

explored to date to study this "ortho effect".

Acknowledgment. I wish to thank Prof. M. Grätzel for his encouragement and for his constructive criticisms on this manuscript. This work was supported with funds from the Swiss National Funds for Scientific Research. I also wish to thank the reviewers for their very useful comments and suggestions in the revision of the manuscript.

Note Added in Proof. Recently, ortho effects arising from steric factors have been shown to cause large differences in the ground- and excited-state properties of tetrakis(2,6-dimethylphenyl)porphyrin and its sulfonato derivative.⁵³

Registry No. ZnTMPyP(2), 59729-18-9; ZnTMPyP(3), 59729-16-7; ZnTMPyP(4), 40603-58-5; ZnTPyP(2), 59729-19-0; ZnTPyP(3), 59729-17-8; ZnTPyP(4), 31183-11-6; ZnT(Cl-P)P(2), 56811-36-0; ZnT(Cl-P)P(3), 56811-38-2; ZnT(Cl-P)P(4), 29116-33-4; ZnTPP, 14074-80-7; ZnT(F)PP, 72076-08-5; H₂TPyP(2), 40904-90-3; H₂TPyP(3), 40882-83-5; H₂TPy(4), 16834-13-2; H₂TMPyP(2), 59728-89-1; H₂TMPyP(3), 59728-91-5; H₂TMPyP(4), 38673-65-3; H₂T(F)PP, 25440-14-6; H₂T(Cl-P)P(2), 22112-77-2; H₂T(Cl-P)P(3), 37083-39-9; H₂T(Cl-P)P(4), 37083-35-5; H₂TPP, 917-23-7.

(53) W. A. Lee, M. Grätzel, and K. Kalyanasundaram, *Chem. Phys. Lett.*, **107**, 308 (1984).

Contribution from the Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7, and Atlantic Research Laboratory, National Research Council, Halifax, Nova Scotia, Canada B3H 3Z1

Magnetic Interactions in Copper Complexes of Tetradentate Binucleating Phthalazine Ligands. Crystal and Molecular Structure of Binuclear μ -Hydroxo-Bridged Copper(II) Complexes of 1,4-Bis(2-pyridylamino)phthalazine and 1,4-Bis((4-methyl-2-pyridyl)amino)phthalazine

LAURENCE K. THOMPSON,*^{1a} A. W. HANSON,^{1b} and BARATHAM S. RAMASWAMY^{1a}

Received July 27, 1983

The dimensions of the binuclear centers in a series of triply bridged binuclear copper(II) complexes involving both a diazine (N-N) and a μ -hydroxo bridge can be varied (tuned) as a result of changing the third anionic bridge group. Cu-O-Cu bridge angles in the range 100-116° are found by varying the anionic bridge from Cl⁻ to SO₄²⁻. The crystal and molecular structure of [Cu₂(PAP4Me)(OH)(H₂O)₂(NO₃)₂]NO₃ (I) (PAP4Me = 1,4-bis((4-methyl-2-pyridyl)amino)phthalazine) and [Cu₂(PAP)(OH)Cl(SO₄)]·2H₂O (II) (PAP = 1,4-bis(2-pyridylamino)phthalazine) are reported and the dimensions of the binuclear centers (e.g. Cu-O-Cu angles and Cu-Cu separation) compared with those of other related complexes in the light of antiferromagnetic exchange between the copper(II) centers. I crystallizes in the monoclinic system, space group *P*2₁/*a*, with *a* = 27.078 (1) Å, *b* = 13.4451 (4) Å, *c* = 7.3744 (6) Å, β = 105.575 (4)°, and four formula units per unit cell. II crystallizes in the monoclinic system, space group *P*2₁/*a*, with *a* = 17.2850 (7) Å, *b* = 9.5248 (6) Å, *c* = 14.5520 (7) Å, β = 117.198 (3)°, and four formula units per unit cell. Refinement by "block-diagonal least squares" gave final *R* factors of 0.039 (I) and 0.030 (II). Both copper atoms in I are distorted six-coordinate, with bridging nitrate and hydroxide groups, a Cu...Cu separation of 3.138 Å, and a Cu-O-Cu bridge angle of 115.3°. In II distorted-square-pyramidal copper centers are found, with bridging sulfate and hydroxide groups, a Cu...Cu separation of 3.211 Å, and a Cu-O-Cu bridge angle of 115.5°. The sulfate acts both as a bidentate intramolecular bridge and also as a tridentate intermolecular bridge. Magnetic susceptibilities of solid samples were determined in the range 77-300 K, and in both cases the systems conform to the Van Vleck equation for exchange-coupled pairs of copper(II) ions with $-2J = 497 \text{ cm}^{-1}$ (I) and $-2J = 532 \text{ cm}^{-1}$ (II).

Introduction

Binuclear copper(II) complexes with nitrogen donor ligands and hydroxide or oxygen-containing bridges between the metal centers usually exhibit antiferromagnetic coupling and are potential models for binuclear copper protein centers which take part in biological reactions involving molecular oxygen, such as oxygen transport² and oxygen activation.^{3,4} Such binuclear copper centers are found in, e.g., the oxygen carrier hemocyanin⁵ and the monooxygenase tyrosinase.⁶ Magnetic

measurements on protein extracts indicate strong antiferromagnetic exchange between the copper(II) centers in *Rhus vernicifera* laccase⁷ ($-2J \geq 1000 \text{ cm}^{-1}$) and in oxyhemocyanin (*Megathura crenulata*; $-2J \geq 1250 \text{ cm}^{-1}$).^{7,8} An oxygen-containing group has been suggested as the bridging entity between the copper(II) centers in these proteins and is thought to be primarily responsible for the exchange.^{9,10} Strong antiferromagnetic exchange is observed in binuclear copper(II) systems involving single hydroxide bridges. For the complexes [Cu₂(tren)₂(OH)](PF₆)₃ and [Cu₂(tren)₂(OH)](ClO₄)₃·H₂O, in which the hydroxide group appears to act as the only bridge between the metal centers, exchange integrals of $-2J = 700$ and 760 cm^{-1} are respectively observed.¹¹ In the complex [Cu₂(L)(OH)](BF₄)₃ (L = 1,4-bis((1-oxa-4,10-dithia-7-azacyclododecan-7-yl)methyl)benzene) in which, in addition to

- (1) (a) Memorial University of Newfoundland. (b) National Research Council.
- (2) Lontie, R.; Vanquickenborne, L. *Met. Ions Biol. Syst.* **1974**, *3*, 183.
- (3) Fee, J. A. *Struct. Bonding (Berlin)* **1975**, *23*, 1.
- (4) (a) Vanneste, W. H.; Zuberbühler, A. In "Molecular Mechanisms of Oxygen Activation"; Hayaishi, O., Ed.; Academic Press: New York, 1974, and references therein. (b) Ochiai, E. "Bioinorganic Chemistry, An Introduction"; Allyn and Bacon: Boston, 1977, and references therein.
- (5) (a) Bannister, J. V., Ed. "Structure and Function of Hemocyanin"; Springer-Verlag: Berlin, 1977. (b) Lontie, R.; Witters, R. In "Copper Proteins"; Spiro, T. G., Ed.; Wiley: New York, 1981; p 229.
- (6) (a) Urbach, F. L. *Met. Ions Biol. Syst.* **1981**, *13*, 73 and references therein. (b) Solomon, E. I. In "Copper Proteins"; Spiro, T. G., Ed.; Wiley: New York, 1981; p 41. (c) Lerch, K. *Met. Ions Biol. Syst.* **1981**, *13*, 143.

