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Different Oxidation States of Copper(I, I/II, II) Thiocyanate Complexes Containing 1,2,4-Triazole as a Bridging Ligand: Syntheses, Crystal Structures, and Magnetic Properties of 2-D Polymer $Cu^I(admtrz)SCN$, Linear Trinuclear $[Cu^I_2Cu^{II}(admtrz)_6(SCN)_2](ClO_4)_2$, and Triangular Trinuclear $[Cu^{II}_3(admtrz)_4(SCN)_3(\mu_3\text{-}OH)(H_2O)](ClO_4)_2\cdot H_2O$ (admtrz = 4-Amino-3,5-dimethyl-1,2,4-triazole)

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Copper thiocyanate compounds with three different oxidation states, $Cu^I(admtrz)SCN$ (**1**), $[Cu^I_2Cu^{II}(admtrz)_6(SCN)_2](ClO_4)_2$ (**2**), and $[Cu^{II}_3(admtrz)_4(SCN)_3(\mu_3\text{-}OH)(H_2O)](ClO_4)_2\cdot H_2O$ (**3**), have been synthesized and characterized (admtrz = 4-amino-3,5-dimethyl-1,2,4-triazole). Compounds **1** and **3** crystallize in the space group *Pbca* of the orthorhombic system with eight formula units in cells of dimensions $a = 8.0221(2)$ Å, $b = 32.3844(1)$ Å, $c = 13.5659(3)$ Å, R1/wR2 = 0.0595/0.1674 for compound **1** and $a = 21.501(3)$ Å, $b = 18.382(2)$ Å, $c = 21.526(2)$ Å, R1/wR2 = 0.0638/0.1519 for compound **3**. Compound **2** crystallizes in the space group *C*2/*c* of the monoclinic system with four formula units in cells of dimensions $a = 18.772(4)$ Å, $b = 11.739(2)$ Å, $c = 22.838(5)$ Å, $\beta = 91.11(3)°$, R1/wR2 = 0.0482/0.1265. The layered-type structure of **1** can be regarded as constructed from the tetranuclear copper units double bridged by one of the two unique thiocyanate and admtrz ligands, which are bridged by the other unique thiocyanate ligands to form a two-dimensional layered structure along the *a* and *b* directions. The linear trinuclear copper cation in mixed-valence compound **2** consists of one two-valence copper and two one-valence copper atoms which are bridged by admtrz ligands, and the external copper(I) atoms are coordinated by terminal thiocyanate. The EPR spectra of **2** show the existence of localized mixed-valence copper ions. The triangle trinuclear copper cation in compound **3** has its Cu_3 triangle capped by one apical μ_3-OH group, each edge bridged by a bridging admtrz ligand and each Cu atom coordinated by a N atom from the terminal thiocyanate, while one of the three edges is further bridged by another admtrz ligand and the opposite Cu1 atom is coordinated by a water molecule. The EPR and magnetic susceptibility of compound **3** were studied, showing antiferromagnetic behavior.

Introduction

The chemistry of polynuclear copper(II), copper(I), and mixed-valence copper(I/II) complexes has drawn great current interest following the discovery of multicopper active sites in several oxidases[1−4] and in the development of novel functional materials showing selective catalysts[5] and molecular ferromagnetism.[6] A trinuclear array of copper(II) centers may be essential functional units in a number of multicopper blue oxidases,[7] such as laccase and ascorbate

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oxidases, which catalyze the four-electron reduction of dioxygen to water with concomitant one-electron oxidation of a variety of substrates, such as ascorbate and polyphenols, and aromatic polyamines.[8] These multicopper blue oxidases, such as ascorbate oxidase and laccase, and nitrous oxide reductase,[9] can exist in fully reduced Cu(I) states. Oxidation of one of the copper(I) centers in a polynuclear species, or partial reduction of polynuclear copper(II) compound with halides or pseudo-halides, such as Cl^- and SCN^- anions, which served both as a reducing agent and as ligand, can afford mixed-valence copper(I/II) complexes.[10] Our attention focuses on the construction of various polynuclear copper complexes by employing one of such bridging ligands that are able to stabilize copper(II), copper(I), and mixed-valence derivatives.

1,2,4-Triazole and, in particular, its derivatives are very interesting bridging ligands. These ligands could provide a 1,2-bridging form; in addition, 4-unsubstituted 1,2,4-triazole also has a 2,4-bridging fashion, which is similar to the 1,3-imidazolate bridging found in an enzyme.[11] Using triazole, we and others have isolated polynuclear copper complexes (mainly trinuclear and more) in different valence states. A mixed-valence copper(I/II) compound, a tetranuclear $[Cu(maamt)(CuCl_3)]_2$ (maamt = 4-amino-3,5-bis[(*N*-methylamino)methyl]-1,2,4-triazole)[12] with single chloride ion as bridging ligand linking Cu(I) and Cu(II) atoms, and a series of one-valent copper(I) polymers[13] containing a tripodal moiety bridge μ_3-1,2,4-trz (trz =1,2,4-triazolate, $C_2N_3H_2^-$) from the copper−cyanide−triazolate−organoamine system have already been reported. Among the copper(II) systems, the linear trinuclear,[14−17] one-dimensional chain,[18,19] two-dimensional network,[20] and triangular trinuclear[21] and hexanuclear[22] complexes with triple triazole bridges or containing small anions (such as Cl^-, OH^-, N_3^-, SCN^-) and triazole as bridges have been structurally characterized. Until our research, no systematic investigation of one-valent copper(I), mixed-valent copper(I/II), and two-valent copper(II) complexes using the same bridging ligand had been reported. In the course of this study, the compounds $Cu^I(admtrz)SCN$ (**1**), $[Cu^I_2Cu^{II}(admtrz)_6(SCN)_2](ClO_4)_2$ (**2**), and $[Cu^{II}_3(admtrz)_4(SCN)_3(\mu_3\text{-}OH)(H_2O)](ClO_4)_2\cdot H_2O$ (**3**) (admtrz = 4-amino-3,5-dimethyl-1,2,4-triazole) were isolated and characterized. Here, we report the syntheses and structural characterizations of a layered structure of a one-valent copper(I) compound containing μ_2-N,S−SCN and triazile bridges (**1**), a linear trinuclear mixed-valence copper(I/II) complex with triple triazole bridges (**2**), and a triangular trinuclear copper(II) complex with μ_3-OH and triazole as co-bridge (**3**), and the EPR (**2** and **3**) and magnetic properties (**3**).

Experimental Section

Materials. All reagents and solvents were purchased from commercial sources and used without further purification. The ligand admtrz was prepared according to the literature.[23] **CAUTION**: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be handled and with great caution.

Synthesis of $Cu^I(admtrz)SCN$ (1). Method A. Solvothermal reactions of CuSCN (98 mg, 0.80 mmol), KSCN (200 mg, 2.0 mmol), admtrz (90 mg, 0.80 mmol) and a mixture of ethanol and water solvents (6.5 mL, volume ratio 1:1.5) in a 25 mL autoclave at 140 °C for 4 days yielded colorless crystals of compound **1**, which were washed with water and ethanol, dried in air, and then hand-picked. Yield: ca. 25%.

