Synthesis, Crystal Structure, Magnetic Susceptibility, and Single-Crystal EPR Studies of $[DafoneH_2][(CuCl_3H_2O)Cl]$

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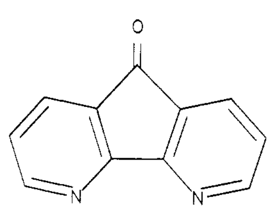
$[DafoneH_2][(CuCl_3H_2O)]Cl$ (dafone = 4,5-diazafluoren-9-one) crystallizes in the monoclinic space group $P2_1/c$ with $a = 14.585(2)$ Å, $b = 14.143(7)$ Å, $c = 7.076(6)$ Å, $\beta = 91.3(2)°$, and $Z = 4$. The crystal contains the unusual chromophore $[(CuCl_3H_2O)Cl]^{2-}$ showing coordinated water and a semicoordinate Cl^-. Moderately strong antiferromagnetic exchange ($J = -72.8$ K, with $\hat{\mathcal{H}}_{ex} = -2J\hat{S}_1\hat{S}_2$) is present. The exchange pathway appears to be via an H-bond involving H_2O and Cl^- of inversion-related molecules. Cl···Cl contacts also exist, but on the basis of geometry, EHMO calculations, and comparison with other systems, they are ruled out as the main exchange pathway. Single-crystal EPR studies ($g_1 = 2.069$, $g_2 = 2.089$, $g_3 = 2.250$) show further weak exchange via H-bonding between the semicoordinate Cl^- and H_2O.

Introduction

The longstanding interest in chlorocuprates[1] stems mainly from their structural diversity. Several examples of the $(CuCl_{n+2})^{n-}$ (n = 2,[2] 3,[3] 4[4]) species are known. These occur in a wide range of geometries. Square planar, square pyramidal, trigonal bipyramidal, and octahedral species have been reported, apart from a host of distorted geometries. The cations of these chlorocuprates may be organic or inorganic. The lattice is usually stabilized by H-bonding. Magneto–structural correlations in these compounds are of interest because of the wide array of superexchange pathways found.

The present crystal structure deals with $[(dafoneH_2)][(CuCl_3H_2O)Cl]$. Examples of dimers and a polymer containing



dafone

the $(CuCl_3H_2O)^-$ unit have been reported recently.[5,6] Monomeric $(CuCl_3H_2O)^-$ species have also been reported in a few crystals previously.[7,8] While one of them[7a] contains magnetically isolated and tetrahedrally distorted $(CuCl_3H_2O)^-$, two others[8] contain a planar anion linked by Cu···Cl bonds to form stacks with very small exchange coupling ($J \leq -3$ K). In contrast, the present system is moderately antiferromagnetic ($J = -72.8$ K) and consists of planar $(CuCl_3H_2O)^-$ units linked by Cl···Cl contacts and H-bonding.

Experimental Section

Syntheses. 4,5-Diazafluorenone (dafone) was prepared by a reported procedure.[9] $(DafoneH_2)[(CuCl_3H_2O)Cl]$ was obtained as large green crystals in 90% yield by the following procedure: Equimolar amounts of $CuCl_2{\cdot}2H_2O$ and dafone were dissolved in concentrated HCl. The solution was heated for ca. 1 h over a water bath and left to cool to room temperature, upon which the crystals separated. The crystals remained stable for about 1 month when kept in contact with the mother liquor. After this they change into dark blue crystals of $Cu(dafone)_2Cl_2$.[10] However the green crystals remain stable indefinitely if they are separated from the mother liquor by filtration inside a nitrogen glovebag and stored in a desiccator. When exposed to air, these crystals were found to decompose to a green powder in a few minutes.

Analyses. C, H, and N analyses were carried out using Perkin-Elmer 240 C analyzer. Anal. Calcd for $CuC_{11}H_{10}N_2OCl_4$: C, 32.41; H, 2.47; N, 6.88. Found: C, 32.40; H, 2.47; N, 7.10.

