4832 *J. Am. Chem. Soc.* **1980**, *102*, 4832-4833

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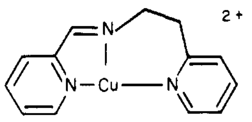
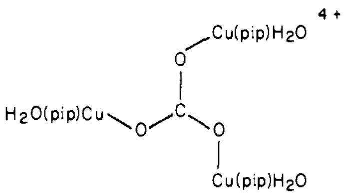
A Tricopper(II) Complex Containing a Triply Bridging Carbonate Group

Sir:

In the course of studies on imidazolate-bridged dicopper(II) complexes,[1] we occasionally isolated a crystalline, carbonate-containing compound from basic aqueous solutions of Cu(pip)-$(NO_3)_2 \cdot H_2O^2$ (I) and imidazole. Use of freshly boiled water and minimal solution stirring inhibited the formation of this compound, suggesting that dissolved carbon dioxide was the source of the carbonate ion. X-ray structural work revealed the novel cation II. Although numerous carbonate complexes are known and exhibit a variety of monodentate, chelating, and bridging geometries,[3,4] to our knowledge II is the first discrete compound to contain a triply bridging carbonate ion. Here we report the syntheses of the perchlorate and nitrate salts of II, their crystal structure, and temperature-dependent magnetic susceptibility studies that reveal ferromagnetic behavior.



$Cu(pip)^{2+}$, I



$[Cu(pip)(H_2O)]_3CO_3{}^{4+}$, II

Table I. Exchange Coupling Constants for Some Carbonate-Bridged Copper(II) Complexes

complex	g	J, cm^{-1}	zJ', cm^{-1}	ref
$[Cu(pip)(H_2O)]_3(CO_3)$-$(NO_3)_4$	2.120 (1)	4.82 (3)	−0.079 (1)	*a*
$[Cu(pip)(H_2O)]_3(CO_3)$-$(ClO_4)_4$	2.139 (1)	4.47 (4)	−0.075 (1)	*a*
$Na_2Cu(CO_3)_2$	2.24 (2)	4.1 (7)	*b*	18

[a] This work. Values for g, J, and zJ' were obtained by least-squares fits of the observed data (~220 points) to the expression $\chi_M{}^{cor}T = (\chi'T)/[1 - (2zJ'\chi')/Ng^2\beta^2]$, where $\chi' = [(Ng^2\beta^2)(1 + 5 \exp(3J/kT))]/[4kT(1 + \exp(3J/kT))]$, in $\chi_M{}^{cor}T$ vs. T plots for $T \leqslant 290$ K. [b] Not applicable.

Slow cooling of a solution containing 10 mmol of Cu(pip)-$(NO_3)_2 \cdot H_2O^{1,2}$ and 4 mmol of K_2CO_3 dissolved in 30 mL of hot water produced well-formed, blue hexagonal bipyramids of $[Cu(pip)(H_2O)]_3(CO_3)(NO_3)_4{}^{5a}$ in 40% yield. The perchlorate salt[5b] was prepared in 75% yield by substituting Cu(pip)-$(ClO_4)_2 \cdot H_2O$ and using 300 mL of water. Carbonate-related IR-active vibrational frequencies[6] occur at 1460 (ν_3), 840 (ν_2), and 752 (ν_4) cm^{-1} for the perchlorate salt.

Both compounds crystallize in the hexagonal system and are isomorphous. The unit cell parameters[7] for the nitrate salt are $a = b = 13.414$ (3) Å, $c = 16.024$ (2) Å, $Z = 2$, $\rho_{obsd} = 1.585$ g cm^{-3}, and $\rho_{calcd} = 1.578$ g cm^{-3}. Intensity data were collected by diffractometer,[9] and the structure was solved by heavy-atom methods in space group $P\bar{6}2c$ and refined (926 data, 133 parameters) to a current value of 0.054 for the residual R_1.[10] The structure and selected geometric features of the cation II are shown in Figure 1.

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(1) Kolks, G.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 5804.

(2) Pip is an abbreviation for the tridentate Schiff base ligand 2-[2-(2-pyridyl)ethyliminomethyl]pyridine (see ref 1).

(3) Gagne, R. R.; Gall, R. S.; Lisensky, G. C.; Marsh, R. E.; Speltz, L. M. *Inorg. Chem.* **1979**, *18*, 771 and references cited therein.

(4) (a) Davis, A. R.; Einstein, F. W. B.; Curtis, N. F.; Martin, J. W. L. *J. Am. Chem. Soc.* **1978**, *100*, 6258. (b) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W.; Watkins, K. O. *Inorg. Chem.* **1979**, *18*, 2296. (c) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W. *Ibid.* **1980**, *19*, 201.

(5) Anal. (a) Calcd for $Cu_3C_{40}H_{45}N_{13}O_{18}$: C, 40.49; H, 3.82; N, 15.35; O, 24.27; Cu, 16.07; CO_3, 5.06. Found: C, 40.35; H, 4.03; N, 15.53; O (by difference), 24.30; Cu, 15.79; CO_3, 5.62. (b) Calcd for $Cu_3C_{40}H_{45}N_9Cl_4O_{22}$: C, 35.95; H, 3.39; N, 9.43; Cl, 10.61. Found: C, 35.84; H, 3.67; N, 9.16; Cl, 10.33.