Method B. A solution of CuSCN (12.2 mg, 0.10 mmol) and NH_4SCN (22.8 mg, 0.30 mmol) in 25 mL of MeCN and a solution of admtrz (11.2 mg, 0.1 mmol) in 25 mL of ethanol were allowed to slowly diffuse in an H-shape tube at ambient temperature. Colorless crystals were obtained after several weeks. Yield: 35%. Anal. Calcd for $C_5H_8N_5SCu$: C, 25.69; H, 3.45; N, 29.96; Cu, 27.18. Found: C, 25.63, H, 3.66, N, 30.05; Cu, 27.10. IR (KBr pellet, cm^{-1}): 3300 (s), 3319 (s), 3199 (s), 2100 (vs), 1633 (m), 1539 (s), 1483 (w), 1419 (s), 1385 (m), 1360 (w), 1325 (w), 1263 (m), 1045 (w), 995 (w), 910 (w), 876 (s), 771 (s), 752 (m), 733 (m), 685 (w), 658 (m).

Synthesis of $[Cu^I_2Cu^{II}(admtrz)_6(SCN)_2](ClO_4)_2$ (2). A solution of $Cu(ClO_4)_2\cdot 6H_2O$ (220 mg, 0.6 mmol) in 2 mL of water was

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Table 1. Summary of X-ray Crystallographic Data for Compounds **1**, **2**, and **3**[a]

	1	**2**	**3**
empirical formula	$C_{10}H_{16}Cu_2N_{10}S_2$	$C_{26}H_{48}Cl_2Cu_3N_{26}O_8S_2$	$C_{19}H_{37}Cl_2Cu_3N_{19}O_{11}S_3$
fw	467.53	1178.54	1065.38
color, habit	colorless, block	brown, block	green, prism
crystal size (mm^3)	0.46 × 0.28 × 0.18	0.26 × 0.22 × 0.15	0.58 × 0.26 × 0.10
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	*Pbca*	*C*2/*c*	*Pbca*
a (Å)	8.0221(2)	18.772(4)	21.501(3)
b (Å)	32.3844(1)	11.739(2)	18.382(2)
c (Å)	13.5659(3)	22.838(5)	21.526(2)
β (deg)		91.11(3)	
V (Å^3)	3524.3(1)	5032(2)	8508(2)
Z, ρ_{calcd} (g cm^{-3})	8, 1.762	4, 1.556	8, 1.664
μ (Mo Kα, mm^{-1})	2.666	1.515	1.830
F(000)	1888	2412	4328
θ range (deg)	1.26−24.97	1.78−24.99	2.22−27.48
h,k,l ranges	−5 to 9, −38 to 30, −10 to 15	−22 to 11, −13 to 11, −27 to 27	0 to 27, 0 to 23, −27 to 0
reflns collected/unique	8836/3061	8488/4403	8882/8882
reflns obsd [$I > 2\sigma(I)$]	2352	3567	3304
params/restraints	217/0	298/0	500/1
GOF on F^2	1.044	1.007	1.004
a, b in weighting scheme	0.1051, 15.5083	0.0992, 0.8435	0.0619, 0
R1, wR2 (obsd)	0.0595, 0.1674	0.0482, 0.1265	0.0638, 0.1519
(Δ/σ) max, mean	0.001, 0.000	0.030, 0.003	0.002, 0.000
max, min peaks (e Å^{-3})	0.678, −0.636	0.834, −0.347	0.688, −0.592

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]^2]^{1/2}$, $GOF = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

added to admtrz (135 mg, 1.2 mmol) dissolved in ethanol (15 mL) with stirring at ambient temperature, followed by the addition of a solution of NH_4SCN (50 mg, 0.6 mmol) in water (1 mL). The resulting green solution was filtered. The deep brown crystals were isolated by slow evaporation of the filtrate at ca. 0−5 °C in a refrigerator for several weeks. Yield: 36%. Anal. Calcd for $C_{26}H_{48}N_{26}Cl_2O_8S_2Cu_3$: C, 26.50; H, 4.10; N, 30.90; Cu, 16.18. Found: C, 26.43; H, 4.31; N, 30.94; Cu, 16.22. IR (KBr pellet, cm^{-1}): 3448 (m), 3277 (s), 3169 (m), 3138 (m), 2964 (w), 2883 (w), 2102 (vs), 1618 (m), 1552 (m), 1529 (m), 1444(m), 1419 (s), 1392 (w), 1383 (w), 1340 (w), 1261 (w), 1146 (vs), 1119 (vs), 1086 (vs), 1049 (m), 995 (m), 941 (m), 779 (m), 768 (m), 741 (w), 663 (w), 636 (s), 627 (s).

Synthesis of [Cu$^{II}_3$(admtrz)$_4$(SCN)$_3$(μ_3-OH)(H$_2$O)](ClO$_4$)$_2$·H$_2$O (3). Compound **3** was prepared following the same procedure described for **2**. The resulting green solution was filtered, and after several days, many well-shaped deep green crystals and some brown small crystals were obtained by free evaporation of the filtrate at ca. 0−5 °C in a refrigerator for several days. The deep green crystals were selected manually. Yield: 48%. Anal. Calcd for $C_{19}H_{37}N_{19}Cl_2O_{11}S_3Cu_3$: C, 21.42; H, 3.50; N, 24.98; Cu, 17.87. Found: C, 21.47; H, 3.66; N, 24.85; Cu, 17.82. IR (KBr pellet, cm^{-1}): 3440 (s), 3319 (vs), 3206 (s), 2974 (m), 2937 (m), 2098 (vs), 1620 (s), 1552 (s), 1421 (s), 1390 (m), 1269 (m), 1144 (vs), 1119 (vs), 1088 (vs), 1043 (m), 1007 (m), 941 (m), 779 (m), 663 (w), 636 (s), 627 (s).

Physical Measurements. Elemental analyses were determined on Perkin-Elmer 240C elemental analyzer. Magnetic susceptibilities on powder samples were carried out with a Quantum Design MPMS SQUID magnetometer in the temperature range 5−300 K. The applied magnetic field was 10000 G, and the data were corrected for diamagnetism using Pascal's constant and the temperature independent paramagnetism estimated at 60 × 10^{-6} emu/mol per Cu(II) ion. The X-band EPR spectra were recorded on a Bruker 2000-D-SRC spectrometer on polycrystalline maeterial at 298 and 110 K, and in frozen DMF solution at 110 K.