X-ray Structure Determination. A single crystal of approximate dimensions 0.41 × 0.25 × 0.13 mm was mounted on a glass fiber and coated with vacuum grease. The data collection was done on an Enraf-Nonius CAD4 diffractometer using Cu Kα radiation. The data were corrected for absorption[11] but not for extinction. The structure was solved using SHELX86 and refined using SHELX76 programs[12] on a Deil-VAX computer. Neutral atom scattering factors were taken from the usual sources.[13] Important crystal parameters and details on intensity collection and refinement are in Table 1. All non-hydrogen positions were located using a combination of heavy atom and direct methods. The ring H-atoms were fixed at calculated positions and allowed to "ride" upon the atoms to which they are bonded. Bond length constraints were applied to the O–H and H–H distances of water. All the non-hydrogen atoms were refined anisotropically. Four reflections with $|F_c - F_o|/\sigma_F > 9$ (002, 020, 041, 131) were excluded. Refinement converged to a final $R = 0.084$ with $R_w = 0.089$. The high R-factor is probably due to the

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(1) (a) Smith, D. W. *Coord. Chem. Rev.* **1976**, *27*, 93. (b) Geiser, U.; Willett, R. D.; Lindbeck, M.; Emerson, J. *J. Am. Chem. Soc.* **1986**, *108*, 1173. (c) Willett, R. D. *Coord. Chem. Rev.* **1991**, *109*, 181.
(2) (a) Halvorson, K. E.; Patterson, C.; Willett, R. D. *Acta Crystallogr., Sect. B* **1990**, *B46*, 508. (b) Dyrek K.; Gosler, J.; Hodorowicz, S. A.; Hoffmann, S. K.; Oleksyn, B. J.; Weselucha-Brczynska, A. *Inorg. Chem.* **1987**, *26*, 1481. (c) Harlow, R. L.; Wells, W. J., III; Watt, G. W.; Simonsen, S. H. *Inorg. Chem.* **1974**, *13*, 2106.
(3) (a) Blanchette, J.; Willett, R. D. *Inorg. Chem.* **1988**, *27*, 843. (b) Antolini, L.; Marcotrigiano, G.; Menabue, L.; Pellacini G. C. *J. Am. Chem. Soc.* **1980**, *102*, 1303.
(4) Tucker, D. A.; White, P. S.; Trojan, K. L.; Kirk, M. L.; Hatfield, W. E. *Inorg. Chem.* **1991**, *30*, 823.
(5) (a) Bond, M. R.; Willett, R. D. *Acta Crystallogr., Sect. C* **1988**, *C43*, 2304. (b) Bond, M. R.; Willett, R. D. *Inorg. Chem.* **1989**, *28*, 3267.
(6) Poitras, J.; Leduc, M.; Beauchamp, A. L. *Can. J. Chem.* **1993**, *71*, 549.
(7) (a) Thompson, L. K.; Woon, T. C.; Murphy, D. B.; Gabe, E. J.; Lee, F. L.; Le Page, Y. *Inorg. Chem.* **1985**, *24*, 4719. (b) Valle, G.; Ettorre, R. *Acta Crystallogr., Sect. C* **1992**, *C48*, 919.
(8) Manfredini, T.; Pellacini, G. C.; Bonamartini-Corradi, A.; Battaglia, L. P.; Guarini, G. T.; Giusti, J. G.; Pon, G.; Willett, R. D. *Inorg. Chem.* **1990**, *29*, 2221.
(9) Henderson, L. J., Jr.; Fonczek, F. R.; Cherry, W. R. *J. Am. Chem. Soc.* **1984**, *106*, 5876.
(10) Balagopalakrishna, C.; Rajasekharan, M. V.; Bott, S.; Atwood, J. L.; Ramakrishna, B. L. *Inorg. Chem.* **1992**, *31*, 2843.
(11) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.
(12) Sheldrick, G. W. *SHELX-A system of computer programs for X-ray structure determination*; University of Cambridge: Cambridge, U.K., 1976, 1986.
(13) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K.; 1974; Vol. 4.

0020-1669/94/1333-0950$04.50/0

Table 1. Crystal Data for (DafoneH$_2$)(CuCl$_3$H$_2$O)Cl

$C_{11}H_{10}N_2O_2CuCl_4$	MW = 407.56
a = 14.585(2) Å	b = 14.143(7) Å
c = 7.076(6) Å	β = 91.3(2)°
V = 1459.3(1) Å^3	D(calcd) = 1.74 gcm^{-3}
monoclinic, $P2_1/c$	Z = 4
Cu Kα	μ = 85.63 cm^{-1}
F(000) = 811.94	N = 2443
N_{param} = 195	R^a = 0.084
$R_w{}^a$ = 0.089	

^{a} $R = (\Sigma|F_o| - |F_c|)/\Sigma|F_o|$. $R_w = [(\Sigma w|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{0.5}$; $w = [\sigma^2(F)]^{-1}$.