(6) Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed.; Wiley-Interscience: New York, 1970; p 98.

(7) Weissenberg and precession photographs of both salts can be indexed according to a hexagonal unit cell in which reflections that obey the condition $h - k = 3n$ are normal, sharp spots; otherwise the reflections appear as weak, diffuse spots. For the *hk0* zone, reflections with $h - k \neq 3n$ are systematically absent. This pattern is indicative of partial ordering, with the disorder occurring along the c axis only.[8a,b] The sharp reflections are associated with a fully disordered subcell. The dimensions of the two cells are related by the expressions $a_s = b_s = 3^{1/2}a$, $c_s = c$, and $Z_s = 3Z$, where the subscript s refers to the supercell and a, c, and Z are the values reported here for the subcell. Data have been collected only for the subcell.

(8) "Advanced Methods of Crystallography", Ramachandran, G. N., Ed.; Academic Press: New York, 1964: (a) Wooster, W. A. p 121; (b) Jagodzinski, H., p 181.

(9) The data were collected by the Molecular Structure Corp., College Station, TX. We thank Drs. Bert Frenz and Jan Troup for this courtesy.

(10) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. Although the space group extinction conditions for $P\bar{6}2c$ are not rigorously obeyed (occasional weak violations were observed), interpretation of the Patterson map was possible only in this space group. The two overlapping images of the pip ligand, required as a result of the crystallographic $\bar{6}$ symmetry axis (vide infra), were readily resolved. Although atoms N9 and Cu (Figure 1) were located at $z = {}^1/_4$ on the Patterson and difference Fourier maps, they rapidly refined to their final positions when placed ~0.25 and 0.10 Å, respectively, from this plane to achieve geometry consistent with other structural studies of the $Cu(pip)^{2+}$ moiety.[11] Six nitrate groups were disordered about the mirror planes at $z = {}^1/_4, {}^3/_4$ [position 6(h)] and were refined as rigid bodies with N–O = 1.20 Å, O–N–O = 120°. Two nitrate groups were badly disordered about position 2a. The Cu, OW, carbonate C, carbonate O, and nitrate group atoms were refined with anisotropic temperature factors. The atoms of the pip ligand were refined with isotropic temperature factors. Hydrogen atoms were fixed at calculated positions, and an overall U_{hyd} was refined to 0.10 $Å^2$. The geometry of the $Cu(pip)^{2+}$ moiety is in excellent agreement with that of the four crystallographically independent units found in $[Cu(pip)]_2(imidazolate)(NO_3)_3 \cdot 2.5H_2O$.[11]

(11) Kolks, G.; Lippard, S. J., to be submitted for publication.

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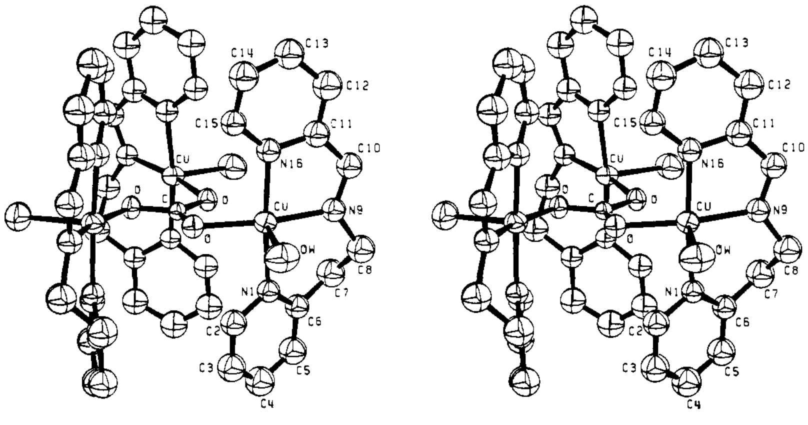

Figure 1. Stereodrawing of the structure of II showing the 35% probability thermal ellipsoids. Hydrogen atoms are omitted. Selected bond distances (in Å; esd ~0.02 Å) are: C–O, 1.294; Cu–O, 1.956; Cu–OW, 2.25; Cu–N1, 2.04; Cu–N9, 1.96; Cu–N16, 2.00. Selected bond angles (in degrees, esd ~0.5°) are: C–O–Cu, 109.2; OW–Cu–O, 97.5; N9–Cu–N1, 92.1; N9–Cu–N16, 81.8; N1–Cu–N16, 172.4. Atoms Cu and O lie –0.06 and 0.42 Å, respectively, out of the best plane fit through N1, N9, and N16. The Cu–Cu distance is 4.63 Å, and each Cu atom has a 2.69-Å contact with another O atom of the CO_3^{2-} group. Only one of the two orientations of the disordered $Cu(pip)(H_2O)^{2+}$ moieties is shown.

