Further Structural and Magnetic Studies of Tricopper Dipyridylamido Complexes

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The compound $Cu_3(dpa)_4Cl_2$, **1** (dpa = the anion of dipyridylamine), which was first synthesized and characterized in 1990, has been structurally characterized in three new crystal forms having Cu···Cu separations of 2.47–2.49 Å. Its magnetic properties have been studied fully. Reaction of $Cu_3(dpa)_4Cl_2$ with 2 equiv of silver tetrafluoroborate yields $Cu_3(dpa)_4(BF_4)_2$ (**2**), a compound with a similar linear trinuclear structure but coordinated BF_4 anions in each axial position and having shorter Cu···Cu distances of 2.40 Å but similar magnetic properties. Least squares fitting of the magnetic susceptibility data for **1** and **2** gave isotropic g values of 2.007 and 2.130 and exchange parameters of −373 and −411 cm^{-1}, respectively. This suggests the possible existence of an exchange pathway in which the metal atoms interact directly with each other.

Introduction

Although more than 10 years have passed since the discovery of the linear trinuclear structure of $Cu_3(dpa)_4Cl_2$, **1** (see Scheme 1), by the groups of Hathaway[1] and Pinkerton,[2] there still exist structural and magnetic inconsistencies about the compound which have not been resolved. The crystal structure of **1** was reported in 1990 and then again 1991. The unit cell dimensions were similar, the space group was the same, and the geometry of the molecule was similar, but one crystal was reported to contain interstitial water molecules[1] whereas the other report stated that the crystal contained no solvent.[2]

Hathaway and co-workers reported also the magnetic moment of **1** at room temperature as 1.40 μ_B (corresponding to $\chi T = 0.245$ emu·K/mol) per Cu atom. Since this is less than the expected spin-only value of 1.73 μ_B (or 0.375 emu·K/mol),[1] they proposed the existence of antiferromagnetic coupling between the three d[9] Cu^{2+} ions, but did not quantify this coupling except to propose that the exchange parameter was >500 cm^{-1}.[1] They also found **1** to be EPR

Scheme 1
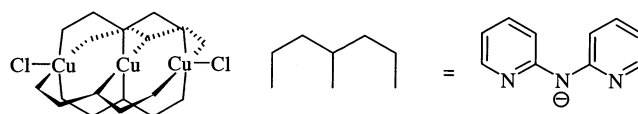
silent, which is a surprising observation for a system containing three Cu^{II} ions where the ground state of the molecule should have either one (in the case of antiferromagnetic coupling) or three (for ferromagnetic coupling) unpaired electrons.

Recently, we have studied linear trinuclear dipyridylamido complexes of Cr,[3] Co,[4] and Ni,[5] which have similar structures and fascinating magnetic properties. We have found that $Cr_3(dpa)_4Cl_2$ and $Co_3(dpa)_4Cl_2$ (like $Ru_3(dpa)_4Cl_2$ and $Rh_3(dpa)_4Cl_2$[6]) all exist in an orthorhombic form (space group *Pnn*2) isomorphous to that reported for **1**.[1,2] The major difference is that the Cr_3, Co_3, Ru_3, and Rh_3 compounds all crystallize with an interstitial molecule of dichloromethane, whereas **1** has been reported to crystallize with a molecule of water,[1] or no solvent at all,[2] which we found to be

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(1) Wu, L.-P.; Field, P.; Morrissey, T.; Murphy, C.; Nagle, P.; Hathaway, B.; Simmons, C.; Thornton, P. *J. Chem. Soc., Dalton Trans.* **1990**, 3835.
(2) Pyrka, G. J.; El-Mekki, M.; Pinkerton, A. A. *J. Chem. Soc., Chem. Commun.* **1991**, 84.
(3) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Pascual, I. *J. Am. Chem. Soc.* **1997**, *119*, 10223.
(4) Cotton, F. A.; Daniels, L. M.; Jordan IV, G. T.; Murillo, C. A. *J. Am. Chem. Soc.* **1997**, *119*, 10377.
(5) Clérac, R.; Cotton, F. A.; Dunbar, K. R.; Murillo, C. A.; Pascual, I.; Wang, X. *Inorg. Chem.* **1999**, *38*, 2655.
(6) Sheu, J.-T.; Lin, C.-C.; Chao, I.; Wang, C.-C.; Peng, S.-M. *Chem. Commun.* **1996**, 315.