X-ray Crystallographic Studies. Table 1 provides the summary of the crystal data, data collection, and refinement parameters for complexes **1**−**3**. Diffraction data were collected on a Siemens Smart CCD diffractometer for compound **1**, on an Enraf Nonius CAD-4 diffractometer for compound **2**, and on a Rigaku Weissenberg RAXISCS3 IP diffractometer for compound **3** with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) by the ω (**1**), $\omega-2\theta$ (**2**), and ω (**3**) scan modes, at 293 K. Empirical correction of absorption was applied for **1**−**3**. The three structures were solved by direct methods and refined anisotropically by full-matrix least squares based on F^2, for all the non-hydrogen atoms apart from the oxygen atoms of the perchlorate anions for **2** and **3**, and the packing water molecules for **3**. For all three compounds, the hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)[U(H) = 1.5U_{eq}(C-Me)]$, and allowed to ride on their parent atoms. Computations were carried out using the SHELXTL PC program system.[24]

Results and Discussion

Synthetic Considerations. Copper(I) thiocyanates are extreme insoluble in common solvents, but a minimum of it can be dissolved in warm saturated KSCN aqueous solution, and in concentrated NH_4SCN acetonitrile solution. Compound **1** was prepared in low yield by the described methods. Well-shaped crystals were obtained from the solvothermal reaction (A) with accompanying original powder CuSCN. Using method B, the small crystals of compound **1** were prepared. Synthesis of compound **2** was achieved by slow reduction of SCN$^-$ anions at low temperature; however, when this reaction system was carried out at room temperature, white powder was isolated. Compound **3** was synthesized

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(24) *SHELXTL Version 5.0*; Siemens Industrial Automation Inc., Analytical Instrumentation: Madison, WI, 1995.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **1**

Cu(1)−N(1A)[a]	1.992(6)	Cu(2)−S(2)	2.347(2)
Cu(1)−N(21)	2.043(6)	S(1)−C(1)	1.652(7)
Cu(1)−N(11)	2.050(6)	S(2)−C(2)	1.649(7)
Cu(1)−S(1)	2.438(2)	N(1)−C(1)	1.156(9)
Cu(2)−N(2B)	1.949(6)	N(2)−C(2)	1.146(9)
Cu(2)−N(12)	2.053(5)	N(11)−N(12)	1.390(7)
Cu(2)−N(22)	2.091(5)	N(21)−N(22)	1.382(7)

N(1A)−Cu(1)−N(21)	113.7(2)	N(12)−Cu(2)−N(22)	105.2(2)
N(1A)−Cu(1)−N(11)	113.1(3)	N(2B)−Cu(2)−S(2)	117.1(2)
N(21)−Cu(1)−N(11)	107.9(2)	N(12)−Cu(2)−S(2)	102.4(2)
N(1A)−Cu(1)−S(1)	103.2(2	N(22)−Cu(2)−S(2)	104.7(2)
N(21)−Cu(1)−S(1)	116.1(2	C(1)−S(1)−Cu(1)	96.0(3)
N(11)−Cu(1)−S(1)	102.5(2	C(2)−S(2)−Cu(2)	105.3(3)
N(2B)−Cu(2)−N(12)	114.5(3)	C(1)−N(1)−Cu(1A)	157.3(6)
N(2B)−Cu(2)−N(22)	111.6(2)	C(2)−N(2)−Cu(2C)	176.3(7)
N(12)−N(11)−Cu(1)	121.8(4)	N(1)−C(1)−S(1)	179.1(7)
N(11)−N(12)−Cu(2)	122.1(4)	N(2)−C(2)−S(2)	178.1(8)
N(22)−N(21)−Cu(1)	122.2(4)		

[a] Symmetry transformations used to generate equivalent atoms: A, $-x + 1, -y + 1, -z + 1$; B, $x + {}^1/_2, -y + {}^3/_2, -z + 1$; C, $x - {}^1/_2, -y + {}^3/_2, -z + 1$.

by crystallization of free evaporation of the solvents at low temperature with a few byproduct brown crystals which were confirmed to be the same as compound **2** by single crystal X-ray diffraction analysis; however, only compound **2** was obtained when the solvents were evaporated much more slowly.

$$3Cu(ClO_4)_2 + 6admtrz + 4NH_4SCN \rightarrow [Cu^I_2Cu^{II}(admtrz)_6(SCN)_2](ClO_4)_2\ (\mathbf{2}) + 4NH_4ClO_4 + (SCN)_2$$

$$3Cu(ClO_4)_2 + 4admtrz + 3NH_4SCN + 3H_2O \rightarrow [Cu^{II}_3(admtrz)_4(SCN)_3(\mu_3\text{-}OH)(H_2O)](ClO_4)_2\cdot H_2O\ (\mathbf{3}) + 3NH_4ClO_4 + HClO_4$$

IR Spectra. The IR spectra show the most intense absorption bands corresponding to thiocyanate anion at ν(CN) 2100 (vs), 2102 (vs), and 2098 (vs) cm^{-1} for **1**, **2**, and **3**, respectively. The perchlorate anion appears at normal frequencies about 1088(vs) and 627 (s) cm^{-1} for both compounds **2** and **3**.

Description of the Structures. Cu^I(admtrz)SCN (1). Compound **1** can be considered as constructed from the basic unit, which is composed of tetranuclear copper atoms double bridged by one of the two unique thiocyanate and triazole ligands, bridged by the other unique thiocyanate ligand to form a two-dimensional network along the *a* and *b* directions, as shown in Figure 1a. Figure 1b illustrates the essential structural features with the atom labeling scheme, and Table 2 gives the bond distances and angles relevant to the copper coordination spheres in **1**.

The Cu1 and Cu2 atoms are each located in a distorted tetrahedral environment, being coordinated by two N atoms from different admtrz ligands, one thiocyanato S atom, and one N atom of another thiocyanate ligand, with bond angles in the range 102.5(2)−116.1(2)° and 102.4(2)−117.1(2)° at Cu1 and Cu2, respectively. The distinct difference between both unique copper atoms is the connection of the μ-1,3-SCN bridges: two Cu1 atoms are bridged by double μ-1,3-SCN ligands to form a planar eight-member ring Cu(SCN)$_2$Cu with Cu···Cu separation of 5.217 Å, while two Cu2 atoms are bridged by only one μ-1,3-SCN ligand with Cu···Cu separation of 5.894 Å. It is notable that the Cu1···Cu2 separation of 3.564 Å double bridged by triazole ligands is much shorter than those by thiocyanate ligands in the present compound. There is a crystallographic inversion center located at the midpoint of the Cu1···Cu1(A) vector. The bond distances of thiocyanate ligand bound to Cu1 atoms in the eight-member ring (Cu1−N1 = 1.992(6) Å, Cu1−S1 = 2.438(2) Å) are longer than those bound to Cu2 atoms (Cu2−N2 = 1.949(6) Å, Cu2−S2 = 2.347(2) Å). The average Cu−N(admtrz) distance of 2.059(6) Å is similar to those (2.018(1)−2.071(8) Å) of usual four-coordinate copper(I) complexes[25] and is slightly longer than those observedin three-coordination copper(I) complexes $(Et_3NH)_2[Cu_4(dmnpz)_6]$, $[Cu(dmnpz)(RNC)]_2$, and $[Cu(dmnpz)(PPh_3)]_2$ (1.951(3)−2.020(2) Å)[26] (Hdmnpz = 3,5-dimethyl-4-nitropyrazole), $[Cu_4(atdz)_6](ClO_4)_4\cdot 2CH_3OH$ (av 1.983 Å)[27](atdz = 2-amino-1,3,4-thiadiazole), and $[Cu_5(CN)_3(trz)_2(bpy)]$, $[Cu_3(CN)_2(trz)(bpy)]$, $[Cu_3(CN)_2(trz)(phen)]$, and $[Cu_4(CN)_3(trz)(phen)]$ (1.936(2)−2.028(2) Å) (Htrz = 1,2,4-triazole),[13] but much longer than those found in the two-coordinate copper(I) complexes $[Cu(dmnpz)]_3$ (av 1.86 Å),[26] $[Cu_6(CN)_5(trz)]$ (1.891(2) Å).[13]