Table 2. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for (DafoneH$_2$)(CuCl$_3$H$_2$O)Cl

atom	x/a	y/b	z/c	U(eqv)^a
Cu(1)	3055(1)	447(1)	1689(2)	8(0)
Cl(1)	3667(1)	1532(2)	4783(3)	16(1)
Cl(2)	4264(1)	−574(1)	1942(3)	15(1)
Cl(3)	1879(2)	1443(2)	1118(4)	28(1)
Cl(4)	2089(1)	−647(2)	2775(4)	17(1)
O(1)	897(5)	−1972(5)	8872(13)	35(3)
O(2)	3776(5)	1205(5)	−166(11)	27(2)
N(1)	3529(5)	−385(5)	6754(11)	9(2)
N(2)	1798(5)	969(5)	6402(12)	12(2)
C(1)	4154(6)	−1083(6)	6894(14)	15(3)
C(2)	3919(7)	−1956(7)	7573(15)	20(3)
C(3)	3023(7)	−2136(7)	8102(14)	21(3)
C(4)	2394(6)	−1388(6)	7949(13)	12(3)
C(5)	1375(7)	−1359(6)	8271(14)	16(3)
C(6)	1088(7)	−387(6)	7712(14)	15(3)
C(7)	249(6)	51(7)	7631(15)	20(3)
C(8)	196(6)	964(7)	6980(16)	24(3)
C(9)	969(6)	1407(7)	6343(16)	20(3)
C(10)	2657(6)	−543(6)	7240(13)	9(3)
C(11)	1857(6)	96(7)	7050(13)	12(3)

^{a} $U(\mathrm{eqv}) = (1/3)(U_{11}a^2a^{*2} + U_{22} + U_{33}c^2c^{*2} + U_{13}a^*c^*ac\cos\beta)$.

Table 3. Selected Bond Distances (Å) and Angles (deg) of (DafoneH$_2$)(CuCl$_3$H$_2$O)Cl

Bond Distances			
Cl(2)–Cu(1)	2.283(2)	Cl(3)–Cu(1)	2.248(2)
Cl(4)–Cu(1)	2.241(2)	O(2)–Cu(1)	2.011(7)
Bond Angles			
O(2)–Cu(1)–Cl(2)	88.5(2)	Cl(4)–Cu(1)–Cl(2)	91.5(1)
O(2)–Cu(1)–Cl(3)	87.5(2)	Cl(4)–Cu(1)–Cl(3)	90.7(1)
O(2)–Cu(1)–Cl(4)	159.2(3)	Cl(3)–Cu(1)–Cl(2)	174.1(1)

inadequate absorption correction and instrument fluctuations as revealed by the random variation (4%) of the intensity of the standard reflections measured at periodic intervals. (There was, however, no linear decay expected for sample decomposition.) This will affect the accuracy of the thermal parameters but not so much the positional parameters. The largest peak in the difference Fourier map corresponds to an electron density of approximately 1 e Å^{-3} and lies in the vicinity of Cl(4). Atom coordinates and equivalent isotropic thermal parameters are given in Table 2. Relevant bond distances and angles are given in Table 3.

Physical Measurements. Magnetic susceptibility measurements were carried out on a powdered sample sealed in a helium-flushed container. The susceptibility was measured on a SQUID-based susceptometer at a field of 3 kG over a temperature range 4.6–283.2 K.

Room-temperature EPR measurements were carried out on a JEOL Fe-3X spectrometer operating at X-band frequency. The powdered sample was transferred into an EPR tube and sealed in a nitrogen glovebag. Suitable single crystals were selected and coated with Apiezon grease inside the glovebag. These proved to be stable, and EPR measurements were performed in three orthogonal planes.