puzzling. Moreover, we found that the metal–metal bond lengths in $Co_3(dpa)_4Cl_2$ change quite dramatically with temperature. Furthermore, at low temperatures the cobalt compound undergoes a phase transition from the orthorhombic *Pnn*2 form to a monoclinic *Pn* form.[7]

We have determined the structure of **1** unambiguously in three different crystal forms at different temperatures, and report only minor changes in the Cu···Cu separations under these conditions. Here, we also report a new analogue of **1**, namely, $Cu_3(dpa)_4(BF_4)_2$, **2**, which also has a linear tricopper chain. Contrary to the earlier reports, we have obtained EPR spectra of **1** at various temperatures, and we also report the EPR spectrum of **2**. The temperature dependences of the magnetic susceptibilities of both compounds have been measured and fit with an appropriate model taking into account isotropic exchange interactions between the three Cu^{II} centers.

Experimental Section

Materials and Methods. All synthetic procedures were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were purified by distillation over an appropriate drying agent in a nitrogen atmosphere prior to use. Di(2-pyridyl)-amine was purchased from Aldrich and sublimed prior to use. Anhydrous $CuCl_2$ and $AgBF_4$ were purchased from Strem Chemicals, and the former was heated in thionyl chloride prior to use. Methyllithium (1.6 M in Et_2O) was purchased from Acros and kept refrigerated prior to use.

Physical Measurements. Unless otherwise specified, solvents of crystallization were removed from samples by vacuum prior to measurements. IR spectra were taken on a Perkin-Elmer 16PC FTIR spectrometer using KBr pellets. X-band EPR spectra were obtained on a Bruker ESP 300 spectrometer. UV–vis spectra were recorded with a Cary 17 spectrophotometer on dichloromethane solutions. Electronic reflectance spectra were obtained in the region from 400 to 1000 nm on an HP 845x UV–visible system with a Labsphere RSA-HP-8453 reflectance spectroscopy accessory. Elemental analysis for compound **2** was performed by Canadian Microanalytical Services in British Columbia, Canada.

$Cu_3(dpa)_4Cl_2$, 1. A flask was charged with Hdpa (0.548 g, 3.20 mmol) dissolved in 35 mL of THF. The solution was cooled to −78 °C, and 2 mL of 1.6 M methyllithium in Et_2O solution was added dropwise. The solution was removed from the cold bath and stirred until it reached room temperature, when a white turbidity was observed. The mixture was added via cannula to a flask containing anhydrous copper(II) chloride (0.323 g, 2.40 mmol). A dark blue color appeared immediately. The reaction mixture was refluxed for 6 h, which resulted in a dark blue solution and a blue precipitate. The solution was filtered, and the precipitate was washed twice with 15 mL portions of THF and ether. Finally, the blue precipitate was dissolved in 30 mL of dichloromethane, and the dark blue solution was layered with 20 mL of ether. After a week, large, block-shaped crystals were collected. Yield: 80%. IR (KBr, cm^{-1}): 3447.8 (w, br), 3067.2 (w), 3025.6 (w), 2483.4 (vw), 1605.3 (s), 1593.1 (s), 1446.2 (m), 1472.6 (vs), 1459.4 (s), 1434.7 (vs), 1423.3 (vs), 1382.0 (m), 1368.5 (s), 1319.3 (m), 1288.3 (w), 1268.3 (w), 1235.2 (w), 1167.0 (m), 1152.7 (m), 1111.3 (w), 1053.7 (w),

1013.1 (m), 921.6 (w), 875.9 (w), 857.3 (w), 760.4 (s), 733.4 (m), 638.4 (w), 532.6 (w), 517.2 (w), 431.5 (m). UV–vis (CH_2Cl_2), nm (ϵ): 246 (39000), 300 (44000), 339 (>64000), 368 (27000), 556 (900), 666 (1200).

Crystals of **1**·CH_2Cl_2 and **1**·Et_2O were obtained by layering dichloromethane solutions of **1** with hexanes and diethyl ether, respectively. Layering a toluene solution of **1** with hexanes gave **1**·toluene.