- (7) Dooley, D. M.; Scott, R. A.; Ellinghaus, J.; Solomon, E. I.; Gray, H. B. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 3019.
- (8) Solomon, E. I.; Dooley, D. M.; Wang, R. H.; Gray, H. B.; Cerdonio, M.; Mogno, F.; Romani, G. L. *J. Am. Chem. Soc.* **1976**, *98*, 1029.
- (9) Burk, P. L.; Osborn, J. A.; Youinou, M.-T.; Agnus, Y.; Louis, R.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1273.
- (10) Coughlin, P. K.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 3228.
- (11) Haddad, M. S.; Hendrickson, D. N. *Inorg. Chim. Acta* **1978**, *28*, L121.

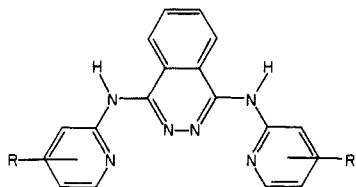


Figure 1. Structure of PAP (R = H) and PAP4Me (R = 4-Me).

a single hydroxide bridge, a rather long (eight-atom) ligand bridge joins the two copper centers, a large exchange ($-2J = 820 \text{ cm}^{-1}$) is observed.⁹ In this system a metal-metal separation of 3.384 \AA and a Cu-O-Cu angle of 132.2° are observed. In another example involving a sexadentate binucleating N_6 macrocycle and a bidentate bridging perchlorate, a large Cu-Cu separation (3.642 \AA) and Cu-O-Cu bridge angle (143.7°) are observed.¹⁰ This system exhibited very strong exchange ($-2J \approx 1000 \text{ cm}^{-1}$). In the complex $[\text{Cu}_2\text{L}(\text{OH})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (L = macrocyclic derived from 2,6-diacetylpyridine and 3,6-dioxaoctane-1,8-diamine) a large Cu-O-Cu angle of 141.7° and a Cu-Cu separation of 3.57 \AA were found but the exchange ($-2J = 240 \text{ cm}^{-1}$) was found to be rather small.¹²

A linear relationship exists between exchange integral ($-2J$ increasing) and the Cu-O-Cu bridge angle (increasing) for some bis(μ -hydroxo)-bridged systems,¹³ and in a rather unusual example of a dialkoxide-bridged binuclear copper(II) complex complete spin pairing is observed at room temperature.¹⁴ Although larger exchange integrals are generally observed for single-hydroxo-bridged species, there does not appear to be a linear relationship between exchange and oxygen bridge angle in the few structurally documented examples, which are not structurally related.

In this report we present the details of a structural and magnetic study of two triply bridged binuclear copper(II) complexes, $[\text{Cu}_2(\text{PAP4Me})(\text{OH})(\text{H}_2\text{O})_2(\text{NO}_3)_2]\text{NO}_3$ (I), (PAP4Me = 1,4-bis((4-methyl-2-pyridyl)amino)phthalazine; Figure 1) and $[\text{Cu}_2(\text{PAP})(\text{OH})\text{Cl}(\text{SO}_4)] \cdot 2\text{H}_2\text{O}$ (II) (PAP = 1,4-bis(2-pyridylamino)phthalazine; Figure 1). Systems of this type have, as a common structural feature, a single hydroxide bridge and a diazine bridge and, in addition, an anionic bridge, which, because of its varying size, allows the binuclear center to be "tuned" in a systematic way. Although the μ -nitrate and μ -sulfato bridges have similar effects on the dimensions of the binuclear center, a comparison of these complexes with related systems involving other anionic groups, which we have reported previously,¹⁵⁻¹⁷ shows how the "tuning" is reflected in the metal-metal separation, Cu-O-Cu bridge angle, and magnetic exchange. A linear relationship is demonstrated between exchange and oxygen bridge angle for systems in which the copper(II) centers have $d_{x^2-y^2}$ ground states.

Experimental Section

The complex $[\text{Cu}_2(\text{PAP4Me})(\text{OH})(\text{H}_2\text{O})_2(\text{NO}_3)_2]\text{NO}_3$ (I) was synthesized as previously described¹⁵ and gave a satisfactory elemental analysis.

Synthesis of $[\text{Cu}_2(\text{PAP})(\text{OH})\text{Cl}(\text{SO}_4)] \cdot 2\text{H}_2\text{O}$ (II). $[\text{Cu}_2(\text{PAP})(\text{OH})\text{Cl}] \cdot 1.5\text{H}_2\text{O}$ ¹⁸ (0.50 g, 0.85 mmol) was dissolved in hot water

Table I. Crystal Data

| | $\text{C}_{20}\text{H}_{23}\text{Cu}_2\text{-N}_9\text{O}_{12}$ (I) | $\text{C}_{18}\text{H}_{19}\text{ClCu}_2\text{-N}_6\text{O}_7\text{S}$ (II) |
|------------------------------------|---|---|
| cryst syst | monoclinic | monoclinic |
| space group | $P2_1/a$ | $P2_1/a$ |
| <i>a</i> , Å | 27.078 (1) | 17.2850 (7) |
| <i>b</i> , Å | 13.4451 (4) | 9.5248 (6) |
| <i>c</i> , Å | 7.3744 (6) | 14.5520 (7) |
| β , deg | 105.575 (4) | 117.198 (3) |
| <i>V</i> , Å ³ | 2586.1 | 2130.9 |
| <i>T</i> , °C | 22 | 22 |
| <i>Z</i> | 4 | 4 |
| ρ (calcd), g cm ⁻³ | 1.820 | 1.951 |
| μ , mm ⁻¹ | 2.72 | 5.03 |
| radiation | Cu K α ; $\lambda_{\alpha_1} = 1.54056 \text{ \AA}$ | |

(80 mL), excess solid sodium sulfate added, and the mixture heated until dark green crystals formed. The product was filtered from the hot mother liquor, washed with water, and air-dried, giving an almost quantitative yield. Anal.¹⁹ Calcd for $\text{C}_{18}\text{H}_{19}\text{ClCu}_2\text{N}_6\text{O}_7\text{S}$: C, 34.5; H, 3.04; N, 13.4; Cu, 20.3. Found: C, 34.6; H, 3.08; N, 13.3; Cu, 20.1.

Spectral Measurements. Electronic spectra were obtained with a Cary 17 spectrometer while infrared spectra were obtained with a Perkin-Elmer Model 283 spectrometer.

Magnetic Measurements. Variable-temperature magnetic measurements (77–300 K) were obtained courtesy of B. Van der Griendt, Department of Chemistry, Gorlaeus Laboratories, State University Leiden, The Netherlands, using a PAR vibrating-sample magnetometer. Room-temperature magnetic moments were checked with use of a Cahn Model 7600 Faraday magnetic susceptibility system, coupled to a Cahn gram electrobalance.

