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Synthesis, Crystal Structure, Magnetic Susceptibility, and Single-Crystal EPR Studies of Bis(diazafluorenone)dichlorocopper(II): A Novel Cu(NN)$_2$X$_2$ System with an Unusual Distortion

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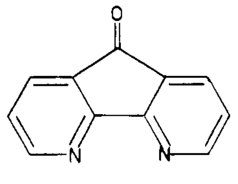
The crystal structure of Cu(dafone)$_2$Cl$_2$ (dafone = 4,5-diazafluoren-9-one) was determined (monoclinic, space group $P2_1/n$ with $a = 6.5911$ (6) Å, $b = 13.0712$ (5) Å, $c = 11.4813$ (9) Å, $\beta = 95.575$ (4)°, and $Z = 2$). This structure represents the first crystallographic example in a family of Cu(NN)$_2$X$_2$ chromophores (NN = 2,2′-bipyridine, 1,10-phenanthroline, or bis(2-pyridyl)amine, and X is an anion) that has retained its octahedral coordination through trans ligation, in spite of the steric effects. The room-temperature magnetic moment is 1.74 μ_B, and it shows little variation down to 5 K. An exchange-averaged EPR spectrum is observed at X-band frequency while the analysis of line shape at Q-band frequency gave a value of $|J| = 0.005$ (3) cm^{-1}. The solid complex has electronic spectral bands at 14.29 kK and 16.95 kK. The molecular g tensor with $g_x = 2.070$, $g_y = 2.066$, $g_z = 2.206$ corresponds to a $|x^2 - y^2\rangle$ ground state.

Introduction

Prodigious literature is now available on the copper(II) complexes with a wide range of ligands, exhibiting a variety of stereochemistries, dominated by nonregular structures involving significant bond length and bond angle distortions, from regular octahedral, tetrahedral, and square-planar geometries.[1] The main factors responsible for this atypical behavior are (i) the Jahn–Teller effect[2] and its secondary consequences, like the plasticity effect,[1a,3] fluxionality,[3] and cooperative Jahn–Teller effect,[4] and (ii) the classical effects,[1b] like the bulk effect, blocking effect, and chelate effect. Hathaway[1b,d,5] has correlated the structural data on these complexes with their electronic properties. Of particular relevance to this paper is the structural pathway (Figure 1) discussed by him for the CuL$_2$X$_2$ chromophores, where L = 2,2′-bipyridine (bpy) and X = Cl$^-$, Br$^-$, I$^-$, CH$_3$COO$^-$, NO$_3^-$, BF$_4^-$, ClO$_4^-$, etc., which are predominantly 5- or 6-coordinate with a wide range of geometries,[3,6] resulting from the bulk effect. Thus, while Cu(en)$_2$X$_2$ (en = ethylenediamine) complexes have a coplanar CuN$_4$ chromophore,[7] the Cu(bpy)$_2$X$_2$ complexes are prevented from assuming this coordination by the steric requirements of the bipyridyl hydrogen atoms.[1b,3,8] Consequently the bpy ligands are forced to twist out of the equatorial plane to yield a cis configuration resulting in 5-coordination, as in [Cu(bpy)$_2$X]X. As many as 34 complexes characterized crystallographically to date show the same behavior.[3,9] The occurrence of similar distortions, also with other chelating ligands like 1,10-phenanthroline and bis(2-pyridyl)amine,[3,9] has shown that this is a general feature of Cu(NN)$_2$X$_2$ chromophores.[10]

In the course of our investigations of weak exchange by EPR spectroscopy in copper(II) complexes, we have synthesized Cu(dafone)$_2$Cl$_2$ (where dafone = 4,5-diazafluoren-9-one). The structure revealed a trans configuration for the two chloride ligands. This is the first example of a new kind of distortion in Cu(NN)$_2$X$_2$ chelates, where the chelating ligands remain coplanar with two short and two long bonds and an overall C_i symmetry. The crystal structure and magnetic properties of this complex are reported here.



