Preparation and Magnetic Properties of Dicopper(II) Hydroxide Tris(pyrazolide)s

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(Received December 10, 1993)

Synopsis. Dicopper(II) hydroxide tris(pyrazolide)s $Cu_2(OH)(4\text{-}Xpz)_3$ (pz=pyrazolide ion; X=H, CH_3, Cl, Br) and $Cu_2(OH)(4\text{-}Xpz)_3(4\text{-}XpzH)_2$ (X=Cl, Br) were prepared and characterized by means of magnetic susceptibility and IR spectroscopy. Their magnetic-moment values increased in the substituent sequence $X=CH_3<H<Br\approx Cl$, and were correlated with the basicities and coordinating angles of the pyrazolido ligands.

Pyrazolide anions may coordinate to metal ions through both nitrogen atoms, forming pyrazolido-bridged polynuclear compounds.[1—8] Ehlert et al. prepared two series of linear-chain polymers, $Cu(4\text{-}Xpz)_2$ and $Cu(4\text{-}Xdmpz)_2$ (pz=pyrazolide ion, dmpz=3,5-dimethylpyrazolide ion; X=H, CH_3, Cl, Br), and attempted to examine whether the strength of their exchange couplings was correlatable with the bridging geometries and/or with the electronic nature of the bridging ligands.[5,7,8] Unfortunately, some of their magnetic data could not be fit to a theoretical expression derived using the Heisenberg linear-chain model. Such unusual behaviors might be attributable to contamination with some basic salts, since pyrazolide ion tends to serve as a bridge in combination with another bridging group, such as a hydroxide ion.[9—12] We thus tried to characterize basic copper(II) pyrazolides in order to elucidate the magnetic properties of pyrazolido-bridged compounds in terms of the ligand basicities and bridging geometries.

The reaction of copper(II) hydroxide with a stoichiometric amount of molten pyrazole (mp 70, 23, 75, and 92 °C for pyrazole and 4-methyl-, 4-chloro-, and 4-bromopyrazoles, respectively) gave a brown powder having an empirical formula $Cu_2(OH)(4\text{-}Xpz)_3$ (X=H, CH_3, Cl, Br).[4] Besides, a reaction with excess pyrazole (6 times) gave a brown powder having an empirical formula $Cu_2(OH)(4\text{-}Xpz)_3(4\text{-}XpzH)_2$ (X=Cl, Br). Their effective magnetic moments (Table 1) were evaluated based on the room-temperature magnetic susceptibilities, which were corrected for any diamagnetic contributions using Pascal constants,[13] and for temperature-independent paramagnetism using a value of 0.75×10^{-9} $m^3\,mol^{-1}$. The susceptibility variations with temperature were determined over the range 80—300 K. The IR spectra of the solid compounds were recorded using Nujol mulls in the 4000—600 cm^{-1} range.

The IR spectra of the obtained dicopper(II) hydroxide tris(pyrazolide)s showed broad bands at ca. 3300 cm^{-1} assignable to the bridging hydroxo groups.[14] Presumably, the copper(II) ions in compounds (**1**)—(**4**) are bridged alternatingly by a pair of pyrazolido groups and a combination of pyrazolido and hydroxo groups to form linear-chain structures. Actually, their variable-temperature susceptibilities could be simulated by the alternating Heisenberg linear-chain model[15] when the following parameters are used: $J_1=-201$ cm^{-1}, $J_2=-111$ cm^{-1}, and $g=2.16$ for (**1**), $J_1=-192$ cm^{-1}, $J_2=-93$ cm^{-1}, and $g=2.17$ for (**2**), $J_1=-180$ cm^{-1}, $J_2=-70$ cm^{-1}, and $g=2.15$ for (**3**), and $J_1=-181$ cm^{-1}, $J_2=-69$ cm^{-1}, and $g=2.16$ for (**4**). These J_2 values are almost the same as the J values reported for binary copper(II) pyrazolides,[5,7] except for copper(II) 4-halopyrazolides, showing a structural resemblance of the doubly pyrazolido-bridged moieties. Also, for compounds (**5**) and (**6**), their susceptibilities were simulated using the alternating Heisenberg linear-chain model. The $J_1=-145$ cm^{-1}, $J_2=0$ cm^{-1}, and $g=2.15$ obtained for (**5**) and $J_1=-150$ cm^{-1}, $J_2=0$ cm^{-1}, and $g=2.16$ obtained for (**6**), however, show that these compounds have dinuclear structures rather than linear-chain structures. All J_1 values of compounds (**1**)—(**6**) are almost the same as each other, indicating a structural resemblance of the hydroxo-bridged moieties.