Extended Hückel Calculations. EHMO calculations were carried out on idealized square planar $CuCl_4^{2-}$ and $CuCl_3H_2O^-$ species. Charge iterations were performed on these species. The bond distances were Cu–Cl = 2.27 Å and Cu–O = 2.02 Å. Previously reported parameters[14] were used. The resulting parameters were used for the calculation of the

(14) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

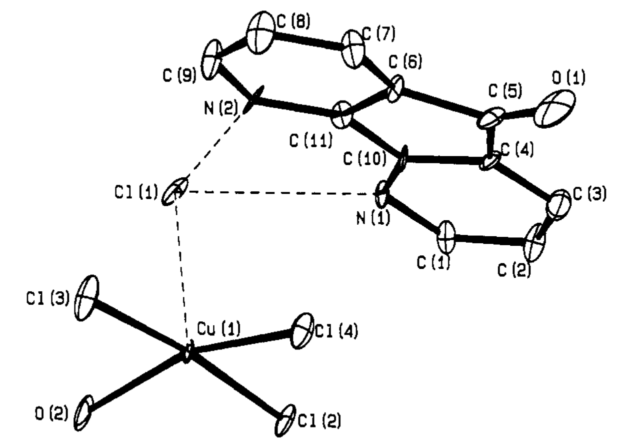
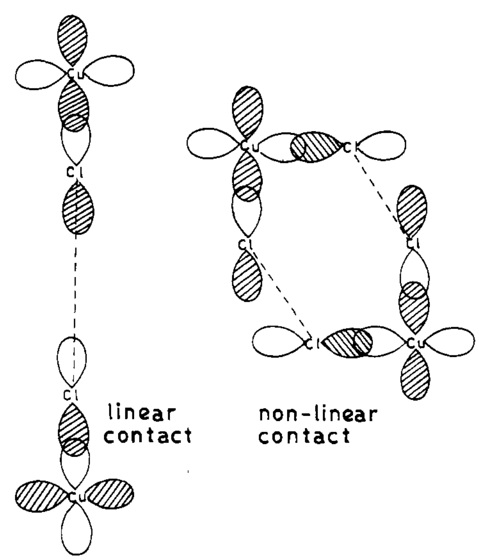


Figure 1. Molecular structure of (dafoneH$_2$)(CuCl$_3$H$_2$O)Cl.

gap between the HOMO and LUMO of the corresponding dimers, with a Cl···Cl distance of 3.6 Å. These calculations were carried out at various Cu–Cl···Cl angles ranging from 180 to 90°. At 180° only one halide–halide contact is possible, whereas, at 90°, there are two short contacts. In order to keep the unit chemically meaningful, neither of the Cl···Cl distances was allowed to become less than 3.6 Å during the angular variation. For the $(CuCl_3H_2O)_2$ dimers, only one short halide contact is observed, which was maintained between 3.6 and 3.8 Å in order to keep the O···Cl distance ≥ sum of the respective van der Waals radii.



Calculations were also done for a $(Cu_2Cl_{12})^{8-}$ dimer with a compressed structure having a d_{z^2} ground state for the purpose of comparison.

Results and Discussion

Description of the Crystal Structure. The X-ray crystal structure reveals the presence of biprotonated dafone as a counterion to $[(CuCl_3H_2O)Cl]^{2-}$, where the copper is weakly bound to a Cl$^-$ ion (Figure 1). The structure is stabilizing by H-bonding between this Cl$^-$ and the cation.

The $(CuCl_3H_2O)^-$ unit assumes a fairly good plane (the root-mean-square deviation of the atoms from the least-squares plane is 0.16 Å). The reason for the preference of a planar geometry may lie in the small size of the water ligand and in the H-bonding of the Cl$^-$ ions, which reduces electronic repulsions. Cu–Cl bond lengths are unequal (Table 3), averaging 2.28 Å as against an average of 2.27 Å for a planar $CuCl_4^{2-}$ anion.[15] The present system differs from other reported examples of $(CuCl_3H_2O)^-$ in being weakly bound to another Cl$^-$ ion (Cu–Cl(1) = 2.802(2) Å)

(15) Hathaway, B. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 5, p 741.

