bridging Cu-Cl-Cu angles of 92.0° and 92.1° and Cl-Cu-Cl of 88.8° and 87.0°.

TABLE III Bond Distances (Å) and Angles (deg) in the Cation $[Cu_2(dien)_2Cl_2]^{2+}$

Cu 1 - Cu 2	3.643(2)		
Cu 1 - Cl 1	2.770(5)	Cu 2 - Cl 2	2.735(5)
Cu 1 - Cl 2	2.313(5)	Cu 2 - Cl 1	2.266(5)
Cu 1 - N 11	2.015(12)	Cu 2 - N 23	2.012(14)
Cu 1 - N 12	1.975(11)	Cu 2 - N 22	2.036(13)
Cu 1 - N 13	2.041(20)	Cu 2 - N 21	1.979(16)
Cl 2-Cu 1-Cl 1	87.0(1)	Cl 1-Cu 2-Cl 2	88.8(2)
N 11-Cu 1-Cl 1	96.4(3)	N 23-Cu 2-Cl 2	97.7(4)
N 11-Cu 1-Cl 2	95.4(4)	N 23-Cu 2-Cl 1	94.5(4)
N 12-Cu 1-Cl 1	86.2(3)	N 22-Cu 2-Cl 2	90.6(3)
N 12-Cu 1-Cl 2	173.2(3)	N 22-Cu 2-Cl 1	179.3(3)
N 12-Cu 1-N 11	85.6(5)	N 22-Cu 2-N 23	85.1(5)
N 13-Cu 1-Cl 1	98.9(6)	N 21-Cu 2-Cl 2	104.3(5)
N 13-Cu 1-Cl 2	92.5(6)	N 21-Cu 2-Cl 1	97.1(4)

MAGNETIC PROPERTIES

The molar magnetic susceptibility of a powdered sample is plotted as a function of temperature in Figure 2. The excellent fitting of the inverse susceptibility to a straight line in the temperature range 2-60 K indicates a very small singlet-triplet splitting. Thus, an application of the magnetic susceptibility expression for a pair of exchanged coupled S = 1/2 ions[10] is inappropriate since the singlet-triplet splitting is smaller than the Zeeman energy $g\mu_B B$, which is about 1.2 cm^{-1} at B = 10 kG. The more general magnetization expression for a pair of S = 1/2 ions[11] was used :

$$M = \frac{Ng\mu_B \sinh(g\mu_B B/kT)}{\exp(-2J/kT)+2\cosh(g\mu_B B/kT)} \tag{1}$$

Equation (1) was fitted to the experimental magnetization data by using a Simplex fitting routine,[12] with g = 2.104

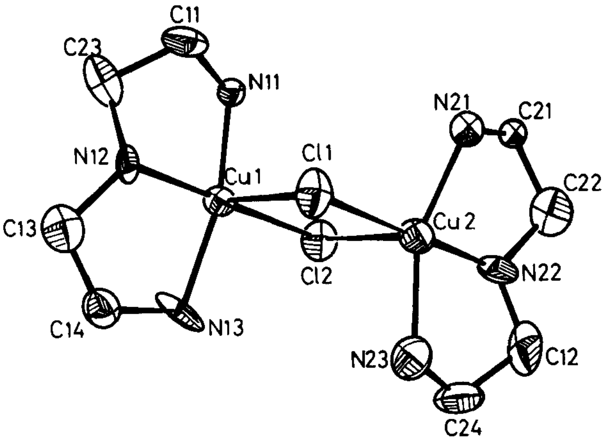

FIGURE 1 MOLECULAR STRUCTURE OF $[Cu_2(dien)_2Cl_2]^-$

as a constant parameter. This g-value is equal to the average value of the g-tensor principal components determined from EPR spectra. The best fit was found with $2J = +0.4(3)cm^{-1}$ and is represented by the solid lines in Figure 2. The intradimer exchange Hamiltonian is of the form $H_{ex} = -2J\ S_1 \cdot S_2$ from which the relationship $\Delta E_{ST} = -2J$ can be derived. The relative accuracy of the singlet-triplet splitting is not very high, but the magnetic data clearly indicate weak ferromagnetic intradimer coupling. A more accurate singlet-triplet splitting value could be obtained by collecting data below 2 K.