The Cu1···Cu2 separation of 3.564 Å is close to that of a four-coordination copper(I) complex $[Cu(dmnpz)(RNC)_2]$ (3.728(2) Å)[26] bridged by double pyrazolate and is rather longer than that of four-coordination copper(I) complexes[28] $[Cu_2(pydz)_3(MeCN)_2][PF_6]_2$ (3.065(2) Å) and $[Cu_2(pydz)_3(cnge)_2][BF_4]_2$ (3.098(3) Å) (cnge = 2-cyanoguanide) bridged by triple pyridazines, but slightly shorter than that of the four-coordination copper(I) complex[29] $[Cu(\mu\text{-}ppdBu)_2\{Cu(cnge)(MeCN)\}_2](BF_4)_3\cdot MeCN$ (3.624(2)−3.634(2) Å) (ppdBu = 3,6-bis[*N*-{3-(*tert*-butyl)pyrazolyl}]) bridged by a pyridazine group. Clearly, when the number of the N^1,N^2-linkage bridges is increased, the Cu−Cu distance tends to shorten.

As shown in Figure 1a, the Cu2 atoms are bridged by SCN$^-$ ligands to form a zigzag (CuSCN)$_\infty$ chain along the *a* direction; such chains are interconnected through the double bridging units −(μ-1,2-admtrz)$_2$−Cu−(μ-1,3-SCN)$_2$−Cu−(μ-1,2-admtrz)$_2$− to lead to a two-dimensional network. This double bridging unit is different from the single bridging organic ligand by varying the length found in the copper(I)

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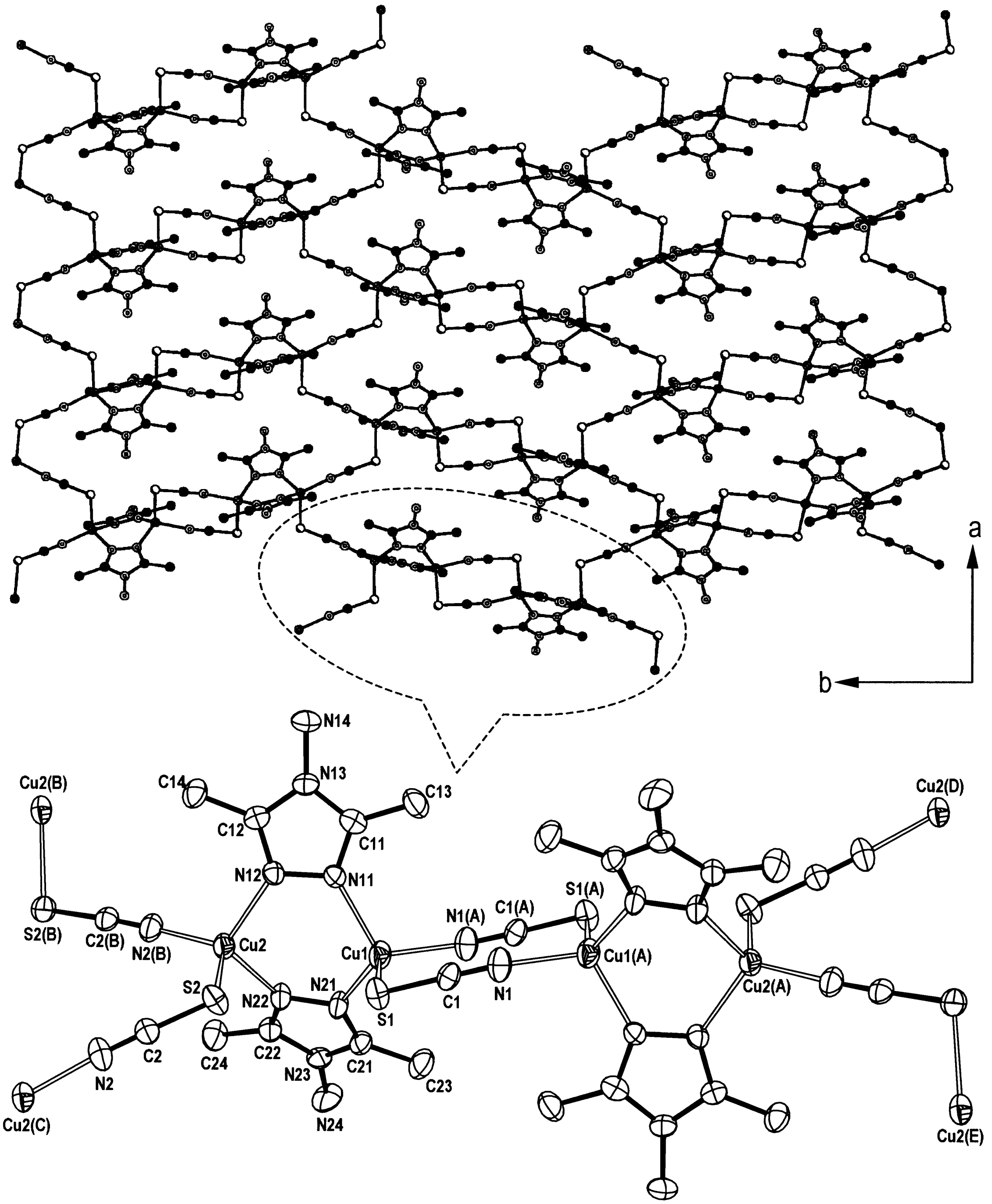

Figure 1. (a) Layered structure of **1** viewed along *c* direction (top). (b) Molecular structure of **1** with atom labeling scheme, symmetry codes are A ($1 - x$, $1 - y$, $1 - z$), B ($\frac{1}{2} + x$, $\frac{3}{2}$ - y, $1 - z$), C ($-\frac{1}{2} + x$, $\frac{3}{2} - y$, $1 - z$), D ($\frac{3}{2} - x$, $-\frac{1}{2} + y$, z), E ($\frac{1}{2} - x$, $-\frac{1}{2} + y$, z) (bottom).

thiocyanate complexes,[30] such as the 2-D sheets CuSCN(pyz) (pyz = pyrazine) and $Cu_2(SCN)_2(bpe)$ (bpe = 1,2-*trans*-(4-pyridyl)ethene), and 3-D networks $Cu_2(SCN)_2(pyz)$, $Cu_2(SCN)_2(4,4'\text{-bipy})$, and CuSCN(bpa) (bpa = 1,2-bis(4-pyridyl)ethane).