$Cu_3(dpa)_4(BF_4)_2$, 2. To a mixture of $Cu_3(dpa)_4Cl_2$ (100 mg, 0.110 mmol) and $AgBF_4$ (41 mg, 0.21 mmol) was added 15 mL of dichloromethane. The solution immediately turned intensely purple. After stirring overnight, a fine white precipitate was observed. The mixture was filtered with the aid of Celite, and the resulting solution was layered with 15 mL of hexanes. Small purple, needle-shaped crystals formed within a day. Yield: 42%. IR (KBr, cm^{-1}): 1606.1 (s), 1596.1 (s), 1473.0 (vs), 1428.1 (vs), 1364.5 (m), 1317.0 (m), 1289.8 (m), 1237.4 (w), 1158.6 (m), 1124.3 (m), 1110.3 (m), 1017.9 (m), 936.8 (m), 919.2 (w), 882.4 (w), 858.7 (w), 762.7 (m), 738.5 (w), 644.7 (w), 531.0 (w), 517.8 (w), 433.9 (w). Electronic reflectance spectrum: 565 nm, broad peak with shoulder at 650 nm. Anal. Calcd for $Cu_3C_{40}H_{32}N_{12}B_2F_8$: C, 45.97; H, 3.06; N, 16.09. Found: C, 45.33; H, 3.05; N, 15.78.

Crystallographic Structural Determinations. Data were collected on a Nonius FAST area detector diffractometer for **1**·toluene and **1**·Et_2O using the program MADNES[8] and on a Bruker SMART 1000 CCD detector diffractometer for **1**·CH_2Cl_2 and **2** using SMART[9] software. In each case, a single crystal was attached to the tip of a quartz fiber with a small amount of stopcock grease and transferred to the goniometer, where the crystal was kept under a stream of cold nitrogen. Unit cell dimensions were obtained by autoindexing routines built into the diffractometer software. For the crystals mounted on the FAST, the unit cell dimensions and Laue symmetry were confirmed by inspection of axial images. In all cases, the data were corrected for Lorentz and polarization effects using PROCOR[10] (for FAST data) or SAINT[11] (for SMART data), and then further corrected for absorption using SORTAV[12] (for FAST data) or SADABS[13] (for SMART data). The structures were solved by direct methods, and the entire structure was determined by least squares refinement on F^2 followed by difference Fourier synthesis using the SHELXL-93 program.[14] In all of the structures, the non-hydrogen atoms were refined with anisotropic displacement tensors. All hydrogen atoms were assigned to calculated positions and were not refined. In **1**·CH_2Cl_2 the interstitial molecules are disordered in two positions over a 2-fold axis as has been shown before for the analogous cobalt compound. The details of each crystal structure are given in Table 1, and Tables 2 and 3 give relevant interatomic distances. Figures 1 and 2 show thermal ellipsoid plots of **1** and **2**, respectively.

(7) Clérac, R.; Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Kirschbaum, K.; Murillo, C. A.; Pinkerton, A. A.; Schultz, A. J.; Wang, X. *J. Am. Chem. Soc.* **2000**, *122*, 6226.

(8) Pflugrath, J.; Messerschmitt, A. *MADNES*, Munich Area Detector (New EEC) System, Version EEC 11/1/89, with enhancements by Enraf-Nonius Corp., Delt, The Netherlands. A description of MADNES appears in the following: Messerschmitt, A.; Pflugrath, J. *J. Appl. Crystallogr.* **1987**, *20*, 306.

(9) *SMART V5.05 Software for the CCD Detector System*; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1998.

(10) (a) Kabsch, W. *J. Appl. Crystallogr.* **1988**, *21*, 67. (b) Kabsch, W. *J. Appl. Crystallogr.* **1988**, *21*, 916.

(11) *SAINTPLUS, V5.00 Software for the CCD Detector System*; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1998.

(12) *SORTAV*. Program for absorption correction for Enraf-Nonius FAST diffractometer using the method of Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(13) *SADABS*. Program for absorption correction using SMART CCD based on the method of Blessing, R. H. See ref 12.

(14) *SHELXTL, Version 5.03*; Siemens Industrial Automation Inc.: Madison, WI, 1994.