dafone

Table I. Crystal Data for Cu(dafone)$_2$Cl$_2$

C$_{22}$H$_{12}$N$_4$O$_2$CuCl$_2$	MW = 498.82
$a = 6.5911$ (6) Å	$b = 13.0712$ (5) Å
$c = 11.4813$ (9) Å	$\beta = 95.575$ (4)°
$V = 984.5$ (1) Å^3	D(calcd) = 1.69 g cm^{-3}
monoclinic, $P2_1/n$	$Z = 2$
Cu Kα	μ(calcd) = 43.67 cm^{-1}
$F(000) = 502$	NO = 1567
NV = 142	$R = 0.052^a$
$R_w = 0.059^a$	GOF = 1.37

[a] $R = (\sum|F_o| - |F_c|)/\sum|F_o|$. $R_w = [(\sum w|F_o| - |F_c|)^2/\sum w|F_o|^2]^{0.5}$. $w = [(\sigma(F))^2 + 0.000625F^2]^{-1}$.

Experimental Section

Preparations. All chemicals were of reagent grade quality and were used as commercially obtained. 4,5-Diazafluoren-9-one (dafone) was prepared following the method of Henderson et al.[11] Cu(dafone)$_2$Cl$_2$ was obtained as dark blue crystals from a saturated solution of CuCl$_2$·2H$_2$O (0.171 g, 1 mmol) and dafone (0.364 g, 2 mmol) in concentrated HCl by slow evaporation at room temperature over a period of 2 weeks. The crystals were collected by filteration and air-dried. Yield:

[†] University of Hyderabad.
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[§] Arizona State University.

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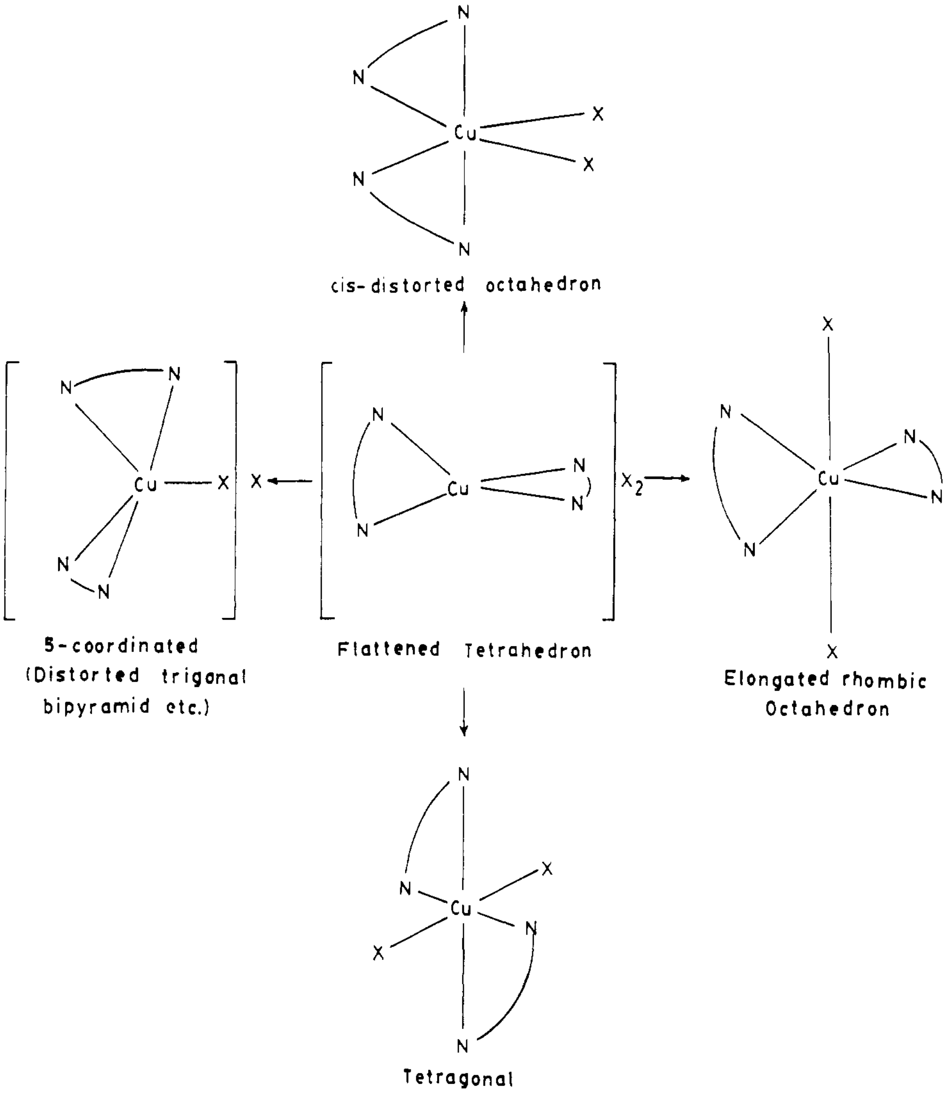