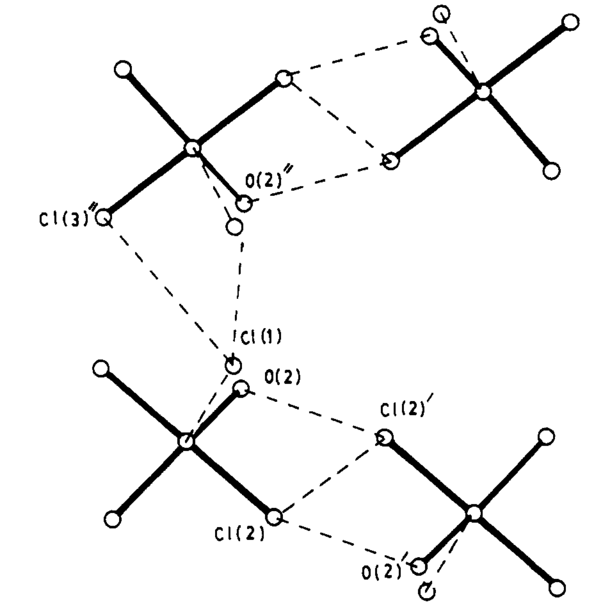


Figure 2. Intermolecular contacts of (dafoneH$_2$)(CuCl$_3$H$_2$O)Cl. The dashed lines correspond to weak contacts. Key: (′) $1-x, -y, -z$; (″) $x, 0.5-y, 0.5+z$.

which is almost perpendicular to the CuCl$_3$H$_2$O plane. The angle between the normal to the mean plane and the Cu–Cl(1) vector is ca. 7.7°, leading to a nearly square pyramidal 4 + 1 coordination. Cl(1) satisfies the criterion for semicoordination[16] in that all Cl(1)–X (X = Cl(2), Cl(3), Cl(4), O(2)) distances are more than the sum of their respective van der Waals radii. The two "trans" X–Cu–X angles are 174 and 159.7°. This kind of geometry with one angle closer to 180° than the other is described as "folded" and has been commonly observed[16] in compounds with 4 + 1 coordination. Correlations of the Cu···Cl semicoordinate distance with the difference between the two trans angles (Δ) have been reported.[17e] The preferred region for most five-coordinate species is defined by the Cu–Cl distance of 2.65–2.75 Å and 15° < Δ < 30°. In the present case, the semicoordinate distance is 2.80 Å and Δ is 14°.

There are four molecules in the unit cell (Figure 2). Inversion related units of (CuCl$_3$H$_2$O)$^-$ are approximately coplanar, forming weak dimers through Cl(2)–Cl(2)′ and Cl(2)–H$_2$O(2)′ H-bonded contacts. Weak interactions between dimers are also observed via Cl(1)–Cl(3)″ and Cl(1)–H$_2$O(2)″ contacts, forming zigzag chains. In other examples of (CuCl$_3$H$_2$O)$^-$,[6] stacks of the planar anions are seen, resulting in an approximately 4 + 2 geometry around Cu. In the present system, the sixth position of the "octahedron" is vacant.

EPR. Polycrystalline EPR at room temperature corresponds to that of an axially symmetric Hamiltonian with $g_1 = 2.242$ and $g_2 = 2.088$. Single-crystal EPR measurements in three orthogonal planes revealed a single exchange-narrowed line. The principal

(16) Willett, R. D., Gatteschi, D., Kahn, O., Eds. *Magneto-Structural Correlations in Exchange Coupled Systems*; NATO ASI Series; Reidel; Dordiecht, The Netherlands, 1985; p 389.
(17) (a) Snively, L. O.; Tuthill, G. F.; Drumheller, J. E. *Phys. Rev. B* **1981**, *24*, 5349. (b) Rubenacker, G. V.; Haines, D. N.; Drumheller, J. E.; Emerson, K. *J. Magn. Magn. Mater.* **1984**, *43*, 238. (c) Brown, D. B.; Hall, J. W.; Helis, H. M.; Walton, E. G.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1977**, *16*, 2675. (d) de Meester, P.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1973**, 424. (e) Blanchette, J. T.; Willett, R. D. *Inorg. Chem.* **1988**, *27*, 843. (f) Zanchini, C.; Willett, R. D. *Inorg. Chem.* **1990**, *29*, 3027. (g) Nilsen, D. M.; Larsen, R. D.; Emerson, K.; Rubenacker, G. V.; Ping, Z.; Drumheller, J. E. *Inorg. Chem.* **1990**, *29*, 2887. (h) Scott, B.; Willett, R. D.; Porter, L.; Williams, J. *Inorg. Chem.* **1992**, *31*, 2483. (i) Patyal, B. R.; Scott, B. L.; Willett, R. D. *Phys. Rev. B* **1990**, *41*, 1657. (j) Scott, B.; Geiser, U.; Willett, R. D.; Patyal, B.; Landee, P.; Greeney, R. E.; Manfredini, T.; Pellacini, G. C.; Corradi, A. B.; Battaglia, L. P. *Inorg. Chem.* **1988**, *27*, 2454. (k) Tucker, D. A.; White, P. S.; Trojan, K. L.; Kirk, M. L.; Hatfield, W. E. *Inorg. Chem.* **1991**, *30*, 823.