For copper(II) 4-chloropyrazolide, Ehlert et. al observed two broad peaks at about 120 and 240 K in its variable-temperature susceptibility curve, and thus reported two different J values.[7] Above the high-temperature peak, the reported susceptibility curve seems to agree very closely with that for compound (**5**), suggesting that the sample was highly contaminated by basic salt. Accordingly, we repeated the metal-molten ligand reactions using the literature methods,[5,7] and collected green crystals with care so as to avoid any contamination with the brown species. The susceptibility curve of the thus-obtained sample exhibited a peak at about 120 K (Fig. 1), and could be analyzed by the Heisenberg linear-chain model with $g=2.13$ and $J=-75$ cm^{-1}.

The room-temperature magnetic moments refined for $Cu(4\text{-}Xpz)_2$ (X=CH_3, H, Cl), being summarized in Table 1, are in harmony with those for $Cu_2(OH)(4\text{-}Xpz)_3$. Hence, it is certain that the strength of the antiferromagnetic couplings for both series of $Cu(4\text{-}Xpz)_2$ and $Cu_2(OH)(4\text{-}Xpz)_3$ decrease according to the substituent sequence $CH_3>H>Br\approx Cl$. This sequence seems to be rationalized by considering the ligand basicity ($pK_{a1}=$ 2.53, 3.09, 0.64, and 0.60 for pyrazole and 4-methyl-, 4-bromo-, and 4-chloropyrazoles, respectively); the more basic pyrazolide ligand forms stronger coordinate-bonds to provide a more efficient pathway for the superexchange couplings. Nevertheless, because of the fairly

Table 1. Analytical Data and Effective Magnetic Moments at 20 °C

Compound		Found (Calcd)/%				μ_{eff}/BM
		Cu	C	H	N	
$Cu_2(OH)(pz)_3$	(**1**)	36.36	31.3	2.93	24.3	1.10
		(36.81)	(31.3)	(2.92)	(24.3)	
$Cu_2(OH)(4\text{-}CH_3pz)_3$	(**2**)	33.36	38.0	4.07	22.1	1.06
		(32.81)	(37.2)	(4.16)	(21.7)	
$Cu_2(OH)(4\text{-}Clpz)_3$	(**3**)	28.79	24.2	1.58	18.8	1.17
		(28.33)	(24.1)	(1.57)	(18.7)	
$Cu_2(OH)(4\text{-}Brpz)_3$	(**4**)	21.99	19.0	1.07	14.9	1.17
		(21.84)	(18.6)	(1.21)	(14.4)	
$Cu_2(OH)(4\text{-}Clpz)_3(4\text{-}ClpzH)_2$	(**5**)	19.70	28.1	1.84	21.7	1.39
		(19.44)	(27.6)	(2.00)	(21.4)	
$Cu_2(OH)(4\text{-}Brpz)_3(4\text{-}BrpzH)_2$	(**6**)	14.99	21.0	1.31	16.2	1.38
		(14.51)	(20.6)	(1.50)	(16.0)	
$Cu(pz)_2$	(**7**)	32.03	36.6	3.09	28.4	1.43
		(32.15)	(36.5)	(3.06)	(28.3)	
$Cu(4\text{-}CH_3pz)_2$	(**8**)	28.08	42.6	4.47	24.8	1.35
		(28.15)	(42.6)	(4.46)	(24.8)	
$Cu(4\text{-}Clpz)_2$	(**9**)	23.79	27.2	1.53	21.2	1.49
		(23.84)	(27.0)	(1.51)	(21.0)	