Figure 1. Structural pathway for $Cu(bpy)_2X_2$ type complexes.

0.401 g, 80%. Anal. Calcd for $C_{22}H_{12}N_4O_2CuCl_2$: C, 52.98; H, 2.43; N, 11.14; Cu, 12.74. Found: C, 52.80; H, 2.30; N, 10.00; Cu, 12.74. Some green prismatic crystals were also isolated along with the blue crystals. These were later identified as $(dafoneH_2)CuCl_4{\cdot}H_2O$. In this paper, we however restrict ourselves to the studies pertaining to the former complex only.

X-ray Structure Determination of $Cu(dafone)_2Cl_2$. A single crystal having approximate dimensions 0.3 × 0.35 × 0.4 mm was sealed in a thin-walled glass capillary. Final lattice parameters were determined from 25 reflections ($2\theta > 70°$) accurately centered on an Enraf-Nonius CAD-4 diffractometer. Intensity data were recorded using methods described earlier,[12] for the range $1° < \theta < 55°$. Out of 2450 reflections measured, 1567 were considered as observed. The details on crystal data, intensity collection, and refinement are listed in Table I. The position of the copper and chlorine atoms were determined from a Patterson map, and subsequent difference Fourier maps allowed the location of all non-hydrogen atoms. Refinement of all atoms with isotropic thermal parameters led to the reduction of the R value by about 4% and allowed the location of the hydrogen atoms which were allowed to "ride" upon the appropriate carbon atoms. Refinement converged at $R = 0.052$ and $R_w = 0.059$. The largest parameter shifts in the final cycles of refinement were less than 0.01 of their estimated standard deviations. Neutral-atom scattering factors were taken from the usual sources.[13] All computer programs were taken from the SHELX suite.[14]

Table II. Positional Parameters, Equivalent Isotropic Thermal Parameters,[a] and Their Estimated Standard Deviations for $Cu(dafone)_2Cl_2$

atom	x	y	z	U(eqv)
Cu	0.0000	0.5000	0.5000	0.037 (2)
Cl	0.1572 (2)	0.4807 (1)	0.3319 (1)	0.038 (3)
N(1)	0.1557 (6)	0.3841 (3)	0.5746 (3)	0.030 (3)
N(2)	−0.2554 (6)	0.3339 (3)	0.4499 (3)	0.033 (3)
O	0.0317 (7)	0.0317 (3)	0.6284 (4)	0.058 (18)
C(2)	0.3451 (8)	0.3908 (4)	0.6348 (4)	0.041 (6)
C(3)	0.4392 (8)	0.3065 (5)	0.6877 (5)	0.046 (17)
C(4)	0.3510 (8)	0.2116 (5)	0.6803 (4)	0.046 (13)
C(5)	−0.3407 (9)	0.1218 (4)	0.4637 (5)	0.050 (11)
C(6)	−0.4736 (8)	0.1895 (5)	0.4031 (5)	0.051 (13)
C(7)	−0.4305 (8)	0.2915 (4)	0.3997 (4)	0.041 (11)
C(8)	0.0725 (7)	0.2926 (4)	0.5682 (4)	0.029 (2)
C(9)	0.1582 (8)	0.2047 (4)	0.6176 (4)	0.035 (4)
C(10)	0.0122 (9)	0.1176 (4)	0.5941 (4)	0.041 (8)
C(11)	−0.1654 (8)	0.1633 (4)	0.5186 (4)	0.038 (4)
C(12)	−0.1319 (7)	0.2672 (4)	0.5064 (4)	0.030 (4)