Table 1. Crystal Data for Compounds **1** and **2**

| | $1 \cdot CH_2Cl_2$ | | | | |
	298 K	160 K	$1 \cdot Et_2O$	$1 \cdot C_7H_8$	**2**
empirical formula	$C_{41}H_{34}Cl_4Cu_3N_{12}$	$C_{41}H_{34}Cl_4Cu_3N_{12}$	$C_{44}H_{42}Cl_2Cu_3N_{12}O$	$C_{47}H_{40}Cl_2Cu_3N_{12}$	$C_{40}H_{32}B_2Cu_3F_8 N_{12}$
fw	1027.22	1027.22	1016.42	1034.43	1045.02
space group	*Pnn*2	*Pnn*2	$P2_1/c$	$Pca2_1$	$P2_1/c$
a, Å	12.95(1)	12.8757(8)	15.9887(9)	18.323(1)	14.376(2)
b, Å	14.11(1)	14.0119(9)	15.7321(5)	14.9167(9)	16.794(2)
c, Å	11.430(9)	11.3144(7)	16.9933(8)	16.431(2)	17.694(2)
β, deg	90	90	99.240(4)	90	103.050(2)
V, Å^3	2089(3)	2041.3(2)	4219.0(3)	4490.8(6)	4161.5(9)
Z	2	2	4	4	4
T, °C	25	−113	−178	−60	−60
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calc}, g/cm^3	1.633	1.671	1.600	1.530	1.668
μ, mm^{-1}	1.817	1.860	1.678	1.576	1.603
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0268, 0.0684	0.0270, 0.0695	0.0459, 0.1121	0.0347, 0.0845	0.0460, 0.1168
R1, wR2 (all data)	0.0297, 0.0701	0.0298, 0.0712	0.0599, 0.1231	0.0371, 0.0875	0.0669, 0.1323

[a] R1 $= \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] wR2 $= [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

Table 2. Main Structural Attributes of $Cu_3(dpa)_4Cl_2$

	$1 \cdot H_2O$	**1**	$1 \cdot CH_2Cl_2$ −113 °C	25 °C	$1 \cdot$ toluene	$1 \cdot Et_2O$
space group	*Pnn*2	*Pnn*2	*Pnn*2	*Pnn*2	$Pca2_1$	$P2_1/c$
Cu$\cdots$Cu, Å	2.471(1)	2.4712(4)	2.4769(3)	2.492(2)	2.4710(9) 2.4688(9)	2.4672(8) 2.4735(8)
Cu−N (outer), Å	2.061[4][a]	2.069[b]	2.070[2]	2.088[3]	2.061[4]	2.066[5]
Cu−N (inner), Å	1.965[4]	1.962[b]	1.966[2]	1.983[3]	1.958[5]	1.967[4]
Cu−Cl, Å	2.465(1)	2.464[b]	2.4718(6)	2.487(2)	2.459(2) 2.465(2)	2.436(1) 2.474(1)
overall torsion angle, deg	48.14	47.1(2)	45.2	46.5	42.4	46.1
ref	1	2	this work	this work	this work	this work

[a] Numbers in square brackets represent errors in average numbers. [b] No standard deviations were reported.

Table 3. Selected Interatomic Distances and Angles for **2**

Cu$\cdots$Cu, Å	2.4035(8) 2.4029(8)	B−F$_{ax}$, Å	1.425(7) 1.421(7)
Cu−N (outer), Å	2.049[4][a]	B−F$_3$,[b] Å	1.373[8][a]
Cu−N (inner), Å	1.972[4][a]	Cu1−Cu2−Cu3, deg	179.46(3)
Cu−F, Å	2.239(3) 2.254(3)	overall torsion angle, deg	41.7

[a] Numbers in brackets denote average values. [b] F$_3$ represents the three F atoms bound only to B atoms.

Magnetic Measurements. A sample from which the interstitial solvent had been removed by vacuum was placed into a plastic bag of known mass and mounted inside an ordinary drinking straw. The straw was then placed inside the Quantum Design SQUID magnetometer MPMS-XL. A field of 1000 G was used for the data collection, which took place from 2 to 400 K. Corrections for diamagnetism were applied: empirically for the straw and sample container (from the measurement of an empty straw and bag), and using Pascal's constants for the diamagnetism of the compounds (-478.48×10^{-6} emu/mol and -509.68×10^{-6} emu/mol for **1** and **2**, respectively.)

Results and Discussion

Syntheses. In the original reports of **1**,[1,2] the compound was synthesized by air oxidation of mononuclear bis-(dipyridylamino)copper(I) chloride, giving a yield of only 31%. While the mechanism of this reaction remains mysterious, we have obtained **1** by a method which we have used extensively to make trinuclear complexes of chromium,[3] cobalt,[4] and nickel,[5] as shown in eq 1. Not only is this
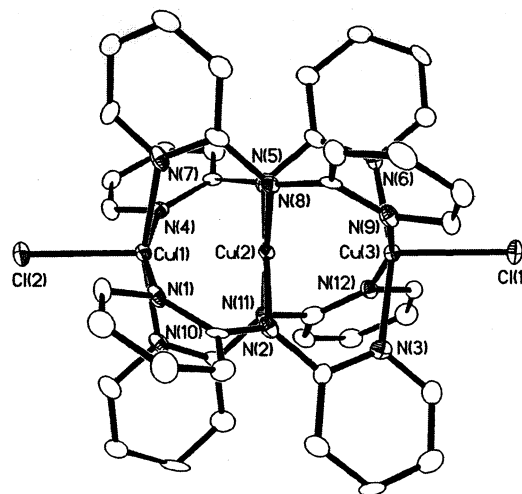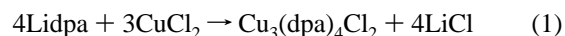