Crystallographic Data Collection and Refinement of the Structure. $[\text{Cu}_2(\text{PAP4Me})(\text{OH})(\text{H}_2\text{O})_2(\text{NO}_3)_2]\text{NO}_3$ (I). Crystals of I were deep blue, with well-formed faces among which {100} and {110} were prominent. The specimen used for all measurements was of extreme dimensions 0.12 and 0.53 mm. The unit-cell constants were derived from a least-squares analysis of the angle settings of 44 well-centered reflections for which $113^\circ < 2\theta < 130^\circ$. The relative intensities of the independent reflections with $2\theta < 130^\circ$ were measured with a Picker four-circle diffractometer using Ni-filtered Cu K α radiation. The θ - 2θ scan method was used, and independent reflection profiles were analyzed as described by Grant and Gabe.²⁰ The standard deviations of the measured intensities were evaluated from counting statistics, and only those for which $I_{\text{net}} > 3\sigma(I_{\text{net}})$ were used in the analysis. These numbered 3710 of a possible 4408. Absorption corrections, ranging from 1.31 to 1.79, were applied to the measured intensities.

The Cu positions were determined by inspection of the $|F_o|^2$ synthesis, and the remaining non-H atoms from the F_o synthesis were phased on the Cu contributions to the structure factors. Refinement was by block-diagonal least squares, minimizing $\sum w(\Delta F)^2$, where $1/w = \sigma^2(F_o) + 0.0005F_o^2$. Where possible, H atoms were placed in their expected positions; otherwise (methyl, hydroxyl, and hydrate H) they were located in a ΔF synthesis. Reasonable isotropic temperature factors were assigned to these atoms. The parameters ultimately refined were scale factor, extinction coefficient,²¹ coordinates, and temperature factors (anisotropic for non-H atoms) of all atoms except for the H atoms bound to C and N. The final *R* index was 0.039 (observed reflections only; 0.049 including unobserved, $R_w = 0.062$). Crystal data are given in Table I.

$[\text{Cu}_2(\text{PAP})(\text{OH})\text{Cl}(\text{SO}_4)] \cdot 2\text{H}_2\text{O}$ (II). Crystals of II were blue, with prominent faces {100}, {001}, and {011}. The specimen used for all measurements was of extreme dimensions 0.10 and 0.15 mm. Except as noted, the analysis proceeded as for I. A total of 46 reflections with $104^\circ < 2\theta < 127^\circ$ were used to determine the cell constants. The independent reflections used in the analysis $I_{\text{net}} > 3\sigma(I_{\text{net}})$ num-

(12) Drew, M. G. B.; McCann, M.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1868.

(13) Crawford, V.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107.

(14) DeCourcy, J. S.; Waters, T. N. *J. Chem. Soc., Chem. Commun.* **1977**, 572.

(15) Bautista, D. V.; Dewan, J. C.; Thompson, L. K. *Can. J. Chem.* **1982**, *60*, 2583.

(16) Bullock, G.; Hartstock, F. W.; Thompson, L. K. *Can. J. Chem.* **1983**, *61*, 57.

(17) Thompson, L. K. *Can. J. Chem.* **1983**, *61*, 579.

(18) Thompson, L. K.; Chacko, V. T.; Elvidge, J. A.; Lever, A. B. P.; Parish, R. V. *Can. J. Chem.* **1969**, *47*, 4141.

(19) Elemental analyses were performed by Canadian Microanalytical Service, Vancouver (C, H, N). Copper analyses were carried out with a Varian Techtron AA-5 after digestion of samples in concentrated HNO_3 (Memorial).

(20) Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1978**, *11*, 114.

(21) Larson, A. C. "Crystallographic Computing"; Munksgaard: Copenhagen, 1970; pp 291–294.

Table II. Final Positional Parameters and Equivalent Isotropic Debye-Waller Temperature Factors (Esd's) for $[\text{Cu}_2(\text{PAP4Me})(\text{OH})(\text{H}_2\text{O})_2(\text{NO}_3)_2]\text{NO}_3$ (I)^a

| atom | x | y | z | $B_{\text{iso}}, \text{\AA}^2$ |
|--------|--------------|-------------|-------------|--------------------------------|
| Cu(1) | -0.06896 (2) | 0.32466 (4) | 0.74806 (7) | 2.28 (2) |
| Cu(2) | 0.05062 (2) | 0.30556 (4) | 0.89631 (7) | 2.21 (2) |
| O(1) | -0.0052 (1) | 0.3580 (2) | 0.7172 (4) | 2.7 (1) |
| O(2) | 0.0953 (1) | 0.4276 (2) | 0.8994 (4) | 3.0 (1) |
| O(3) | 0.0976 (1) | 0.3674 (2) | 0.6303 (4) | 3.8 (2) |
| O(4) | 0.1333 (1) | 0.5085 (2) | 0.7213 (4) | 3.7 (1) |
| O(5) | 1.0345 (1) | 0.3927 (2) | 0.1476 (4) | 3.5 (1) |
| O(6) | 0.9555 (1) | 0.3428 (2) | 0.0881 (4) | 3.6 (1) |
| O(7) | 0.9878 (1) | 0.4336 (2) | 0.3327 (3) | 3.3 (1) |
| OW(8) | -0.0988 (1) | 0.4601 (2) | 0.6740 (4) | 2.8 (1) |
| OW(9) | 0.8926 (1) | 0.2787 (2) | 0.3928 (4) | 4.2 (2) |
| O(10) | 0.3507 (1) | 0.4245 (3) | 0.2215 (5) | 5.4 (2) |
| O(11) | 0.3033 (1) | 0.4862 (3) | 0.3891 (5) | 6.0 (3) |
| O(12) | 0.2694 (2) | 0.4469 (4) | 0.1045 (6) | 7.3 (3) |
| N(1) | -0.1327 (1) | 0.2786 (2) | 0.7957 (4) | 2.3 (1) |
| N(2) | -0.1230 (1) | 0.1184 (2) | 0.6783 (4) | 2.2 (1) |
| N(3) | -0.0412 (1) | 0.1845 (2) | 0.7908 (4) | 1.9 (1) |
| N(4) | 0.0111 (1) | 0.1744 (2) | 0.8502 (4) | 2.0 (1) |
| N(5) | 0.0856 (1) | 0.0804 (2) | 0.9017 (4) | 2.2 (1) |
| N(6) | 0.1095 (1) | 0.2342 (2) | 1.0574 (4) | 2.3 (1) |
| N(7) | 0.1087 (1) | 0.4341 (2) | 0.7465 (4) | 2.6 (1) |
| N(8) | 0.9919 (1) | 0.3894 (2) | 0.1907 (4) | 2.4 (1) |
| N(9) | 0.3082 (1) | 0.4487 (3) | 0.2441 (5) | 4.0 (2) |
| C(1) | -0.1620 (1) | 0.3435 (3) | 0.8640 (5) | 2.9 (2) |
| C(2) | -0.2117 (1) | 0.3235 (3) | 0.8618 (6) | 3.3 (2) |
| C(3) | -0.2336 (1) | 0.2350 (3) | 0.7882 (5) | 2.8 (2) |
| C(4) | -0.2887 (2) | 0.2116 (4) | 0.7791 (8) | 4.6 (3) |
| C(5) | -0.2037 (1) | 0.1672 (3) | 0.7254 (5) | 2.6 (2) |
| C(6) | -0.1529 (1) | 0.1902 (3) | 0.7348 (5) | 2.2 (1) |
| C(7) | -0.0708 (1) | 0.1077 (3) | 0.7233 (5) | 2.0 (1) |
| C(8) | -0.0495 (1) | 0.0125 (2) | 0.6937 (4) | 2.0 (1) |
| C(9) | -0.0801 (1) | -0.0688 (3) | 0.6082 (5) | 2.6 (2) |
| C(10) | -0.0570 (1) | -0.1554 (3) | 0.5775 (5) | 3.0 (2) |
| C(11) | -0.0037 (2) | -0.1649 (3) | 0.6320 (5) | 2.9 (2) |
| C(12) | 0.0265 (1) | -0.0882 (3) | 0.7228 (5) | 2.6 (2) |
| C(13) | 0.0040 (1) | 0.0028 (2) | 0.7526 (5) | 2.1 (1) |
| C(14) | 0.0334 (1) | 0.0887 (2) | 0.8386 (5) | 2.1 (1) |
| C(15) | 0.1213 (1) | 0.1405 (3) | 1.0264 (5) | 2.2 (1) |
| C(16) | 0.1693 (1) | 0.0987 (3) | 1.1114 (5) | 2.5 (2) |
| C(17) | 0.2060 (1) | 0.1548 (3) | 1.2384 (5) | 2.9 (2) |
| C(18) | 0.2582 (2) | 0.1128 (4) | 1.3282 (7) | 4.0 (2) |
| C(19) | 0.1932 (1) | 0.2500 (3) | 1.2762 (6) | 3.2 (2) |
| C(20) | 0.1452 (1) | 0.2883 (3) | 1.1865 (6) | 2.9 (2) |
| HO(1) | -0.003 (1) | 0.412 (3) | 0.687 (5) | 3.9 (10) |
| HW(8)A | -0.085 (2) | 0.513 (4) | 0.720 (7) | 7.8 (15) |
| HW(8)B | -0.108 (2) | 0.471 (4) | 0.562 (7) | 6.9 (14) |
| HW(9)A | 0.877 (1) | 0.251 (3) | 0.303 (5) | 3.5 (9) |
| HW(9)B | 0.904 (1) | 0.316 (3) | 0.358 (6) | 3.5 (9) |