$[Cu^I_2Cu^{II}(admtrz)_6(SCN)_2](ClO_4)_2$ (2). The crystal structure of **2** consists of linear trinuclear copper cations shown in Figure 2 and noncoordinated perchlorate anions. Selected bond distances and angles are given in Table 3. In the cation, the central copper(II) ion lies on the crystallographic inversion center and shows distorted (4 + 2) octahedral coordination with six N-donating admtrz ligands. The equatorial plane is a perfect plane, formed by four nitrogen atoms with Cu−N distances in the range 2.053(2)−2.130(2) Å. The average Cu−N bond length of 2.092 Å is an intermediate value between those found in $[Cu_3(metz)_6(H_2O)_4](CF_3SO_3)_6(H_2O)_4$ (2.14(5) Å)[14] (where metrz = 3-merhyl-4-ethyl-1,2,4-triazole) and in the related triazole complex $[Cu(hyetrz)_3](ClO_4)_2\cdot 3H_2O$ (2.038 Å on average in equatorial plane)[18] (where hyetrz = 4-(2-hydroxyethyl)-1,2,4-triazole). Two admtrz

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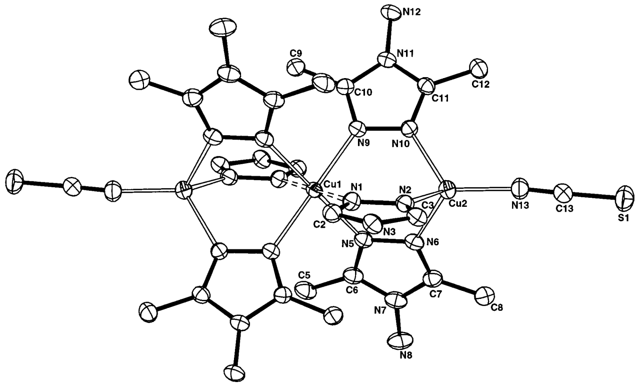

Figure 2. Molecular structure of $[Cu^{I}_2Cu^{II}(admtrz)_6(SCN)_2]^{2+}$ cation in **2**. C1, C4, and N4 atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex **2**

Cu(1)−N(9)	2.053(2)	Cu(2)−N(10)	2.083(2)
Cu(1)−N(5)	2.130(2)	N(1)−N(2)	1.379(3)
Cu(1)−N(1)	2.380(2)	N(5)−N(6)	1.392(3)
Cu(2)−N(13)	1.917(2)	N(9)−N(10)	1.390(2)
Cu(2)−N(2)	2.069(2)	S(1)−C(13)	1.627(3)
Cu(2)−N(6)	2.079(2)	N(13)−C(13)	1.150(3)

N(9)−Cu(1)−N(5A)[a]	87.15(7)	N(13)−Cu(2)−N(10)	120.06(9)
N(9)−Cu(1)−N(5)	92.85(7)	N(2)−Cu(2)−N(10)	101.77(7)
N(9)−Cu(1)−N(1)	94.06(6)	N(6)−Cu(2)−N(10)	95.29(7)
N(9)−Cu(1)−N(1A)	85.94(6)	C(13)−N(13)−Cu(2)	170.8(2)
N(5)−Cu(1)−N(1A)	85.03(7)	N(13)−C(13)−S(1)	178.5(3)
N(5)−Cu(1)−N(1)	94.97(7)	N(2)−N(1)−Cu(1)	119.5(1)
N(1)−Cu(1)−N(1A)	180.00(9)	N(1)−N(2)−Cu(2)	118.7(1)
N(9A)−Cu(1)−N(9)	180.0(1)	N(6)−N(5)−Cu(1)	122.1(1)
N(5A)−Cu(1)−N(5)	180.0(1)	N(5)−N(6)−Cu(2)	119.5(1)
N(13)−Cu(2)−N(2)	118.21(9)	N(10)−N(9)−Cu(1)	121.5(1)
N(13)−Cu(2)−N(6)	118.09(8)	N(9)−N(10)−Cu(2)	121.7(1)
N(2)−Cu(2)−N(6)	99.05(7)		

[a] Symmetry transformations used to generate equivalent atoms: A, $-x + {}^1/_2, -y + {}^1/_2, -z$.

ligands coordinate axially to the copper(II) at the significantly longer distance of 2.380(2) Å, which falls in the range 2.369(6)−2.404(6) Å observed in the related complex.[18] This central atom is bridged to each of the two external copper(I) atoms through triple triazole ligands. Cu(I) presents a distorted tetrahedral coordination involving three bridging admtrz ligands and one terminal SCN^- anion. The Cu(I)−N(admtrz) bond distances around the Cu2 atom are 2.069(2), 2.079(2), and 2.083(2) Å, respectively. These bond distances lie within the range found in complex **1** (2.043(6)−2.091(5) Å). The Cu(I)−N(SCN) bond distance is 1.917(2) Å, slightly shorter than 1.927(6) Å found in the μ_4-N,S,S,S−SCN bridging compound CuSCN,[31] in which each sulfur atom is shared by three Cu(I) tetrahedrons and the nitrogen coordinating to the other Cu(I). It is also clearly shorter than that observed in the μ_3-N,S,S−SCN bridging copper(I) complexes $[Cu_2(SCN)_2(L)]_\infty$ (1.936(1)−2.047(4) Å) (L = pyrazone, 4,4′-bipy, or *trans*-1,2-bis(4-pyridyl)ethene),[30a,32] in the single μ_2-N,S−SCN bridging copper(I) complexes $[CuSCN(bpa)]_\infty$, $[CuSCN(pyrazine)]_\infty$, and $[CuSCN(L)_2]_\infty$ (L = 2-, 3-, 4-methylpyridine, respectively, 2,4-dimthylpyridine, or quinoline) (1.94(1)−2.00(1) Å),[30b,30c,33] and in the double μ_2-N,S−SCN bridging copper(I) complex **1** (1.992(6) Å). The thiocyanate anion can coordinate to metal ions through either S or N atoms. In general, Cu(I) shows a preference for the softer S donor over the less polarizable nitrogen donor atom, which is in accordance with the HSAB principle,[34] but in the present complex, the thiocyanate ion coordinates to Cu(I) only through N atoms. To our knowledge, this coordination mode of Cu(I)−N(SCN) is very rare, with only a few known examples being found.[35] This distortion of the CuN_4 core from T_d symmetry is also seen in some important angles associated with Cu(I) coordination environment (85.94(6)−94.97(7)°). The bond angles around the Cu(2) atom are in the range 95.29(7)−120.06(9)°. The SCN groups are almost linear (N(13)−C(13)−S(1) = 178.5(3)°), whereas the Cu−NC(S) linkages are bent (Cu(2)−N(13)−C(13) = 170.8(2)°).