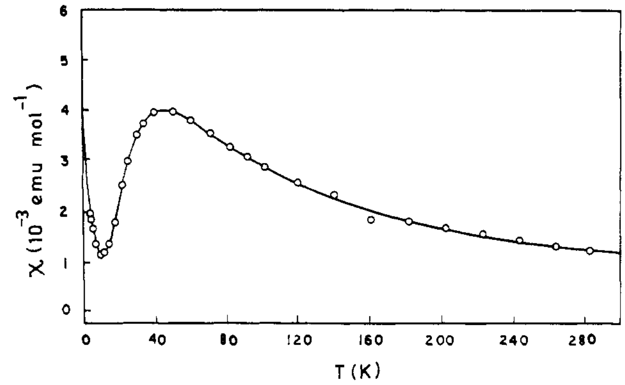


Figure 3. Temperature dependence of molar magnetic susceptibility of (dafoneH$_2$)(CuCl$_3$H$_2$O)Cl in the range 4.6–283.2 K. The solid line represents the best fit to the modified Bleany-Bowers equation wtih parameters $g = 1.97$, $\phi = -2.37$ K, $J = -72.8$ K, and $\rho = 0.036$.

values of the **g**-tensor matrix evaluated using the Schnland[18] method are 2.069, 2.089, and 2.250.

Complete exchange at all orientations indicates interactions between magnetically nonequivalent centers. Exchange through Cl(1)–Cl(3)″ (distance is 4.001(3) Å) and Cl(1)–O(2)″ H-bonds (distance is 3.205(7) Å) is observed. This exchange is necessarily weak as it is along an axis almost perpendicular to the CuCl$_3$O plane. However it should suffice to explain the EPR data.

Magnetic Susceptibility. Magnetic susceptibility results indicate antiferromagnetic coupling within the lattice. The behavior of this compound in the temperature range 4.3–283.2 K reveals a maximum at ca. 50 K and a small Curie-type tail below 10 K. An attempt was made to fit the molar magnetic susceptibility in the temperature range 81.5–283.2 K to the Curie–Weiss law. The result suggests the presence of antiferromagnetic interactions $(\bar{g}) = 1.68$ and $\Theta = -40.55$ K). This is also indicated in the plot of $\chi_m T$ vs T, where, as expected for systems with $J < 0$, $\chi_m T$ decreases on cooling and tends to zero. A least-squares fit to the Hall and Hatfield[17k] expression yielded very poor results. Consequently, the data were fitted to the Bleany–Bowers[19] expression which was modified to include monomeric impurities.

$$\chi_m = N^2g^2\beta^2/3k(T-\Theta)[1 + \{^1/_3\exp(-2J/kT)\}]^{-1} \times (1-\rho) + [Ng^2\beta^2/k(T-\Theta)]\rho + N\alpha$$

where ρ is the mole fraction of the paramagnetic impurity used as a floating parameter and $N\alpha$ is the temperature-dependent paramagnetism for a mononuclear Cu(II) complex given a value of 60×10^{-6} emu mol^{-1}. A nonlinear routine was used for fitting the data in the range 4.6–283.2 K. The best fit parameters are $g = 1.97$, $\Theta = -2.37$ K, $J = -72.8$ K, $\rho = 0.036$, and $F = 0.3766 \times 10^{-3}$. The J value is indicative of moderately strong antiferromagnetic coupling. The g-value used in this fit is smaller than the average EPR g-value (2.139). Such discrepancies are common among Cu(II) compounds.[20] The good fit obtained by the Bleany–Bowers equation points to dimeric interactions in the compound (Figure 3).

Magneto–Structural Correlations. A square planar d^9 complex favors a $d_{x^2-y^2}$ ground state. By the renaming of the Cartesian axes appropriate for the low symmetry, the ground state may be described as d_{xy}.