A strong correlation has been found between the singlet-triplet splitting and the quotient ϕ/R in symmetrical bis(μ-chloro) copper(II) bimetallic complexes.[3,4,13] A summary of the available data is presented in Table IV, and the relationship is plotted in Figure 3. The dimeric unit in $[Cu_2(dien)_2Cl_2](ClO_4)_2$ is not symmetrical, so a value for ϕ/R = 33.5 deg/Å was calculated by averaging bond distances and angles. The new

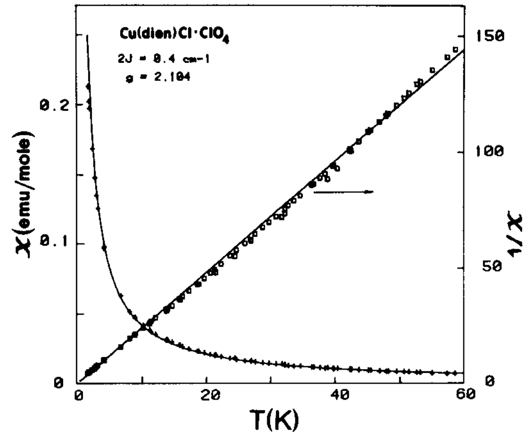

FIGURE 2 MAGNETIC DATA FOR $[Cu_2(dien)_2Cl_2](ClO_4)$

($\Delta E_{ST}=2J,\phi/R$) data point is marked by the filled circle in Figure 3, where it may be seen that the magnetic and structural data for $[Cu_2dien_2Cl_2](ClO_4)_2$ adhere to the magneto-structural correlation that has been found for all known bis(μ-chloro) bridged copper(II) complexes.

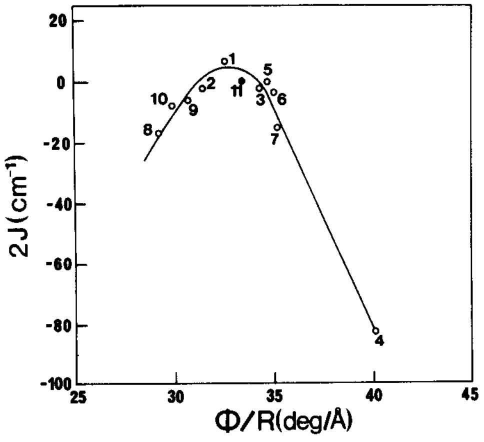

FIGURE 3 MAGNETO-STRUCTURAL CORRELATION FOR CHLORO-BRIDGED COPPER (II) DIMERS

TABLE IV Structural and Magnetic Properties of Bis(μ-chloro)-Bridged Copper(II) Dimers[a]

Compound	ϕ/R deg/A	2J cm^{-1}	ref.
1 $[Cu(dmg)Cl_2]_2$	32.6	+6.3	14-16
2 $[Cu(Me_3en)Cl_2]_2$	31.4	-2.1	17,18
3 $[Cu(4\text{-}Meox)_2Cl_2]_2$	34.4	-2.6	4
4 $[Cu(Guan)Cl_3]_2 \cdot 2H_2O$	40.0	-82.6	19,20
5 $[Cu(Et_3en)Cl_2]_2$	34.8	+0.1	3
6 $[Cu(4\text{-}Metz)(DMF)Cl_2]_2$	35.0	-3.4	3
7 $[Co(en)_3]_2[Cu_2Cl_8]Cl_2$	35.2	-14.6	21,22
8 $[Cu(TMSO)Cl_2]_2$	29.3	-17.0	23
9 $[Cu(tmen)Cl_2]_2$	30.7	-5.6	18,24
10 $[Cu(2\text{-}pic)_2Cl_2]_2$	29.9	-7.4	25-27
11 $[Cu(dien)Cl]_2(ClO_4)_2$	33.5	+0.4	this work

[a] Abbreviations: dmg = dimethylglyoxime; Me_3en = N,N,N'-trimethylethylenediamine; 4-Meox =4-methyloxazole; Guan = guaninium; Et_3en = N,N,N'-triethylethylenediamine; 4-Metz = 4-methylthiazole; en = ethylenediamine; TMSO = tetramethylene sulfoxide; tmen = N,N,N',N'-tetramethylethylenediamine; 2-pic = 2-methylpyridine; dien = diethylenetriamine.