The Cu1···Cu2 separation of 3.558 Å is much longer than that of four-coordination copper(I) complexes[28] $[Cu_2(pydz)_3(MeCN)_2](PF_6)_2$ (3.065(2) Å) and $[Cu_2(pydz)_3(cnge)_2](BF_4)_2$ (3.098(3) Å) (cnge = 2-cyanoguanide) bridged by triple pyridazine, but clearly shorter than that of six-coordination copper(II) complexes $[Cu_3(pytrz)_{10}(H_2O)_2](ClO_4)_6{\cdot}7H_2O$ (3.8540(7) Å) (pytrz = 4-(2-pyridyl)-1,2,4-triazole)[15] and $[Cu(hyetrz)_3](ClO_4)_2{\cdot}3H_2O$ (3.853(2) Å) (hyetrz = 4-(2-hydroxyethyl)-1,2,4-triazole)[18] with triple triazole bridge, indicating that when one or both monovalent copper(I) atoms linked by triple N^1,N^2-linkage bridges are replaced by divalent copper(II) ions, the Cu−Cu distance tends to lengthen even more. The dihedral angles between three bridging triazoles are 111.29°, 121.08°, and 127.60°: three planes are intersected in the central line through the three Cu atoms.

$[Cu^{II}_3(admtrz)_4(SCN)_3(\mu_3\text{-}OH)(H_2O)](ClO_4)_2{\cdot}H_2O$ (3). The structure of **3** consists of trinuclear complex cation $[Cu_3(admtrz)_4(\mu_3\text{-}OH)(SCN)_3(H_2O)]^{2+}$, two noncoordinated perchlorate anions, and one lattice water molecule. The selected bond distances and angles are listed in Table 4. The $[Cu_3(admtrz)_4(\mu_3\text{-}OH)(SCN)_3(H_2O)]^{2+}$ has its Cu_3 triangle capped by one apical μ_3-OH group, with each edge bridged by a bridging admtrz ligand and each Cu atom coordinated by a N atom from the terminal thiocyanate, while one of the three edges is further bridged by another admtrz ligand and the opposite Cu1 atom is coordinated by a water molecule, as shown in Figure 3. The coordination geometry around each of the Cu(II) ions is best described as a distorted square pyramid with Cu−N and Cu−O (equatorial) bond lengths being normal for Cu(II) in this geometry. The Cu−O (axial) bond length is 2.292(2) Å for Cu1−O1W, and Cu−N (axial) bond lengths vary from 2.249 (2) Å for Cu2−N31 to 2.195-

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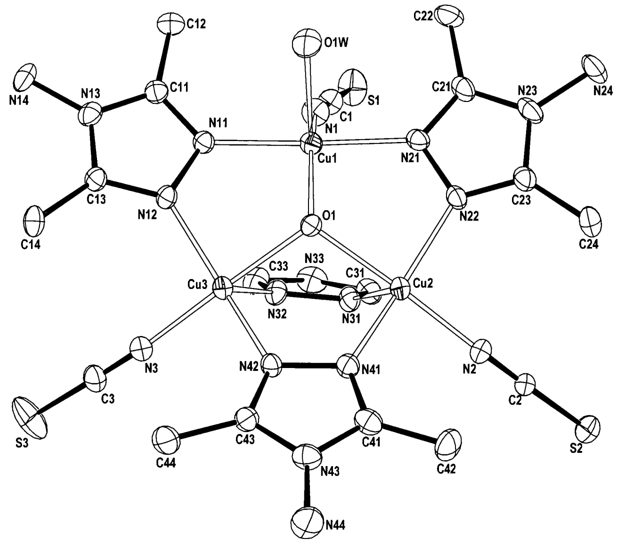

Figure 3. Molecular structure of $[Cu^{II}_3(admtrz)_4(SCN)_3(\mu_3\text{-}OH)(H_2O)]^{2+}$ cation in **3**. C32, C34, and N34 are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex **3**

Cu(1)−N(1)	1.937(2)	Cu(3)−O(1)	2.022(2)
Cu(1)−N(21)	1.979(2)	Cu(3)−N(32)	2.195(2)
Cu(1)−N(11)	1.995(2)	S(1)−C(1)	1.607(3)
Cu(1)−O(1)	2.021(2)	N(1)−C(1)	1.142(3)
Cu(1)−O(1W)	2.292(2)	S(2)−C(2)	1.630(3)
Cu(2)−N(2)	1.929(2)	N(2)−C(2)	1.153(4)
Cu(2)−N(41)	1.998(2)	S(3)−C(3)	1.604(3)
Cu(2)−N(22)	2.012(2)	N(3)−C(3)	1.126(4)
Cu(2)−O(1)	2.015(2)	N(11)−N(12)	1.376(3)
Cu(2)−N(31)	2.249(2)	N(21)−N(22)	1.375(3)
Cu(3)−N(3)	1.937(2)	N(31)−N(32)	1.382(3)
Cu(3)−N(42)	1.989(2)	N(41)−N(42)	1.390(3)
Cu(3)−N(12)	1.996(2)		
N(1)−Cu(1)−N(21)	91.54(9)	N(2)−Cu(2)−N(22)	93.75(9)
N(1)−Cu(1)−N(11)	93.24(8)	N(41)−Cu(2)−N(22)	159.14(8)
N(21)−Cu(1)−N(11)	173.68(8)	N(2)−Cu(2)−O(1)	175.08(8)
N(1)−Cu(1)−O(1)	149.85(9)	N(41)−Cu(2)−O(1)	87.05(7)
N(21)−Cu(1)−O(1)	88.14(7)	N(22)−Cu(2)−O(1)	87.78(7)
N(11)−Cu(1)−O(1)	89.79(7)	N(2)−Cu(2)−N(31)	93.93(9)
N(1)−Cu(1)−O(1W)	109.76(9)	N(41)−Cu(2)−N(31)	102.59(8)
N(21)−Cu(1)−O(1W)	87.51(8)	N(22)−Cu(2)−N(31)	96.56(8)
N(11)−Cu(1)−O(1W)	86.99(8)	O(1)−Cu(2)−N(31)	81.24(7)
O(1)−Cu(1)−O(1W)	100.35(7)	N(3)−Cu(3)−N(42)	94.34(9)
N(2)−Cu(2)−N(41)	93.11(9)	N(3)−Cu(3)−N(12)	92.83(9)
N(42)−Cu(3)−N(12)	155.93(8)	N(3)−C(3)−S(3)	177.8(3)
N(3)−Cu(3)−O(1)	175.35(9)	Cu(2)−O(1)−Cu(1)	110.61(7)
N(42)−Cu(3)−O(1)	86.71(7)	Cu(2)−O(1)−Cu(3)	107.44(7)
N(12)−Cu(3)−O(1)	87.99(7)	Cu(1)−O(1)−Cu(3)	108.83(7)
N(3)−Cu(3)−N(32)	95.74(9)	N(12)−N(11)−Cu(1)	119.0(1)
N(42)−Cu(3)−N(32)	104.94(8)	N(11)−N(12)−Cu(3)	116.7(1)
N(12)−Cu(3)−N(32)	97.15(8)	N(22)−N(21)−Cu(1)	120.7(1)
O(1)−Cu(3)−N(32)	79.62(7)	N(21)−N(22)−Cu(2)	117.4(1)
C(1)−N(1)-Cu(1)	166.2(2)	N(32)−N(31)−Cu(2)	112.9(1)
N(1)−C(1)−S(1)	178.4(3)	N(31)−N(32)−Cu(3)	116.6(1)
C(2)−N(2)−Cu(2)	166.5(2)	N(42)−N(41)−Cu(2)	117.3(1)
N(2)−C(2)−S(2)	178.5(3)	N(41)−N(42)−Cu(3)	118.5(1)
C(3)−N(3)−Cu(3)	169.9(3)		