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

Table III. Selected Bond Lengths (Å) and Bond Angles (deg)

Cu–Cl	2.292 (1)	Cu–N(1)	1.978 (4)
Cu–N(2)	2.773 (4)		
N(1)–Cu–Cl	91.3 (1)	N(2)–Cu–Cl	93.11 (9)
N(1)–Cu–N(2)	76.6 (1)		

Physical Measurements. The magnetic susceptibility measurements on a powdered sample in the temperature range 4.5–280 K and at a field

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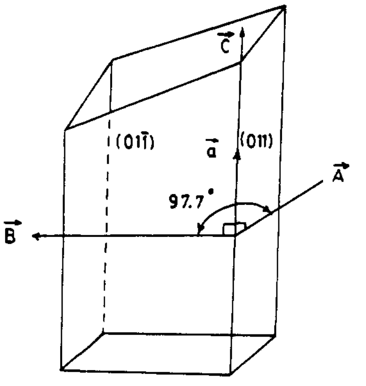

Figure 2. Morphology of the Cu(dafone)$_2$Cl$_2$ crystal used for EPR measurements. The directions $\hat{A}$, $\hat{B}$, and $\hat{C}$ correspond to crystal rotation axes.

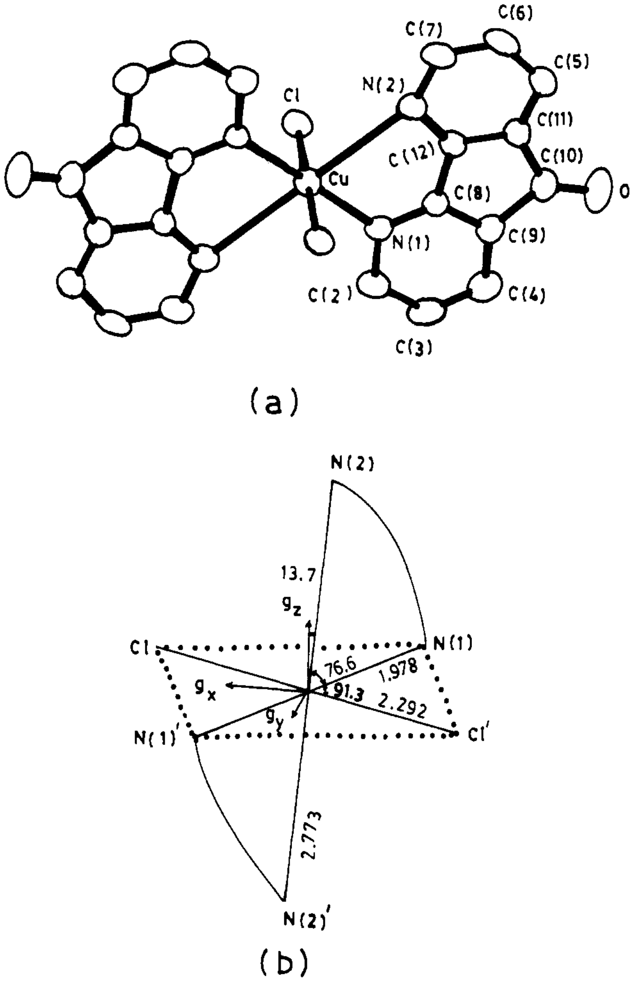

Figure 3. Molecular structure of Cu(dafone)$_2$Cl$_2$ showing (a) atom-numbering scheme and (b) geometry of the *trans*-CuN$_4$Cl$_2$ coordination polyhedron. The bond lengths (Å) and bond angles (deg) are also indicated. g_x, g_y, and g_z refer to molecular g tensor directions.