Dimeric contacts are seen between inversion-related molecules (the Cu–Cu distance is ca. 6.3 Å). The shortest intermolecular Cu–Cl distance is 4.73 Å, which is too long for any significant exchange. Instead, Cl–Cl contacts are considered as a likely

(18) Schönland, D. S. *Proc. Phys. Soc. London* **1959**, *73*, 788.
(19) Bleany, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.
(20) (a) Marsh, W. E.; Patel, K. C.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1983**, *22*, 511. (b) Sikarov, S.; Bkouche-Waksman, I.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 490.

Table 4. Examples of Exchange through Halide–Halide Contacts

system no.	X	unit	X–X (Å)	bridge geometry	J/k (K)	ref
			Planar			
1	Cl	$CuCl_4^{2-}$	3.63	linear	−13.7	17a
2	Cl,Br	$CuCl_2Br_2^{2-}$	3.70	linear	−31	17a
3	Br	$CuBr_4^{2-}$	3.80	linear	−68	17b
4	Cl	$CuCl_4^{2-}$	3.99	nonlinear double bridge	−7.3	17f
5	Cl	$CuCl_3^-$	3.71	nonlinear	−1.21	17g
6	Cl	$Cu_2Cl_6^{2-}$	3.94	nonlinear double bridge	−23.9	17j
7	Cl	$CuCl_3H_2O^-$	3.88	nonlinear double bridge	−72.81	this work[a]
			Flattened Tetrahedral			
8	Br	$Cu_2Br_4^-$	4.09	nonlinear double bridge	−1.8	17h
9	Br	$CuBr_4^{2-}$	4.1, 4.3	nonlinear double bridge	−6.64, −0.66	17i
10	Cl	CuN_2Cl_2	3.75	nearly linear	−10.8	17c
11	Br	CuN_2Br_2	3.79	nearly linear	−5.2	17c,d
			Trigonal Bipyramidal			
12	Br	$Cu_2Br_6^{2-}$	3.73	nonlinear	−38.7	17e
			Compressed Octahedral			
13	Cl	$CuCl_6^{4-}$	3.99	linear	−8	17k

[a] Comparisons in this table as well as EHMO calculations indicate that the Cl···Cl contact cannot explain the large J value in this case (see text).

pathway for exchange. These kinds of contacts resulting in antiferromagnetic coupling have been reported.[17]

The $(CuCl_3H_2O)^-$ ion is approximately coplanar with its inversion-related counterpart. There is, thus, "edgewise" interaction between the two molecules. The principle behind halide–halide short contacts is that, if the distance between the halides is less than the sum of their respective van der Waals radii + 0.5 Å, exchange of electron density is possible through a two-halide bridge. Thus, superexchange is via a 4-atom, 6-electron cluster. The distance between $Cl(2)^-$ ions of adjacent inversion-related chromophores fulfills the criterion for two-halide exchange (the Cl(2)–Cl(2)′ distance is 3.883(3) Å).

Some of the examples of halide–halide contacts leading to antiferromagnetic coupling are tabulated (Table 4). From this table, some trends emerge. For four-coordinate structures, planarity of the chromophore and linearity of the Cu–X···X–Cu bridge favor stronger exchange. Br···Br contacts are generally more efficient than Cl···Cl contacts. Planarity favors the overlap between the (in-plane) magnetic orbitals of the intermolecular dimer. Somewhat puzzling is the moderately large J-value of **12**, which, in spite of extensive d_{z^2}, $d_{x^2-y^2}$ mixing shows moderate coupling. The reason probably lies in the unusually short Br···Br contact. The odd member of the table is by far the present system (no. **7**), which shows the strongest coupling in spite of relatively long Cl···Cl contacts and a Cu–Cl···Cl angle of 97°.

EHMO calculations revealed that "linear" contact between halides results in the maximum energy gap between the HOMO and the LUMO. As shown in Figure 4, energy gaps for $(CuCl_4)_2$ as well as $(CuCl_3H_2O)_2$ dimers go through a minimum. In the former case, due to the presence of two Cl···Cl contacts, there is a sharp increase as the angle tends to 90°. However, for the $(CuCl_3H_2O)_2$ dimers, the energy gap at 90° is much less than at 180°. In fact, the energy gap of the present case is close to a minimum. The structure with a d_{z^2} ground state gave a smaller gap than others, even with linear contact. This is in agreement with the experimental data.[17k] Only the present compound remains unexplained due to these calculations. Therefore, we have to turn our attention to alternative modes of exchange to rationalize our data.