Figure 1. Thermal ellipsoid plot of **1** in $1 \cdot Et_2O$ with ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity.

reaction more straightforward, but the yield (typically at least 80%) is significantly better.

$$4\text{Lidpa} + 3\text{CuCl}_2 \rightarrow \text{Cu}_3(\text{dpa})_4\text{Cl}_2 + 4\text{LiCl} \quad (1)$$

Conversion to **2** proceeds by metathesis using silver tetrafluoroborate to precipitate silver chloride from the reaction solution, as shown in eq 2.
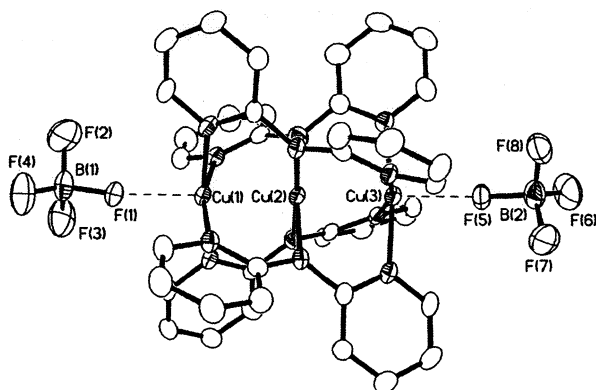
$$\text{Cu}_3(\text{dpa})_4\text{Cl}_2 + 2\text{AgBF}_4 \rightarrow \text{Cu}_3(\text{dpa})_4(\text{BF}_4)_2 + 2\text{AgCl} \quad (2)$$

Figure 2. Thermal ellipsoid plot of **2** with ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Figure 3. Electronic reflectance spectrum of **2**.

Crystallography. The orthorhombic *Pnn*2 form of **1** was reported in 1990 and 1991 as containing either an interstitial water molecule or no interstitial solvent.[1,2] All of the other trinuclear dipyridylamido complexes in the *Pnn*2 space group have an interstitial molecule of dichloromethane. We therefore felt this situation was unusual and decided to find out if any of the structural parameters of **1** are different in other solvates by crystallizing **1**·CH$_2$Cl$_2$, **1**·Et$_2$O, and **1**·toluene. For comparison, data from all structural determinations of **1** are given in Table 2. While all of the *Pnn*2 forms contain exactly equal Cu···Cu distances because the central Cu atom resides on a crystallographic 2-fold axis, in the other two forms the Cu$_3$ chains are not required to be precisely symmetrical but nevertheless the Cu···Cu separations are nearly the same. We collected data sets of **1**·CH$_2$Cl$_2$ at two different temperatures to see if any of the main features of the molecule are temperature dependent, since we found that many of the features of Co$_3$(dpa)$_4$Cl$_2$ depend quite a bit on temperature.[7] From Table 2, it is clear that temperature makes little or no difference to the main geometrical features of the structure. The Cu···Cu separations have been found to vary by only 0.03 Å, the Cu−N distances vary only within a range of 0.02 Å, and the Cu−Cl distances change by at most 0.05 Å.

Compound **1** has different crystal forms which are available via different methods of crystallization. When crystallized from dichloromethane and hexanes, **1**·CH$_2$Cl$_2$ (space group *Pnn*2) results. If ether is used instead of hexanes, **1**·Et$_2$O (space group *P*2$_1$/*c*, *Z* = 4) results, and from toluene and hexanes, **1**·toluene (space group *Pca*2$_1$) is obtained. This is consistent with our findings for the isomorphous trichromium,[15] tricobalt,[7] and trinickel[5] M$_3$(dpa)$_4$Cl$_2$ compounds. Trinuclear dipyridylamido complexes of Ru and Rh have been reported only in the orthorhombic *Pnn*2 form.[6] While we have found dramatic changes in the metal−metal distances for Co$_3$(dpa)$_4$Cl$_2$ upon changing temperature or crystal form, it can be seen from Table 2 that the interatomic distances of **1** vary only slightly with temperature, as well as from one crystal form to another.