^a Hydrogen atoms whose parameters were not refined have been omitted.

bered 2566 of a possible 3631. Absorption corrections ranged from 1.38 to 1.98. The coordinates and isotropic temperature factors of all the H atoms were included in the refinement. The final *R* index was 0.030 (observed reflections only; 0.056 including unobserved; $R_w = 0.040$). Crystal data are given in Table I.

The computer program system has been described by Larson and Gabe.²² The atomic scattering factors were taken from ref 23.

Final positional parameters for compounds I and II are given in Tables II and III, respectively, while thermal parameters are found in Tables VII and VIII (supplementary material). Bond distances and bond angles relevant to the copper coordination sphere for compounds I and II are given in Tables IV and V, respectively, while Tables IX and X (supplementary material) contain other bond length and bond angle data pertaining to the ligand and anionic groups. Angles between the mean planes of the aromatic rings in I and II are found in Tables XI and XII, respectively (supplementary material), while distances and angles involving H atoms that may serve as hydrogen

Table III. Final Positional Parameters and Equivalent Isotropic Debye-Waller Temperature Factors (Esd's) for $[\text{Cu}_2(\text{PAP})(\text{OH})\text{Cl}(\text{SO}_4)] \cdot 2\text{H}_2\text{O}$ (II)

| atom | x | y | z | $B_{\text{iso}}, \text{\AA}^2$ |
|--------|-------------|--------------|-------------|--------------------------------|
| Cu(1) | 0.15383 (3) | 0.24089 (6) | 0.44746 (4) | 1.84 (2) |
| Cu(2) | 0.16374 (3) | 0.25671 (6) | 0.23266 (4) | 2.01 (3) |
| S | 0.23850 (6) | 0.51948 (10) | 0.40058 (7) | 1.70 (4) |
| Cl | 0.28373 (7) | 0.19230 (12) | 0.21324 (8) | 3.04 (5) |
| O(1) | 0.2088 (2) | 0.1803 (3) | 0.3673 (2) | 2.0 (1) |
| O(2) | 0.1986 (2) | 0.4561 (1) | 0.4608 (2) | 2.7 (1) |
| O(3) | 0.1858 (2) | 0.4900 (3) | 0.2908 (2) | 2.7 (1) |
| O(4) | 0.2423 (2) | 0.6758 (3) | 0.4175 (2) | 1.9 (1) |
| O(5) | 0.3275 (2) | 0.4702 (3) | 0.4385 (2) | 3.0 (1) |
| OW(6) | 0.3675 (2) | 0.3934 (3) | 0.6882 (2) | 3.4 (2) |
| OW(7) | 0.3384 (2) | 0.4149 (4) | 0.8524 (3) | 4.3 (2) |
| N(1) | 0.0818 (2) | 0.2906 (4) | 0.5149 (2) | 1.9 (1) |
| N(2) | -0.0302 (2) | 0.1338 (3) | 0.4112 (2) | 2.1 (2) |
| N(3) | 0.0417 (2) | 0.1989 (4) | 0.3170 (2) | 1.8 (1) |
| N(4) | 0.0449 (2) | 0.2096 (3) | 0.2236 (2) | 1.9 (2) |
| N(5) | -0.0199 (2) | 0.1774 (4) | 0.0456 (2) | 2.1 (2) |
| N(6) | 0.1020 (2) | 0.3250 (3) | 0.0890 (2) | 2.0 (1) |
| C(1) | 0.1118 (3) | 0.3889 (4) | 0.5917 (3) | 2.3 (2) |
| C(2) | 0.0672 (3) | 0.4283 (5) | 0.6437 (3) | 2.8 (2) |
| C(3) | -0.0124 (3) | 0.3650 (5) | 0.6191 (3) | 3.1 (2) |
| C(4) | -0.0435 (3) | 0.2650 (5) | 0.5428 (3) | 2.7 (2) |
| C(5) | 0.0049 (2) | 0.2321 (4) | 0.4904 (3) | 1.9 (2) |
| C(6) | -0.0195 (2) | 0.1252 (4) | 0.3242 (3) | 1.7 (2) |
| C(7) | -0.0761 (2) | 0.0330 (4) | 0.2420 (3) | 1.7 (2) |
| C(8) | -0.1296 (3) | -0.0681 (4) | 0.2539 (3) | 2.3 (2) |
| C(9) | -0.1795 (3) | -0.1552 (4) | 0.1728 (3) | 2.5 (2) |
| C(10) | -0.1781 (3) | -0.1414 (4) | 0.0790 (3) | 2.4 (2) |
| C(11) | -0.1260 (3) | -0.0435 (5) | 0.0657 (3) | 2.4 (2) |
| C(12) | -0.0745 (2) | 0.0463 (4) | 0.1467 (3) | 1.8 (2) |
| C(13) | -0.0147 (2) | 0.1476 (4) | 0.1410 (3) | 1.9 (2) |
| C(14) | 0.0238 (2) | 0.2794 (4) | 0.0194 (3) | 2.0 (2) |
| C(15) | -0.0154 (3) | 0.3313 (5) | -0.0822 (3) | 2.4 (2) |
| C(16) | 0.0279 (3) | 0.4315 (5) | -0.1090 (3) | 3.0 (2) |
| C(17) | 0.1091 (3) | 0.4759 (5) | -0.0385 (3) | 2.9 (2) |
| C(18) | 0.1436 (3) | 0.4221 (5) | 0.0592 (3) | 2.6 (2) |
| HO(1) | 0.250 (2) | 0.186 (4) | 0.398 (3) | 1.4 (8) |
| HW(6)A | 0.339 (2) | 0.333 (4) | 0.664 (3) | 1.8 (8) |
| HW(6)B | 0.341 (3) | 0.464 (5) | 0.652 (3) | 4.1 (11) |
| HW(7)A | 0.305 (3) | 0.470 (5) | 0.839 (4) | 4.8 (12) |
| HW(7)B | 0.357 (4) | 0.408 (7) | 0.823 (5) | 9.1 (19) |
| HN(2) | -0.075 (2) | 0.102 (3) | 0.404 (2) | 0.6 (7) |
| HN(5) | -0.065 (2) | 0.151 (4) | -0.006 (3) | 2.3 (9) |
| HC(1) | 0.166 (3) | 0.432 (5) | 0.603 (3) | 3.3 (10) |
| HC(2) | 0.096 (2) | 0.506 (4) | 0.701 (3) | 2.5 (9) |
| HC(3) | -0.048 (2) | 0.387 (4) | 0.653 (3) | 2.1 (8) |
| HC(4) | -0.096 (2) | 0.224 (4) | 0.518 (3) | 2.0 (8) |
| HC(8) | -0.131 (2) | -0.083 (4) | 0.317 (3) | 1.5 (7) |
| HC(9) | -0.215 (2) | -0.217 (4) | 0.179 (3) | 2.7 (9) |
| HC(10) | -0.207 (2) | -0.199 (4) | 0.024 (3) | 3.0 (10) |
| HC(11) | -0.130 (2) | -0.038 (4) | 0.003 (3) | 2.8 (9) |
| HC(15) | -0.072 (2) | 0.299 (4) | -0.127 (3) | 2.8 (9) |
| HC(16) | 0.001 (3) | 0.456 (5) | -0.170 (3) | 4.1 (11) |
| HC(17) | 0.137 (2) | 0.541 (4) | -0.065 (2) | 1.0 (7) |
| HC(18) | 0.190 (2) | 0.440 (4) | 0.100 (3) | 1.3 (7) |