(2) Å for Cu3−N32. In compound **3**, there is a pair of similar coordination environments for Cu2 and Cu3 atoms which is different from that for the Cu1 atom.

The capping oxygen atom O(H) is located 0.690 Å above the Cu_3 plane. The oxygen atom of the central hydroxyl OH^- is in a roughly tetrahedral coordination sphere with the Cu−O(H)−Cu angles in the range 107.44(7)−110.61(7)°, indicative of sp^3 configuration for the hydroxy oxygen atom. The Cu···Cu distances, Cu−O(H)−Cu angles, and O(H)···Cu_3 plane distance in **3** are comparable with those found in complexes $Cu_3(OH)(pao)_3(SO_4)$ (3.22 Å, 108.2°, 0.697 Å)[36] (pao = pyridino-2-carbaldehyde oximate), $[Cu_3(\mu_3\text{-}OH)(pz)_3(\mu_4\text{-}NO_3)(Hpz)_3]_2(\mu\text{-}NO_3)_2$ (3.303(4) Å, 111.2(9)°, 0.605 Å),[37] $[Cu_3(OH)(aat)_3(NO_3)(H_2O)_2](NO_3)\cdot 2H_2O$ (3.341(1) Å, 112.4(2)°, 0.564(3) Å), $[Cu_3(OH)(aat)_3(CF_3SO_3)(H_2O)_2](CF_3SO_3)$ (3.355(2) Å, 114.6(3)°, 0.473(6) Å), and $[Cu_3(OH)(aat)_3(ClO_4)(H_2O)_2](ClO_4)$ (3.371(3) Å, 115.4(3)°, 0.433(6) Å)[38] (Haat = (3-acetylamino-1,2,4-triazole), but in the μ_3-O complex $Cu_3O(dpeo)_3$ the values are 3.177 Å, 116.5°, and 0.352 Å[39] (depo = 2-methylimino-1,2-diphonylthanone oximate). It is worthy to note that the Cu···Cu distances increase with the increase of Cu−O(H)−Cu angles and the decrease of the distance of the hydroxyl oxygen atom to Cu_3 plane, suggestive of more sp^2 character for the central hydroxyl oxygen atom.

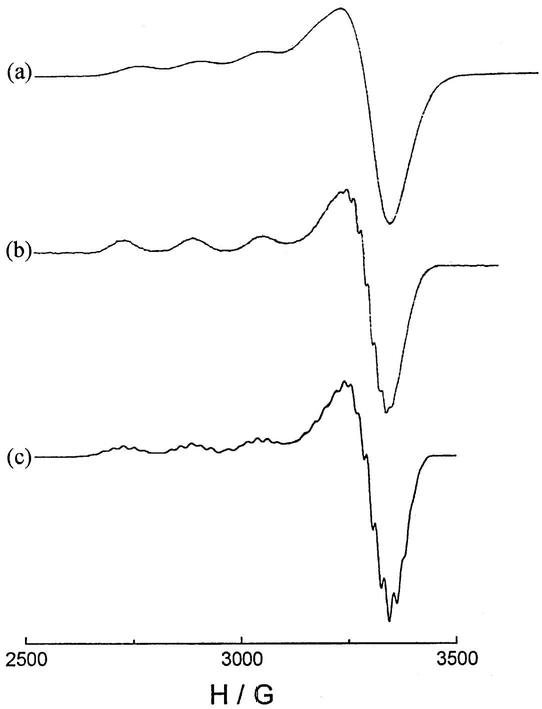

Figure 4. X-band EPR spectra of complex **2**: (a) powder at 110 K; (b) in DMF at 110 K; (c) simulation of (b).

EPR Studies. The X-band EPR spectra of **2** were recorded on a crystalline solid (110 and 298 K) and on a frozen DMF solution (110 K). The spectra measured at 110 K were shown in Figure 4, together with a simulation for the DMF solution. The simulations were based on the spin Hamiltonian

$$\mathbf{H} = g_z\beta H_z\cdot S_z + g_y\beta H_y\cdot S_y + g_x\beta H_x\cdot S_x + A_z(S_z\cdot I_z) + A_y(S_y\cdot I_y) + A_x(S_x\cdot I_x) + A_{Nz}(S_z\cdot I_{Nz}) + A_{Ny}(S_y\cdot I_{Ny}) + A_{Nx}(S_x\cdot I_{Nx})$$

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The following EPR parameters were obtained: $g_\perp = g_{x,y} = 2.0550$, $g_\parallel = g_z = 2.2850$, $A_\perp = A_{x,y} = 14.0$ G, $A_\parallel = A_z = 166.0$ G, $A_{Nx} = 16.0$ G, and $A_{Ny} = 25.0$ G. In a $d_{x^2-y^2}$ ground-state Cu(II) in complex **2**, when ^{14}N on an equatorial metal ligand is directly coordinated to the metal ion, the electronuclear interaction is large and dominates the electromagnetic coupling, and the ^{14}N on metal axial position is weakly coordinated to the center copper(II), this electronuclear interaction can been taken as zero.

The spectra on a polycrystalline at 110 and 298 K are quite similar. The hyperfine splittings are observed on room temperature and below. An additional feature of the frozen DMF solution EPR spectrum is the observation of superhyperfine (SHF) splitting of the g component, which is due to electronuclear interaction from four donor N atoms of admtrz ligands lying approximately in an equatorial plane of the Cu(II) ion.

The metal hyperfine coupling constant, A_z, increases in DMF (recorded at 110 K), indicating that in solution the geometry at the copper(II) center becomes less of a tetrahedral distortion of the CuN_4 core within the equatorial coordinating plane. However, this difference is small, suggesting that the solid state structure is essentially retained in solution. The EPR spectra are typical of a Cu(II) ion coordinated in a distorted octahedron[40] with the $d_{x^2-y^2}$ ground state, in agreement with its crystal structure, suggesting that the valences of mixed-valence Cu(I,II,I) complex **2** are localized.