The only other model which can explain the moderately strong antiferromagnetic exchange is hydrogen bonding between inversion-related chromophores. The Cl(2)–O(2)′ distance is 3.222(1) Å, which is less than the sum of their van der Waals radii. Fairly strong antiferromagnetic coupling (J = −100 to −195 K) has been reported for H-bonded contacts between water molecules.[21] There is a case of ferromagnetic exchange[22] via N–H···Cl bonds where the contact is through an organic counterion containing the N–H part. In the present case there is direct H-bonding between the chromophores, which is more like the former. Strong H-bonds have been reported between water and chloride[23] in copper complexes. (O···Cl is between 3.10 and 3.26 Å). However, to the best of our knowledge magnetic correlations have not been performed.

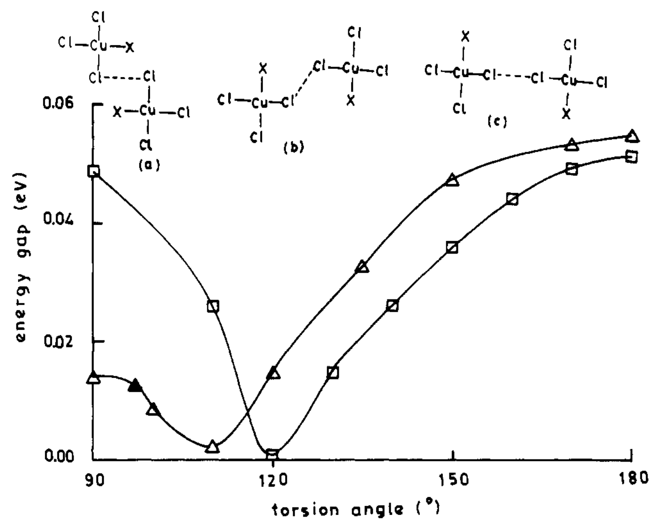


Figure 4. Variation of the HOMO–LUMO energy gap with torsion angle. Δ represents the points for the $(CuCl_3H_2O)_2^{2-}$ unit, while □ represents the points for the $(CuCl_4)_2^{4-}$ units. ▲ is the calculated energy gap at the experimental angle. The drawings at the top of the figure correspond to (a) 90°, (b) 120° for X = Cl or 110° for X = H_2O, and (c) 180°.

Conclusions. The presence of a planar $(CuCl_3H_2O)$ unit with a semicoordinate Cl^- is significant in that it rules out any inherent instability of the $CuCl_3H_2O^-$ species. The fact that a water molecule coordinates to copper in preference to the chloride ion implies that the structure is better stabilized by H-bonding in the former case. Moderately strong antiferromagnetic coupling is

(21) (a) Bertrand, J. A.; Black, T. D.; Eller, P. G.; Holm, F. T.; Mahmood, R. *Inorg. Chem.* **1976**, *15*, 2965. (b) Bertrand, J. A.; Fujitha, E.; Van Derveer, D. G. *Inorg. Chem.* **1980**, *19*, 2022. (c) Muhonen, H. *Inorg. Chem.* **1986**, *25*, 4692.

(22) Groenendijk, H. A.; Blöte, H. W.; Van Duyneveldt, A. J.; Gaura, R. M.; Landee, C. P.; Willett, R. D. *Physica* **1981**, *106B*, 47.

(23) (a) De Munno, G.; Denti, G.; Dapporte, P. *Inorg. Chim. Acta* **1982**, *74*, 1990. (b) Ghedini, M.; De Munno, G.; Denti, G.; Lanfredi, A. M.; Tripicchio, A. *Inorg. Chim. Acta* **1982**, *57*, 87. (c) Dyrek, K..; Gosler, J.; Hodorowicz, S. A.; Hoffmann, S. K.; Oleksyn, B. J.; Weselucha-Brycyznska, A. *Inorg. Chem.* **1987**, *26*, 1481.

observed which is explained on the basis of H-bonds. Cl···Cl interactions are rejected as the primary pathway for spin exchange.

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Supplementary Material Available: Tables of crystal data, H-atom parameters, anisotropic thermal parameters, and complete bond distances and angles (Tables S1–S3) (6 pages). Ordering information is given on any current masthead page.