bridges are given in Table XIII (supplementary material). Unrefined positional parameters and temperature factors for H atoms in I are given in Table XIV (supplementary material) while observed and calculated structure factors for I and II are deposited in Tables XV and XVI, respectively (supplementary material).

Results and Discussion

Description of the Structure of $[\text{Cu}_2(\text{PAP4Me})(\text{OH})(\text{H}_2\text{O})_2(\text{NO}_3)_2]\text{NO}_3$ (I). The structure of I is given in Figure 2, and interatomic distances and angles relevant to the copper coordination spheres are given in Table IV. The two copper(II) centers are bridged by the phthalazine group (N-(3)N(4)), a bidentate nitrate, and a hydroxide group. The stereochemistry at Cu(1) can be described in terms of a somewhat distorted, axially elongated, octahedron. Axial bond lengths to O(6) and O(9) (H_2O) are considerably longer than the equatorial bond lengths. The stereochemistry at Cu(2) is at least five-coordinate with the CuN_2O_3 (excluding O(3))

(22) Larson, A. C.; Gabe, E. J. "Computing in Crystallography"; Delft University Press: Delft, Holland, 1978; pp 81-89.

(23) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, Table 2.2B.

Table IV. Interatomic Distances (Å) and Angles (deg) (Esd's) Relevant to the Copper Coordination Sphere in $[\text{Cu}_2(\text{PAP4Me})(\text{OH})(\text{H}_2\text{O})_2(\text{NO}_3)_2]_2\text{NO}_3$ (I)

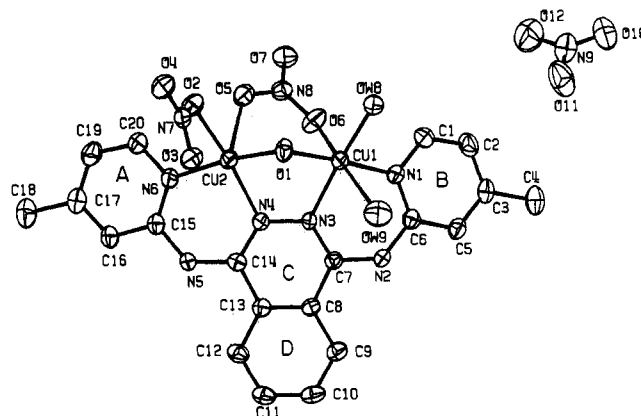
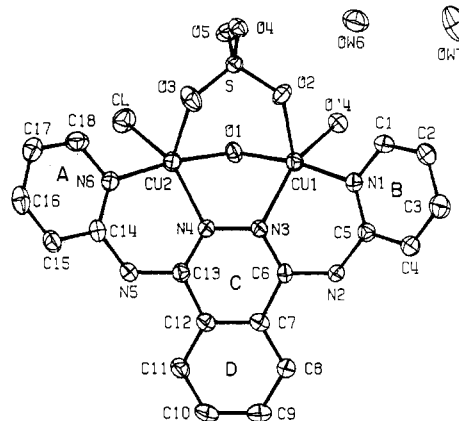
| | | | |
|-------------------|-----------|-----------------|-----------|
| Cu(1)-O(1) | 1.856 (2) | Cu(2)-O(1) | 1.859 (2) |
| Cu(1)-O(6) | 2.428 (3) | Cu(2)-O(5) | 2.330 (3) |
| Cu(1)-OW(8) | 2.007 (3) | Cu(2)-O(2) | 2.035 (3) |
| Cu(1)-OW(9) | 2.620 (3) | Cu(2)-O(3) | 2.738 (3) |
| Cu(1)-N(1) | 1.952 (3) | Cu(2)-N(6) | 1.964 (3) |
| Cu(1)-N(3) | 2.022 (3) | Cu(2)-N(4) | 2.042 (3) |
| Cu(1)-Cu(2) | 3.138 (1) | N(3)-N(4) | 1.372 (4) |
| O(1)-Cu(1)-O(6) | 95.6 (1) | O(1)-Cu(2)-O(5) | 94.8 (1) |
| O(1)-Cu(1)-OW(8) | 93.8 (1) | O(1)-Cu(2)-O(2) | 94.0 (1) |
| O(1)-Cu(1)-OW(9) | 93.9 (1) | O(1)-Cu(2)-O(3) | 79.7 (1) |
| O(1)-Cu(1)-N(1) | 174.3 (1) | O(1)-Cu(2)-N(6) | 171.3 (1) |
| O(1)-Cu(1)-N(3) | 85.7 (1) | O(1)-Cu(2)-N(4) | 85.4 (1) |
| O(6)-Cu(1)-OW(8) | 99.7 (1) | O(5)-Cu(2)-O(2) | 79.8 (1) |
| O(6)-Cu(1)-OW(9) | 168.9 (1) | O(5)-Cu(2)-O(3) | 129.8 (1) |
| O(6)-Cu(1)-N(1) | 81.7 (1) | O(5)-Cu(2)-N(6) | 93.4 (1) |
| O(6)-Cu(1)-N(3) | 86.9 (1) | O(5)-Cu(2)-N(4) | 111.4 (1) |
| OW(8)-Cu(1)-OW(9) | 85.4 (1) | O(2)-Cu(2)-O(3) | 51.3 (1) |
| OW(8)-Cu(1)-N(1) | 91.5 (1) | O(2)-Cu(2)-N(6) | 90.2 (1) |
| OW(8)-Cu(1)-N(3) | 173.4 (1) | O(2)-Cu(2)-N(4) | 168.8 (1) |
| OW(9)-Cu(1)-N(1) | 88.4 (1) | O(3)-Cu(2)-N(6) | 97.1 (1) |
| OW(9)-Cu(1)-N(3) | 88.1 (1) | O(3)-Cu(2)-N(4) | 117.8 (1) |
| N(1)-Cu(1)-N(3) | 89.2 (1) | N(6)-Cu(2)-N(4) | 89.0 (1) |
| Cu(1)-N(3)-N(4) | 116.8 (2) | Cu(2)-N(4)-N(3) | 114.7 (2) |
| Cu(1)-O(1)-Cu(2) | 115.3 (1) | | |