Table 3 contains the metrical information for **2**. Here, we see that upon replacing the chloride ions by BF$_4$− ions (often
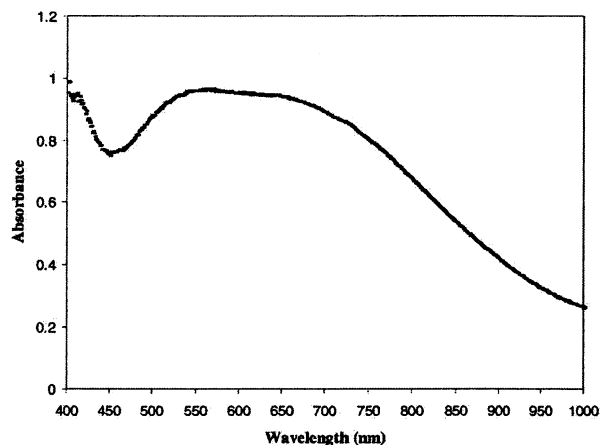
considered noncoordinating, but rather strongly coordinated here with Cu−F distances of 2.24 Å), the Cu···Cu distance decreases significantly (about 0.07 Å). Indeed, the Cu···Cu separation of 2.40 Å in **2** is even shorter than the shortest Cu···Cu distance for any dicopper(II) tetragonal paddle-wheel-type complex. For example, for Cu$_2$(amidinate)$_4$ these distances are typically ca. 2.46 Å.[16] Shorter Cu···Cu distances of 2.34 Å are found, however, in Cu(I) compounds or mixed-valent Cu(I)−Cu(II) complexes with only two[17] or three[18] "paddles" on the paddlewheel structural motif. Also, the BF$_4$− anions are distorted somewhat with the B−F distance to the fluorine atom bound to the Cu atom being 0.05 Å longer than the remaining B−F distances. Thus, there seems to be a relatively strong attraction between the fluorine atoms and the external copper atoms. The elongation of the B−F bond length appears to correspond to an intermediate state in the process of formation of a fluoride anion and a BF$_3$ molecule. Complete cleavage of the B−F bond was observed earlier in a similar compound, [Cr$_3$(dpa)$_4$(BF$_4$)F]BF$_4$.[19]

Spectroscopy. Hathaway et al. have already reported the electronic reflectance spectrum of **1**,[1] and the solution electronic spectrum we obtained is consistent with the earlier findings. The electronic spectra of compounds **1** and **2** are very similar, despite the difference in the Cu···Cu separations observed in the solid state. Both spectra feature a large broad peak in the visible region with a distinct shoulder. Compound **2** was found to decompose in solution when exposed to air, so only the reflectance spectrum of the solid was obtained. This is shown in Figure 3.

Hathaway et al. mention in their study of **1** that the compound is EPR silent.[1] We have found that for **1**·CH$_2$Cl$_2$ this is not the case: the X-band EPR spectrum at 8 K is

(15) Clérac, R.; Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Murillo, C. A.; Pascual, I. *Inorg. Chem.* **2000**, *39*, 748.

(16) See, for example: (a) Halfpenny, J. *Acta Crystallogr.* **1995**, *C51*, 2542. (b) Kilner, M.; Pietrzykowski, A. *Polyhedron* **1983**, *2*, 1379.

(17) Clérac, R.; Cotton, F. A.; Daniels, L. M.; Gu, J.; Murillo, C. A.; Zhou, H.-C. *Inorg. Chem.* **2000**, *39*, 4488.

(18) (a) Beck, J.; Strahle, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 409. (b) LeCloux, D. D.; Davydov, R.; Lippard, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 6810. (c) LeCloux, D. D.; Davydov, R.; Lippard, S. J. *Inorg. Chem.* **1998**, *37*, 6814. (d) Al-Obaidi, A.; Baranovic, G.; Coyle, J.; Coates, C. G.; McGarvey, J. J.; McKee, V.; Nelson, J. *Inorg. Chem.* **1998**, *37*, 3567. (e) Schmid, R.; Strahle, J. *Z. Naturforsch.* **1989**, *B44*, 105.