of 3 kG were done on a SQUID based susceptometer supplied by the SHE Corp. Diamagnetic corrections (245 × 10^{-6} emu mol^{-1}) were estimated from Pascal's constants.[15]

The room-temperature EPR spectra were obtained with a Varian E-112 spectrometer at both X- and Q-band frequencies, following procedures described else where.[16] The EPR angular variation was followed by rotating the crystal about the $\hat{A}$, $\hat{B}$, and $\hat{C}$ axes where, $\hat{A} = \hat{a} \times (\hat{b}^* + \hat{c}^*)$, $\hat{B} = \hat{a} \times (\hat{b}^* - \hat{c}^*)$, and $\hat{C} = \hat{a}$. $\hat{A}$ makes an angle of 97.7° with $\hat{B}$, while $\hat{C}$ is perpendicular to both (Figure 2).

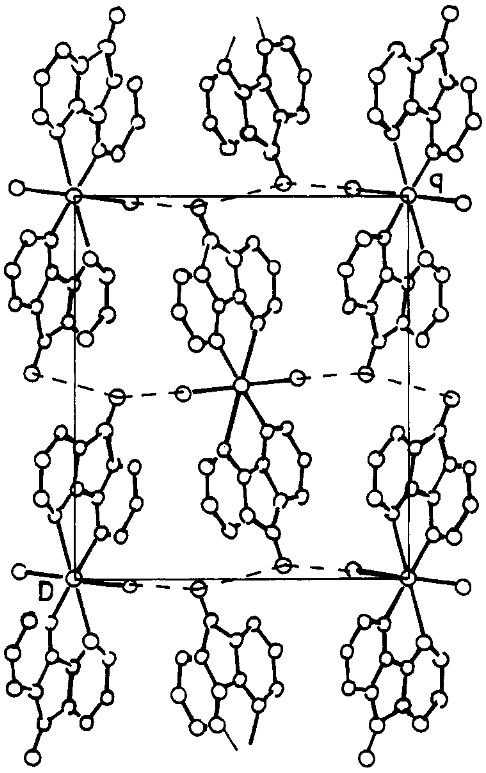

Figure 4. Molecular packing in the *bc* plane of Cu(dafone)$_2$Cl$_2$. The dashed lines correspond to intermolecular short contacts.

Results

Crystal Structure. The structural data are summarized in Tables II and III and in Figures 3 and 4. The unit cell consists of two magnetically inequivalent Cu(dafone)$_2$Cl$_2$ molecules. Each molecule is centrosymmetric (C_i). The basal plane is built up of two nitrogens and two chloride ions arranged in a trans fashion. The apical positions are occupied by two weakly bonding nitrogen atoms, thus completing a distorted (2 + 2 + 2) octahedron (Figure 3b). The tetragonality[17] in the present complex is 0.77, quite different from the unity expected for an ideal octahedron.

Magnetism and EPR Spectra. The corrected magnetic susceptibility in the temperature range 4.5–280 K exhibits a Curie–Weiss dependence with a negligible Weiss correction (Θ = 0.002 K). The room-temperature magnetic moment is 1.74 μ_B. Since there is no change even down to 4.5 K, the exchange interaction[18] in the lattice should be less than 4.5 K. The polycrystalline EPR spectrum at X-band frequency is rhombic with $g_1 = 2.151$, $g_2 = 2.088$, and $g_3 = 2.063$. The X-band single-crystal EPR spectrum showed a single line in all the three planes which is the result of coalescence of spectra from two magnetically inequivalent sites at all orientations. Due to complete exchange averaging, the crystal g tensor will have the full symmetry of the crystal unit cell, which in the present case means that one of the principal axes will lie along the crystal *b* axis. It is necessary in such situations to use a decoupling procedure to obtain the true molecular g tensor.[1b] Since the initial measurements were made in three nonorthogonal planes, the method of Wallers and Rogers[19] was used to obtain the crystal g tensor, which was decoupled using a procedure described elsewhere,[16] to give the molecular g values as $g_x = 2.070$, $g_y = 2.066$, $g_z = 2.206$.