Table V. Interatomic Distances (Å) and Angles (deg) (Esd's) Relevant to the Copper Coordination Sphere in $[\text{Cu}_2(\text{PAP})(\text{OH})\text{Cl}(\text{SO}_4)] \cdot 2\text{H}_2\text{O}$ (II)

| | | | |
|------------------|-----------|-----------------|-----------|
| Cu(1)-O(1) | 1.900 (3) | Cu(1)-Cu(1)' | 5.606 (1) |
| Cu(1)-O(2) | 2.169 (3) | Cu(1)-Cu(2)' | 6.282 (1) |
| Cu(1)-O(4)' | 2.060 (3) | Cu(2)-Cu(1)' | 6.506 (1) |
| Cu(1)-N(1) | 1.963 (3) | Cu(2)-Cu(2)' | 8.420 (1) |
| Cu(1)-N(3) | 2.039 (3) | Cu(1)-Cu(2) | 3.211 (1) |
| Cu(2)-O(1) | 1.892 (3) | N(3)-N(4) | 1.389 (4) |
| Cu(2)-O(3) | 2.346 (3) | S-O(2) | 1.469 (3) |
| Cu(2)-Cl | 2.301 (1) | S-O(3) | 1.459 (3) |
| Cu(2)-N(6) | 1.973 (3) | S-O(4) | 1.506 (3) |
| Cu(2)-N(4) | 2.047 (3) | S-O(5) | 1.454 (3) |
| O(1)-Cu(1)-O(2) | 94.8 (1) | O(1)-Cu(2)-O(3) | 93.9 (1) |
| O(1)-Cu(1)-O(4)' | 91.8 (1) | O(1)-Cu(2)-Cl | 93.3 (1) |
| O(1)-Cu(1)-N(1) | 171.7 (1) | O(1)-Cu(2)-N(6) | 172.4 (1) |
| O(1)-Cu(1)-N(3) | 84.1 (1) | O(1)-Cu(2)-N(4) | 84.7 (1) |
| O(2)-Cu(1)-O(4)' | 94.6 (1) | O(3)-Cu(2)-Cl | 106.8 (1) |
| O(2)-Cu(1)-N(1) | 90.5 (1) | O(3)-Cu(2)-N(6) | 89.4 (1) |
| O(2)-Cu(1)-N(3) | 114.6 (1) | O(3)-Cu(2)-N(4) | 102.9 (1) |
| O(4)'-Cu(1)-N(1) | 94.0 (1) | Cl-Cu(2)-N(6) | 92.3 (1) |
| O(4)'-Cu(1)-N(3) | 150.7 (1) | Cl-Cu(2)-N(4) | 150.2 (1) |
| N(1)-Cu(1)-N(3) | 87.9 (1) | N(6)-Cu(2)-N(4) | 87.9 (1) |
| Cu(1)-N(3)-N(4) | 116.8 (2) | Cu(2)-N(4)-N(3) | 116.2 (2) |
| Cu(1)-O(1)-Cu(2) | 115.5 (1) | | |
| O(2)-S-O(3) | 110.2 (2) | O(3)-S-O(4) | 109.1 (2) |
| O(2)-S-O(4) | 107.8 (2) | O(3)-S-O(5) | 112.1 (2) |
| O(2)-S-O(5) | 110.2 (2) | O(4)-S-O(5) | 107.3 (2) |

^a Related to tabulated atoms by 2_1 axis.

chromophore corresponding to a distorted square pyramid. Cu(1) is displaced by 0.040 Å from the mean plane of O(1), O(8), N(1), and N(3) toward O(6) while Cu(2) is displaced by 0.159 Å from the mean plane of O(1), O(2), N(4), and N(6) toward O(5). In addition the O(3) atom of the coordinated nitrate is involved as a potential ligand with a bond distance (Cu(2)-O(3)) of 2.738 Å. It has been suggested that in unsymmetrically coordinated bidentate nitrate groups the difference between the Cu-O bond lengths, involving the two coordinated oxygen atoms, falls in the range 0.2-0.7 Å.²⁴ We recently reported the structure of a nitrate complex, where, even though the Cu-O bond length difference was 0.84 Å, other structural and spectral evidence suggested a weak in-

**Figure 2.** View of the binuclear cation $[\text{Cu}_2(\text{PAP4Me})(\text{OH})(\text{H}_2\text{O})_2(\text{NO}_3)_2]^+$ with the hydrogen atoms omitted for clarity. Various rings are labeled A-D.**Figure 3.** View of the binuclear complex $[\text{Cu}_2(\text{PAP})(\text{OH})\text{Cl}(\text{SO}_4)] \cdot 2\text{H}_2\text{O}$ with the hydrogen atoms omitted for clarity. Various rings are labeled A-D.

teraction involving the distant nitrate oxygen atom.²⁵ Since the difference between the Cu-O bond lengths in this case is 0.703 Å, it is reasonable to assume that the perturbation of O(3) at the copper center is significant and that the structure at Cu(2) is best described as a severely distorted octahedron.

Of particular interest in this structure is the presence of three different types of nitrate: the unsymmetrical bidentate nitrate already mentioned, an ionic nitrate, and a bidentate nitrate group bridging the two metal centers. Copper-oxygen, apical bond distances to this group are quite long, which is perhaps to be expected considering the likely $d_{x^2-y^2}$ ground state for both copper centers. For comparison $\text{Cu}(\text{NO}_3)_2(\text{H}_2\text{O})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ has one Cu-O bond length in a bridging nitrate group of 2.391 Å.^{26,27} The ionic nitrate in I links adjacent molecules together by H bonding.