(19) Clérac, R.; Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Murillo, C. A.; Pascual, I. *Inorg. Chem.* **2000**, *39*, 752.
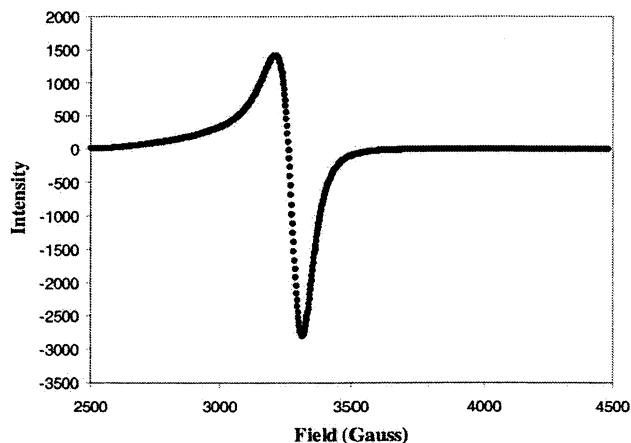
Figure 4. X-band EPR spectrum of **1** taken in dichloromethane glass at 8 K. The spectrum of **2** is very similar.

shown in Figure 4. The signal remains the same in the range from 5 to 180 K and is somewhat unsymmetrical but centered at $g = 2$. From the shape of the spectrum, we believe that the g value is slightly anisotropic, as one would expect for an axial Cu^{II} system. The EPR spectrum of **2** at 8 K is essentially the same as that for **1**.

Magnetism. Plots of χT vs T for compounds **1** and **2** are shown in Figures 5 and 6, respectively. It is readily apparent that the ground state which is populated at low temperatures in each case is a doublet, and that at higher temperatures a higher multiplicity state is partially populated. These data were modeled as three interacting $S = {}^1/_2$ magnetic centers,[20] with the following zero-field Hamiltonian:

$$H = -J(S_A \cdot S_B + S_{A'} \cdot S_B) - J'(S_A \cdot S_{A'})$$

in which J represents the exchange parameter between nearest neighbor Cu^{2+} ions, J' is the exchange parameter between terminal Cu^{2+} ions, and the copper atoms are labeled $A-B-A'$ along the linear chain. The eigenvalues of this Hamiltonian are two doublet states, and a quartet state, with the following relative energies:

$$E(S,S'): \quad S = S' + S_B; \quad S' = S_A + S_{A'}$$

$$E({}^1/_2, 1) = 0$$

$$E({}^1/_2, 0) = -J + J'$$

$$E({}^3/_2, 1) = -3J/2$$

Thus, the quartet excited state is separated in energy by $-3J/2$ above the doublet ground state. On this basis, we can derive the following expression for χ using the van Vleck equation:

$$\chi = \frac{N_A g^2 \beta^2}{4kT} \frac{(1 + e^{J/kT} + 10e^{3J/2kT})}{(1 + e^{J/kT} + 2e^{3J/2kT})}$$

where N_A is Avogadro's constant, g is the Landé factor, β is the Bohr magneton, k is the Boltzmann constant, and T is

(20) Kahn, O. *Molecular Magnetism*; Wiley-VCH: New York, 1993.

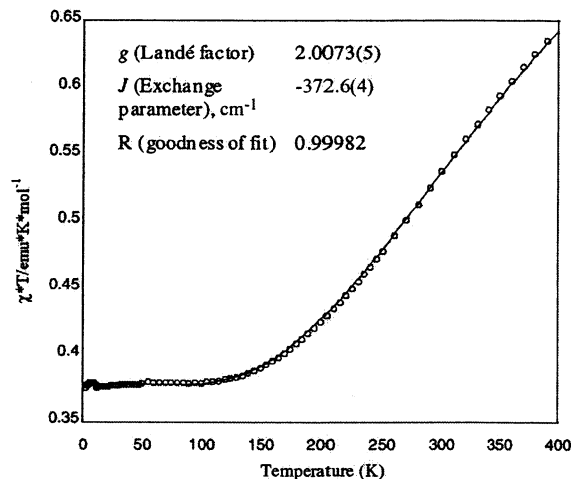| g (Landé factor) | 2.0073(5) |
| J (Exchange parameter), cm⁻¹ | -372.6(4) |
| R (goodness of fit) | 0.99982 |

Figure 5. Plot of $\chi_m T$ for **1** with data points taken from 2 to 400 K. The solid line corresponds to the least squares fit of the data.