References

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(2) Roundhill, S. G. N.; Roundhill, D. M.; Bloomquist, D. R.; Landee, C.; Willett, R. D.; Dooley, D. M.; Gray, H. B. Inorg. Chem. (1979), 18, 831.

(3) Marsh, W. E.; Patel, K. C.; Hatfield, W. E.; Hodgson, D. J. Inorg. Chem. (1983), 22, 511.

(4) Marsh, W. E. Ph.D. Dissertation, The University of North Carolina, Chapel Hill, 1982.

(5) Computations were carried out on a NOVA 3 (General Data) computer with use of SHELXTL (G. M. Sheldrick, Göttingen, West Germany, 1980).

(6) Brown, D. B.; Crawford V. H.; Hall, J W.; Hatfield,

W. E. J. Phys. Chem. (1977), 81 ,1303.

(7) Figgis, B. N.; Nyholm, R. S. J. Chem. Soc. (1958), 4190.

(8) Lewis, D. L.; Hodgson, D. J. Inorg. Chem. (1974), 13, 143.

(9) Lewis, D. L.; Hatfield, W. E.; Hodgson, D. J. Inorg. Chem. (1974), 13, 147.

(10) Bleaney, B.; Bowers, K. D. Proc. Roy. Soc. London, Ser.A (1952), 214, 451.

(11) Meyers, B. E.; Berger, L.; Friedberg, S. A. J. Appl. Phys. (1969), 40, 1149.

(12) Hatfield, W. E.; Weller, R. R.; Hall, J. W. Inorg. Chem. (1980), 19, 3285.

(13) Hatfield, W. E. Comments Inorg.Chem. (1981), 1, 105.

(14) Svedung, D. H. Acta. Chem. Scand. (1969), 23, 2865.

(15) Watkins, N. T.; Dixon, E. E.; Crawford, V. H.; McGregor, K. T.; Hatfield W. E. J. Chem. Soc. Chem., Comm. (1973), 133.

(16) Megnamisi-Bélombé, M.; Novotny, M. A. Inorg. Chem. (1980), 19, 2470.

(17) Phelps, D. W.; Goodman, W. H.; Hodgson, D. J. Inorg. Chem. (1976), 15, 2266.

(18) Estes, W. E. Ph.D. Dissertation, The University of North Carolina, Chapel Hill, 1977.

(19) Carrabine, J. A.; Sundaralingam, M. J. Am. Chem. Soc. (1970), 92,369. DeClerq, J. P.; Debboudt, M.; vanMeersche, M. Bull. Soc. Chim. Belg. (1971), 80, 527. Sundaralingam, M.; Carrabine, J.A. J. Mol. Biol. (1971), 61, 287.

(20) Drake, R. F.; Crawford, V. H.; Laney, N. W.; Hatfield, W. E.; Inorg. Chem. (1974), 13, 1246. Villa, J. F. Inorg. Chem. (1973), 12, 2054.

(21) Hodgson, D. J.; Hale, P. K.; Hatfield , W. E. Inorg. Chem. (1971), 10, 1061.

(22) Barnes, J. A.; Hatfield, W. E.; Hodgson, D. J.; Chem. Phys. Lett. (1970), 7, 374. McGregor, K. T.; Losee, D. B.; Hodgson, D. J.; Hatfield, W. E. Inorg. Chem. (1974), 13, 756.

(23) Swank, D. D.; Needham, G. F.; Willett, R. D. Inorg. Chem. (1979), 18, 761.

(24) Estes, E. D.; Estes, W. E.; Hatfield, W. E.; Hodgson, D. J. Inorg. Chem. (1975), 14, 106.

(25) Marsh, W. E.; Hatfield, W. E.; Hodgson, D. J. Inorg. Chem. (1982), 21, 2679.

(26) Duckworth , V. F.; Stephenson, N. C. Acta Cryst. B (1969), 25, 1975 .

(27) Jeter, D.Y.; Hodgson, D. J.; Hatfield, W. E. Inorg. Chim. Acta (1971), 5, 257.