The binuclear center is characterized by a metal-metal separation of 3.138 Å, an oxygen bridge angle of 115.3°, and Cu-O(1) separations of 1.859 and 1.856 Å (Table IV). The metal-metal separation and oxygen bridge angle are larger than those found in the complex $[\text{Cu}_2(\text{PAP})(\text{OH})\text{Cl}_3] \cdot 1.5\text{H}_2\text{O}$ (III).^{28,29} This appears to be the result of replacing the smaller chlorine bridge with a bidentate nitrate bridge. The angles Cu(2)-N(4)-N(2) and N(4)-N(3)-Cu(1) in I are larger, as

(25) Thompson, L. K.; Ball, R. G.; Trotter, J. *Can. J. Chem.* **1980**, *58*, 1566.

(26) Garaj, J. *Acta Chem. Scand.* **1968**, *22*, 1710.

(27) Morosin, B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *B26*, 1203.

(28) Dewan, J. C.; Thompson, L. K. *Can. J. Chem.* **1982**, *60*, 121.

(29) Marongiu, G.; Lingafelter, E. C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 620.

(24) Addison, C. C.; Logan, N.; Wallwork, S. C.; Garner, C. D. *Q. Rev., Chem. Soc.* **1971**, *25*, 289.

Table VI. Magnetic and Key Structural Parameters for μ -Hydroxy-Bridged Copper Complexes of Some Substituted Phthalazines

| complex | Cu--Cu, Å | Cu-O, Å | Cu-O-Cu, deg | $-2J$, cm^{-1} | $\langle g \rangle$ | μ_{RT} , μ_{B} | ref |
|--|----------------------|-------------|----------------------|--------------------------|---------------------|--------------------------------------|-----|
| [Cu ₂ (PAP4Me)(OH)(H ₂ O) ₂ (NO ₃) ₂][NO ₃] (I) | 3.138 (1) | 1.856-1.859 | 115.3 (1) | 497 | 2.10 | 1.02 | |
| [Cu ₂ (PAP)(OH)Cl(SO ₄) ₂] \cdot 2H ₂ O (II) | 3.211 (1) | 1.892-1.900 | 115.5 (1) | 532 | 2.20 | 1.01 | |
| [Cu ₂ (PAP)(OH)Cl ₃] \cdot 1.5H ₂ O (III) | 3.001 (2), 2.972 (2) | 1.929-1.942 | 100.1 (2), 101.8 (2) | 201 | 2.28 | 1.60 | 17 |
| [Cu ₂ (PAP)(OH)Br ₃] \cdot 1.5H ₂ O (IV) | 3.010 (2), 2.986 (3) | 1.920-1.937 | 101.3 (3), 102.9 (3) | 191 | 2.20 | 1.66 | 17 |
| [Cu ₂ (PAP)(OH)(IO ₃) ₃] \cdot 4H ₂ O (V) | 3.165 (1) | 1.882-1.897 | 113.8 (2) | 290 | 2.21 | 1.49 | 45 |
| [Cu ₂ (MIP)(OH)Cl ₃ (H ₂ O)] \cdot H ₂ O (VI) | 3.425 | 1.920 | 126.2 | 800 | 2.00 | 0.62 | 45 |

would be expected, while the Cu-O(1) bond lengths are shorter than those found in III.

The ligand has a great deal of flexibility about the exocyclic nitrogen atoms (N(5), N(2)), and pyridine rings A and B are bent with respect to the mean plane of the phthalazine group by angles of 22.5 and 18.1°, respectively (Table XI). Comparable angles in the complex [Cu₂(PAP)(OH)Cl₃] \cdot 1.5H₂O are found to be on average 29° for a system with an oxygen bridge angle of about 100°. This bending of the pyridine rings is, no doubt, the result of the stereochemical demands of the copper centers and the oxygen bridge angle. The phthalazine group itself is not completely planar, and the angle between the fused benzene ring (D) and the diazine ring (C) is 4°.

Description of the Structure of [Cu₂(PAP)(OH)Cl(SO₄)₂] \cdot 2H₂O (II). The structure of II is given in Figure 3, and interatomic distances and angles relevant to the copper coordination spheres are given in Table V. The two copper(II) centers are bridged by the phthalazine group (N(3)N(4)), a sulfate, and a hydroxide group. The stereochemistry at both copper centers is square pyramidal with the bridging sulfate supplying both apical sites (O(2) and O(3)). Three sites per copper in the basal plane are provided by phthalazine and pyridine nitrogens and the hydroxide bridge. The fourth site at one copper center is occupied by a terminal chlorine atom while at the other copper center an oxygen atom from a sulfate on a neighboring molecule completes the basal plane. The sulfate groups are in fact tridentate, bridging three copper centers in a polymeric chain arrangement. Sulfate oxygen O(4) is bound to Cu(1) in a neighboring molecule and performs an equivalent function to oxygen O(4)'. The intermolecular sulfate-bridged structure is illustrated in Figure 4, and relevant bond distances and angles involving the sulfate bridge itself are given in Table V. The sulfate group behaves as both an intramolecular and an intermolecular bidentate bridge, and the Cu-Cu separations generated by intermolecular bridging (5.61 and 6.28 Å) are much larger than the intramolecular separation (3.211 Å).

The binuclear center is characterized by a metal-metal separation of 3.211 Å, an oxygen bridge angle of 115.5°, and Cu-O(1) separations of 1.900 and 1.892 Å. Copper-nitrogen bond distances involving the ligand are comparable with those observed for I and also for the parent compound [Cu₂(PAP)(OH)Cl₃] \cdot 1.5H₂O (III). The Cu-Cl bond length is similar to that found in III.

The sulfate group can coordinate in a number of ways, acting as a monodentate,³⁰⁻³² a bridging bidentate,³³ a bridging tridentate,^{34,35} and a chelating bidentate ligand.³⁶ The axial Cu-O distances to the tridentate sulfate group in II are quite different (2.346 and 2.169 Å), and this possibly reflects the

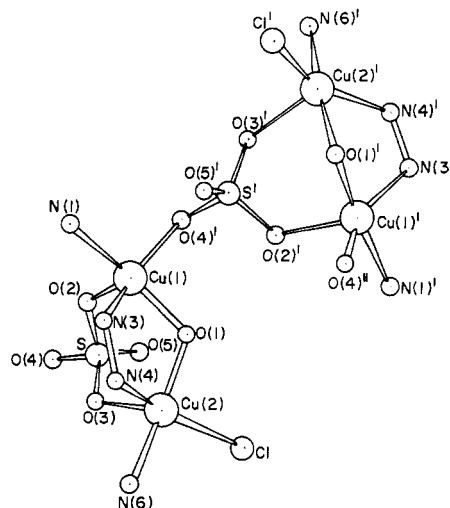


Figure 4. View of the polymeric sulfate-bridged chains in II (the ligand has been abbreviated N(1)N(3)N(4)N(6) for clarity).

difference in the basal ligand grouping at the two copper centers. These axial Cu-O distances are longer than the axial Cu-O(SO₄) separation of 1.98 Å found in the complex Cu₄(N-ino)₄(OH)₂(SO₄)(H₂O)₄,³⁷ in which the sulfate acts as a bidentate bridging group (N-ino = isonicotinate N-oxide), and also longer than the comparable Cu-O distance of 2.15 Å found in the complex (μ_3 -hydroxo)tris(μ -pyridine-2-carbaldehyde oximate)(μ_3 -sulfato)tricopper(II)-16.3-water, which contains a tridentate sulfate.^{34,35}

Pyridine rings A and B are bent by angles of 35.4 and 32.6°, respectively, with reference to the mean plane of the phthalazine unit and are mutually inclined at 63.4°. The twisting of the ligand about the exocyclic nitrogen center is larger in this case than in all previously reported structures of this sort. Again the phthalazine group is not planar and the mean planes of the diazine ring (C) and the fused benzene ring (D) are inclined at an angle of 7.9°.