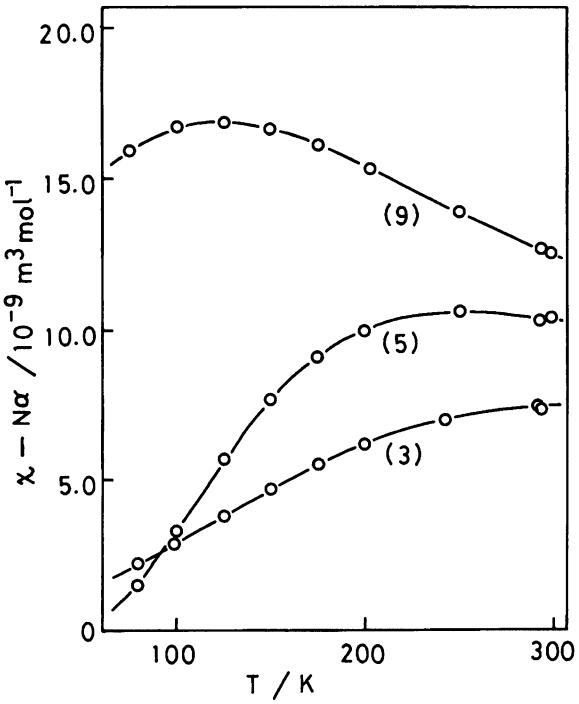

Fig. 1. Observed and calculated magnetic susceptibilities of compounds (**3**), (**5**), and (**9**). The solid curves were obtained as described in the text.

flexible nature of the diazolido-coordination modes,[16,17] the substituents on the pyrazolido ligands may cause a variation in their bridging geometries (Fig. 2). Actually, the coordinating angle θ (dihedral angle between the plane and coordinating bond) of the pyrazolido ligand in $Cu(4\text{-}Xpz)_2$ varies greatly from 9.1° (X=H)[5] to 7.7° ($X=CH_3$) and 11.0° (X=Cl).[7] The increase in J with increasing θ is qualitatively understood based on the Goodenough–Kanamori rule[18] or molecular orbital

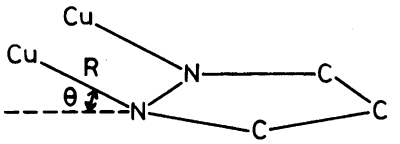

Fig. 2. Coordinate systems for pyrazolido-bridged copper(II) compounds.

analyses;[19] the greater p character in the hybrid orbitals used by the bridging atoms produces a decreased antiferromagnetic coupling.

Glerup et al. have formulated the influence of the structural parameters on the strength of the exchange couplings for chromium(III) compounds.[20] Taking into account the ligand-basicity dependence,[21,22] we can modify the expression for doubly pyrazolido-bridged copper(II) compounds (in cm^{-1}) as follows:

$$J = -215 \times 10^2 (pK_{a1} + 30) R^{-12} [\cos^4\theta/(1+ A \sin^2\theta)^2 + B], \quad (1)$$

where K_{a1} is the acid dissociation constant of the pyrazolium ion and R=1.96 Å is the Cu–N bond length.[5,7] By substituting the relevant values for J, pK_{a1}, and θ of binary copper(II) pyrazolides, the following fitting parameters were obtained: A=2.3 and B=−0.05. As a result, the basicity and coordinating-angle dependencies were collaborated and evaluated separately. The strength of the exchange couplings (J_1 and J_2) for the present compounds is affected by changes in the electron densities and in the p character of the orbitals on the pyrazolido nitrogen.

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