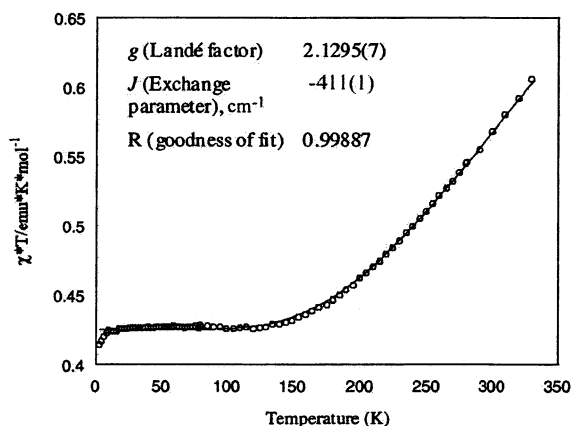| g (Landé factor) | 2.1295(7) |
| J (Exchange parameter), cm⁻¹ | -411(1) |
| R (goodness of fit) | 0.99887 |

Figure 6. Plot of $\chi_m T$ for **2** with data points taken from 2 to 350 K. The solid line is the least squares fit of the data.

temperature. Since J' has no net effect on the measured magnetic properties, it has been set equal to zero. Once both sides of this equation are multiplied by T, the resulting equation can be used to fit the magnetic data for each compound. The results are shown graphically in Figures 5 and 6, with the refined parameters shown as insets. The g values of 2.01 and 2.13 for **1** and **2**, respectively, agree with those obtained by EPR (2.10 for both **1** and **2**). The small differences between the refined g values from the SQUID data and those from the EPR spectrum can be attributed to the unresolved axial anisotropy of the EPR spectra and the fact that the g values obtained from the SQUID data are only refined isotropically. The exchange parameters for each compound are indicative of very strong antiferromagnetic coupling ($J = -373$ and -411 cm⁻¹ for **1** and **2**, respectively). This corresponds to an energy gap of 560 and 620 cm⁻¹ between the doublet ground states and quartet excited states of **1** and **2**, respectively.

The larger antiferromagnetic coupling in **2** compared to that in **1** has a bearing on the mechanism of the coupling. It is known for the classical case of dicopper(II) tetracarboxylates that the mechanism of antiferromagnetic coupling is via spin polarization through the bridging ligands.[21] In this work, we have the same bridging ligands in both **1** and **2**, and the difference in the path length from Cu1 to Cu2

through the ligand for **1** and **2** is less than 0.01 Å, a difference which would not lead to such a large variation in the exchange parameters through that pathway. It appears, therefore, that a direct exchange mechanism such as metal−metal interaction may contribute to the antiferromagnetic coupling. Since the metal−metal distances are extremely short for this type of compound, and those in **2** are ca. 0.07 Å shorter than those in **1**, this makes a change in the doublet−quartet energy gap of 60 cm^{-1} more reasonable. It is interesting to compare the present situation with one addressed many years ago by Goodgame et al.[22] They showed that while the Cu to Cu distance in $[Cu_2(O_2CH)_4(NCS)_2]^{2-}$ is appreciably longer (2.716(2) Å) than that in $[Cu_2(O_2CCH_3)_4(NCS)_2]^{2-}$ (2.643(3) Å), the values of the magnetic coupling constants are −485 and −305 cm^{-1}, respectively. This was taken as evidence that direct orbital overlap between the copper atoms is not responsible for the antiferromagnetic interaction. Since the Cu···Cu separations in **1** and **2** are more than 0.2 Å shorter than those in the dicopper carboxylates discussed above, the likelihood of a direct metal atom to metal atom interaction is much greater and, apparently, occurs.

Concluding Remarks

Here we present further studies of $Cu_3(dpa)_4Cl_2$, as well as a new derivative, $Cu_3(dpa)_4(BF_4)_2$. The compounds are very similar with respect to their spectroscopy and the overall geometry of the crystal structures. Compound **2**, however, has significantly shorter Cu···Cu distances than **1**, leading to an appreciable difference in the magnetic properties of the two compounds. Even though both are simple exchange-coupled trinuclear systems, the degree of antiferromagnetic coupling in **2** is much greater. We should note here also that the more labile BF_4^- ligands in **2** make this compound very suitable for axial ligand substitution reactions, so that it may be possible to make a series of related compounds with varying Cu···Cu separations by which we can test the possible antiferromagnetic exchange mechanisms.

(21) Rodríguez-Fortea, A.; Alemany, P.; Alvarez, S.; Ruiz, E. *Chem. Eur. J.* **2001**, *7*, 627.
(22) Goodgame, D. M. L.; Hill, N. J.; Marsham, D. F.; Skapski, A. C.; Smart, M. L.; Troughton, P. G. H. *J. Chem. Soc., Chem. Commun.* **1969**, 629.