The EPR angular variation of the single crystal at Q-band frequency at room temperature showed resolution of the exchange-averaged line at most of the orientations. A merging effect

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(17) The tetragonality is defined as the mean in-plane distance/mean out-of-plane distance.[1b]

(18) The exchange integral J is defined by the Hamiltonian $\mathcal{H} = -2J\mathbf{S}_1 \cdot \mathbf{S}_2$, with positive J implying ferromagnetic interaction.

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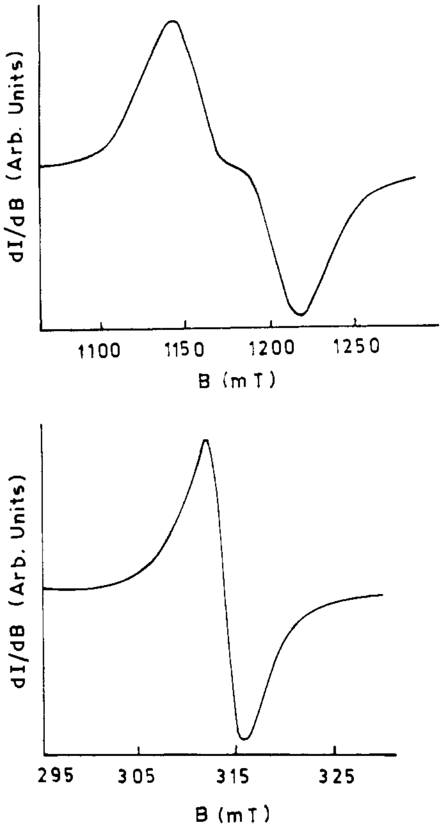

Figure 5. Single-crystal EPR spectra of Cu(dafone)$_2$Cl$_2$ recorded at two different frequencies: (a, top) Q-band; (b, bottom) X-band. The magnetic field is in the plane perpendicular to the rotation axis $\tilde{A}$, making a 10° angle with the crystallographic *a* axis. The spectra are simulated with the following set of parameters: (a) $\mathbf{g}_1 = 2.189$; $\mathbf{g}_2 = 2.094$; $\tau_1 = 217.0$; $\tau_2 = 220.0$; $|J| = 0.005$ (3) cm^{-1}. (b) $\mathbf{g}_1 = 2.191$; $\mathbf{g}_2 = 2.100$; $\tau_1 = 13.0$; $\tau_2 = 13.0$; $|J| = 0.005$ (3) cm^{-1}. Note that the **g** values used in the X-band and Q-band fittings agree within experimental error. In both cases the simulated spectrum exactly overlaps with the experimental spectrum.

seen at some orientations is indicative of the closeness of the exchange energy to the splitting due to *g* anisotropy at the Q-band frequency of ca. 1.2 cm^{-1}. The line shape arising from weak exchange was simulated (Figure 5) using a previously described model,[20] giving a value of 0.005 (3) cm^{-1} for $|J|$.

Discussion

Structure. A notable feature of the present complex is the way in which it relieves the bulk strain due to the crowding of the hydrogens adjacent to the nitrogen atoms of the dafone ligands. Unlike in all other reported structures of Cu(NN)$_2$X$_2$ complexes, Cu(dafone)$_2$Cl$_2$ has a coplanar CuN$_4$ coordination in which the strain is relieved by lengthening of one pair of trans Cu–N bonds. The Cu–N(2) bond length (2.773 Å) is the highest observed in this type of complex.[3] The present structure is more akin to the trans complex Cu(pyridine)$_2$Cl$_2$.[21] In this case, the fifth and sixth coordination positions are occupied by weakly binding Cl$^-$ from the neighboring molecules, leading to extended interaction in the lattice. In Cu(dafone)$_2$Cl$_2$ on the other hand, the fifth and sixth coordination sites are filled in an intramolecular fashion by weak ligation with the second nitrogen atom of the dafone molecules.[22] It appears that the presence of the polar C=O group in the ligand is responsible for the trans structure which allows for cancellation of the two dipoles as well as maximum π-bonding. However the effect of π-back-donation on the C=O bond is not large enough to affect significantly its length (1.192 Å) or IR stretching frequency (1720 cm^{-1}).