The carbonate group[12] lies on a crystallographically required $\bar{6}$ symmetry axis. The $Cu(pip)(H_2O)^{2+}$ moieties (I) are oriented approximately perpendicular to, and are of necessity disordered across, the plane of the carbonate group.[10,13] A water molecule is weakly bound to a fifth, axial, site of each copper atom while an oxygen atom of the carbonate group occupies the space at the other axial position. Hydrogen bonding from the coordinated water molecule to the lattice nitrate groups links units of II into sheets at $z = {}^1/_4, {}^3/_4$, with each unit being associated with six others.

The disposition of Cu atoms about the carbonate group in $[Cu(pip)(H_2O)]_3(CO_3)(NO_3)_4$ is similar to that found for the mineral azurite, $Cu_3(OH)_2(CO_3)_2$.[14] In azurite, the carbonate group is a triply bridging, tridentate ligand with hydroxide ions further linking the $Cu_3CO_3^{4+}$ units into an infinite network.

Magnetic susceptibility data were obtained for both the nitrate and perchlorate salts of II over the range $1.6 \leq T \leq 290$ K by using the Faraday method. Plots of $\chi_M^{cor}T$ vs. T showed ferromagnetic coupling within the $[Cu(pip)(H_2O)]_3CO_3^{4+}$ cations and a very weak intercation antiferromagnetic interaction,[15] perhaps mediated by the hydrogen-bonding linkages described above. Molar susceptibility expressions were derived by assuming isotropic intracluster exchange ($\mathcal{H}' = -2J\sum_{i,j}\hat{S}_i\cdot\hat{S}_j$)[16] and allowing for intercluster exchange by the molecular field approximation ($\mathcal{H}'' = -2zJ'\hat{S}^z\langle\hat{S}^z\rangle$).[17] The results are summarized in Table I along with values reported for the polymeric compound $Na_2Cu(CO_3)_2$.[18] The agreement between the magnitude of exchange coupling in the trinuclear and polymeric compounds must be viewed with caution since the bridging carbonate geometries are so different. In the salts of II, the copper atoms interact mainly through the σ system of the carbonate group whereas in the polymer the copper atoms lie 1.64 and –0.38 Å out of the carbonate plane and the superexchange pathway could involve both the σ and π orbitals of the carbonate group.[19]

Acknowledgments. This work was supported by NIH Research Grant GM-16449 from the National Institute of General Medical Sciences and Grant CHE79 12436 from the National Science Foundation.

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(12) Refinement of the bridging ligand as either a carbonate or a nitrate group showed a clear preference for the former as judged by crystallographic significance tests and evaluation of the thermal parameters. The isomorphism and identical magnetic behavior of the nitrate and perchlorate salts of II leave no doubt that carbonate ion is the bridging ligand.

(13) Partial ordering of the $Cu(pip)^{2+}$ orientations about the carbonate group may be responsible for the diffuse reflections of the supercell. Collection of the supercell data is planned, and the details of the ordering will be reported at a later time.

(14) Gattow, G.; Zemann, J. *Acta Crystallogr.* **1958**, *11*, 866.

(15) Zero-field splitting of the cluster quartet state was considered but rejected since it gave a poorer fit to the data and required an unreasonably large value of $|D| = 1.2$ cm^{-1}. No evidence for zero-field splitting occurred in the powder X-band ESR spectrum which consisted of a single symmetric signal at $g = 2.125$ for both complexes.

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(17) Ginsberg, A. P.; Lines, M. E. *Inorg. Chem.* **1972**, *11*, 2289.

(18) (a) Gregson, A. K.; Healy, P. C. *Inorg. Chem.* **1978**, *17*, 2969. (b) Healy, P. C.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1972**, 1913.

(19) **Note Added In Proof**: It has just been reported[20] that in $[Cu\{O(CH_2CO_2)_2\}]\cdot 0.5H_2O$ the copper atoms, bridged by $-CO_2^-$ groups with geometry similar to that in II, are ferromagnetically coupled with J = 4.66 cm^{-1}.

(20) Corvan, P. J.; Estes, W. E.; Weller, R. R.; Hatfield, W. E. *Inorg. Chem.* **1980**, *19*, 1297.

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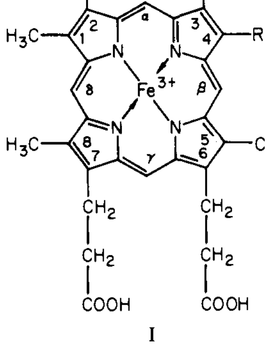
Proton NMR Characterization of Heme Rotational Disorder in Reconstituted Horseradish Peroxidase

Sir:

Elucidation of structure–function relationships in hemoproteins has relied heavily on the comparison of the properties of the native proteins with those of proteins reconstituted with modified porphyrins. The degree that various porphyrins yield different trends in properties in models and in proteins has been interpreted in terms of the nature of the interaction between the 2,4-substituents of I and the apoprotein.[1,2] In particular, deuterohemin (I, R =



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