The X-band EPR spectra of complex **3** were recorded on powder samples at 100 K. This compound displays an axial spectrum giving $g_\perp = 2.0898$, $g_\parallel = 2.2549$, and $A_\parallel = 116.67$ G, which are in agreement with the square-pyramidal (C_4v) geometry around each copper.[41] The average g value ($g_{av} = (g_\parallel + 2g_\perp)/3$) of 2.1448 is very close to that ($g = 2.15(1)$) obtained by fitting the variable temperature magnetic susceptibility data according to a Heisenberg model (discussed in the following section).

Magnetic Properties. The temperature dependence of $\chi_M T$ for compound **3** is shown in Figure 5. The $\chi_M T$ value is 0.86 cm^3 K mol^{-1} at 300 K, which is much lower than the value expected for three uncoupled copper(II) ions. The value of $\chi_M T$ decreases upon cooling, reaching a value of 0.44 cm^3 K mol^{-1} at ca. 75 K, which corresponds to the spin-only value of 0.437 cm^3 K mol^{-1} ($g = 2.17$) for one unpaired electron. This behavior indicates a strong antiferromagnetic interaction between the Cu(II) ions, with $S = {}^1/_2$ ground state per Cu_3 unit. The value of $\chi_M T$ keeps on decreasing as the temperature lowers, reaching the value of 0.26 cm^3 K mol^{-1} at 5 K.

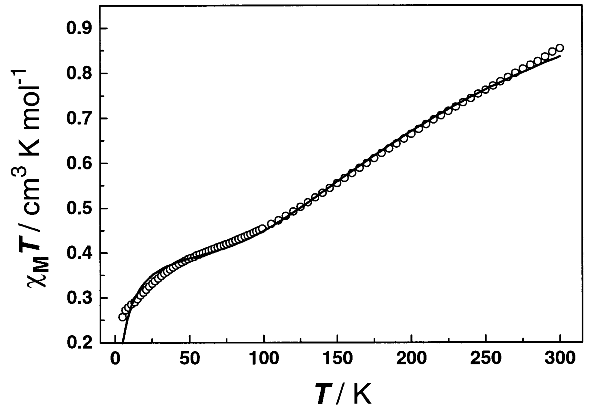

Figure 5. Experimental (○) and calculated (−) temperature dependence of $\chi_M T$ for **3**.

As seen from the known structure of **3**, all atoms in the present trimer are crystallographically independent. However, the linkage between Cu1 and Cu2 ions through μ_2-N1,N2-triazole and μ_3-OH bridges on metal equatorial positions is similar to the linkage between Cu1 and Cu3 ions. The Cu_3 cluster can be taken as an isosceles triangle array. An equation which uses two different J values ($J = J_{12} = J_{13}$, $J' = J_{23}$) was tried. For this case, the exchange Hamiltonian takes on the form $\mathbf{H} = -2J(S_1 \cdot S_2 + S_1 \cdot S_3) - 2J'(S_1 \cdot S_2)$. The corresponding molar magnetic susceptibility is expressed by eq 1, in which Weiss-like parameter Θ was considered to analyze the experimental variation of $\chi_M T$ at low temperature. The symbols in the following equation have their usual meaning. Assuming that the g values for all three copper atoms are equal, the following equation applies:

$$\chi_M = \frac{Ng^2\beta^2}{4K(T-\Theta)} \times \frac{\exp(-2J/KT) + \exp(-2J'/KT) + 10\exp(J/KT)}{\exp(-2J/KT) + \exp(-2J'/KT) + 2\exp(J/KT)}$$

The least-squares fitting of the experimental $\chi_M T$ (χ_M is magnetic susceptibility per trinuclear copper(II) unit) gives $g = 2.15(1)$, $J = -53.2(5)$ cm^{-1}, $J' = -120.1(6)$ cm^{-1}, $\Theta = -5.93(3)$ K, and $R = 1.31 \times 10^{-4}$ ($R = \sum|(\chi_M T)_{exp} - (\chi_M T)_{calcd}|^2/\sum(\chi_M T)_{exp}{}^2$).

The copper centers would be defined by a ground state [$d_{x^2-y^2}$] that is based on the equatorial plane that includes just the μ_3-OH and admtrz bridges, and exchange interaction in the Cu_3 cluster would be expected to depend predominantly on these bridges. The apical admtrz (μ-N31−N32), bridging the Cu2 and Cu3 atoms, is considered orthogonal in a magnetic sense and so would be considered to contribute little to the overall exchange process. As a result, the J' value of $-120.1(6)$ cm^{-1} is much higher than the J value of -53.2 (5) cm^{-1}; the dihedral angle of 137.89° between the equatorial planes of Cu(2) and Cu(3) atoms is larger than the dihedral angles of 132.48° and 132.37° between the equatorial planes of Cu(1) and Cu(2), and Cu(1) and Cu(3), respectively. The closer this kind of dihedral angle is to 180°, the larger the magnetic orbital $d_{x^2-y^2}$ overlap, and the stronger the magnetic exchange interaction. The similar dihedral angles give the similar value of J. In addition, the value of $-120.1(6)$ cm^{-1} in this complex is considerably lower than the values reported for trinuclear hydroxo-bridged complexes

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with pyrrazolatoin complex $Cu_3(OH)(pz)_3$ (-200 cm^{-1})[42] and 3-acetylamino-1,2,4-triazolate ligands in $[Cu_3(OH)(aat)_3A(H_2O)_2]A\cdot xH_2O$ ($A = CF_3SO_3$, NO_3, ClO_4; $x = 0, 2$) (-190.9 to -198.2 cm^{-1})[38] wherein the coordination planes are much more coplanar. But the value of $-53.2(5)$ cm^{-1} in the present complex is far higher than the value of -12 cm^{-1} found in $[(CuL^0)_3(OH)](ClO_4)_2$ (L^0 = 7-amino-5-aza-4-methyl-3-octene-2-one)[43] and -15 cm^{-1} in $[(CuL^1)_3(OH)](ClO_4)_2$ (L^1 = 8-amino-5-aza-4-methyl-3-octene-2-one)[44] wherein the coordination planes are roughly orthogonal. These observations imply that the degree of coplanarity of the coordination equatorial planes influences the magnetic coupling between the paramagnetic ions.

The Θ value of $-5.93(4)$ K that resulted from the fitting is significantly large, similar to that reported for the complex $[Cu_3(OH)(aat)_3(CF_3SO_3)(H_2O)_2](CF_3SO_3)\cdot xH_2O$ ($-5.1(1)$ K),[38] indicating that it is possible for an antisymmetric exchange phenomenon to exist.[45]

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Supporting Information Available: X-ray crystallographic files, in CIF format, for $Cu^I(admtrz)SCN$, $[Cu^I_2Cu^{II}(admtrz)_6(SCN)_2](ClO_4)_2$, and $[Cu^{II}_3(admtrz)_4(SCN)_3(\mu_3\text{-}OH)(H_2O)](ClO_4)_2\cdot H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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