Spectral and Magnetic Properties. Even though the exact point group is only C_i, the ligand field has a near D_{4h} symmetry, as reflected in the axial nature of the molecular **g** tensor. Since $g_\parallel \gg g_\perp > 2.0$, the ground state is $|x^2 - y^2\rangle$. It may be noted that the rhombic features exhibited by the polycrystalline spectrum do not reflect the molecular symmetry, as it corresponds neither to the crystal nor to the molecular **g** tensor. The electronic spectrum[23] shows two bands, a broad band at 14.29 kK and a higher energy band at 16.95 kK. Twin peaked electronic spectra are seen also in the case of other elongated tetragonal complexes like Cu(NH$_3$)$_4$(NO$_2$)$_2$ (17.1, 13.4 kK)[5] and Cu(NH$_3$)$_4$(SCN)$_2$ (17.5, 14.3 kK).[24] EPR and electronic spectral data can help in distinguishing the present tetragonal structure from the other 6-coordinate structures of Figure 1. The cis-distorted octahedron has one *g* value close to 2 corresponding to a ground state dominated by the $|z^2\rangle$ component.[3] The elongated rhombic octahedron on the other hand has a higher *g* value with significant in-plane anisotropy.[6f] Further, this structure gives a single broad band in the electronic spectrum. Tris chelate complexes having effective D_2 symmetry and high tetragonality (T, 0.9)[25] have the lowest energy band at 8–9.5 kK.[1b] It is more difficult to distinguish the tetragonal geometry from the compressed tetrahedral geometry. This latter type also has only one crystallographically characterized member which has a dihedral angle of 44.6°.[6b] Due to the low value of this angle, its d–d transition energies and *g* values are somewhere midway between those of the tetragonal stereochemistry and those expected for the nonexistent square-planar structure.

Only a weak magnetic exchange is observed ($|J| = 0.005$ cm^{-1}) owing to the large distances between metal ions, the shortest Cu–Cu distance being 6.591 Å, and due to the nonavailability of any bridges. Hence the exchange effects are "direct" in nature. Recently, it was found that the exchange interaction between the magnetic subsystems (oligomers, chains, and layers in the system) may become quite significant when there are short halide–halide contacts.[26] It appears that significant exchange occurs ($|J| > 1$ cm^{-1}) when X···X contact distance is within $2r + 0.5$ Å, where r is the van der Waals' radius of the halide ion. In this context, the apparently attractive interactions marked by dashed lines in Figure 4 are most likely responsible for the weak exchange.

Conclusion

The structural pathway predicted by Hathaway for Cu(NN)$_2$X$_2$ complexes is far from complete. It would be interesting to pursue studies further with dafone and a variety of anions (X) to arrive at a more generalized pathway.

Acknowledgment. We thank the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras, for extending their facilities. C.B. thanks the Council of Scientific and Industrial Research, New Delhi, for the award of a fellowship.

Supplementary Material Available: Tables SI–SVI, listing derived hydrogen positions, anisotropic thermal parameters, bond distances and angles, summary of the mean plane data, intermolecular contacts, and **g** tensor data (6 pages); a table of calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

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(22) [Cu(dafone)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ also has an exactly symmetric structure with Cu at an inversion center. Relevant bond distances (Å): Cu–N(1), 2.002 (2); Cu–N(2), 2.608 (2); Cu–O, 1.981 (2). Balagopalakrishna, C.; Rajasekharan, M. V. Unpublished results.

(23) Measured using a PAR Model 3000 photoaccoustic spectrometer with carbon black as reference.

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