Spectroscopic Measurements. Both complexes are characterized by sharp infrared absorptions (3580 cm^{-1} , I; 3620 cm^{-1} , II) due to bridging hydroxide. Four nitrate combination mode ($\nu_1 + \nu_4$) absorptions are observed for I at 1751, 1753, 1766, and 1784 cm^{-1} .³⁸ The ionic nitrate can be associated with one of the absorptions around 1750 cm^{-1} and the monodentate nitrate with the other band and the 1766- cm^{-1} band. The very high energy band at 1784 cm^{-1} is assumed to be associated with the bridging nitrate group. Four major absorptions are observed for II at 960, 1030, 1116, and 1140 cm^{-1} , associated with the sulfate groups,³⁹ while a band at 262 cm^{-1} is assigned to a Cu-Cl stretch.

Compound I is characterized by a d-d absorption at 16 300 cm^{-1} in the solid-state (mull transmittance) spectrum, associated with six-coordinated copper(II) centers. The electronic

(30) Hoskins, B. F.; Williams, F. D. *J. Chem. Soc., Dalton Trans.* **1975**, 1267.

(31) Tedenac, J. C.; Phung Dinh, N.; Avinens, C.; Maruin, M. *J. Inorg. Nucl. Chem.* **1975**, *38*, 85.

(32) Ahuja, I. S. *Indian J. Chem.* **1970**, *9*, 173.

(33) Korvenranta, J. *Suom. Kemistil. B* **1973**, *46*, 240.

(34) Beckett, R.; Hoskins, B. F. *J. Chem. Soc., Dalton Trans.* **1972**, 291.

(35) Beckett, R.; Colton, R.; Hoskins, B. F.; Martin, R. L.; Vince, D. G. *Aust. J. Chem.* **1969**, *22*, 2527.

(36) Barraclough, C. G.; Tobe, M. L. *J. Chem. Soc.* **1961**, 1993.

(37) Knuuvttila, P. *Inorg. Chim. Acta* **1982**, *58*, 201.

(38) Lever, A. B. P.; Mantovani, E.; Ramaswamy, B. S. *Can. J. Chem.* **1971**, *49*, 1957.

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

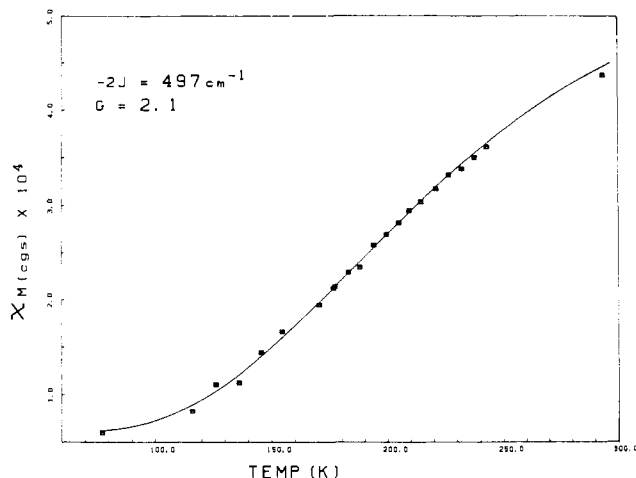


Figure 5. Magnetic susceptibility data (half-filled boxes) for $[\text{Cu}_2\text{-(PAP4Me)(OH)(H}_2\text{O)}_2\text{(NO}_3\text{)}_2]\text{NO}_3$. The solid line was calculated from eq 1 with $g = 2.10$, $-2J = 497 \text{ cm}^{-1}$, and $N\alpha = 120 \times 10^{-6} \text{ cgsu}$.

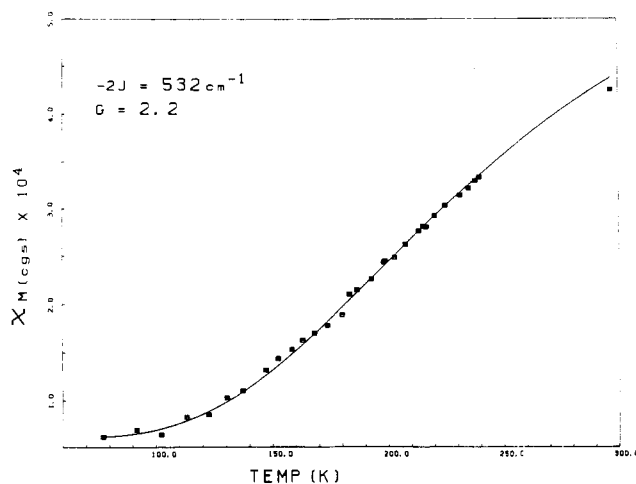


Figure 6. Magnetic susceptibility data (half-filled boxes) for $[\text{Cu}_2\text{-(PAP)(OH)Cl(SO}_4\text{)}]\cdot 2\text{H}_2\text{O}$. The solid line was calculated from eq 1 with $g = 2.20$, $-2J = 532 \text{ cm}^{-1}$, and $N\alpha = 120 \times 10^{-6} \text{ cgsu}$.

spectrum of II (solid state, mull transmittance) is characterized by an absorption at 14800 cm^{-1} with a shoulder at 13900 cm^{-1} , indicative of a weaker ligand field than in the nitrate complex. The unsymmetrical nature of the binuclear center is not clearly reflected in the d-d absorption although the low-energy shoulder could be associated with the copper center to which chlorine is bound. Splitting of the d-d band in this way has, however, been associated with square-pyramidal copper(II) centers in other systems, especially at low temperature.^{17,18}

Magnetic Measurements. Magnetic susceptibility measurements were performed on powdered samples in the range 77–300 K. The results are summarized in Table VI, along with data on other related systems, and also in Figures 5 and 6. The best-fit lines were calculated from the Van Vleck equation⁴⁰ for exchange-coupled pairs of copper(II) ions (eq 1). In this expression $2J$ (in the spin Hamiltonian $\mathcal{H} =$

$$\chi_M = \frac{N\beta^2 g^2}{3kT} \left[1 + \frac{1}{3} \exp(-2J/kT) \right]^{-1} + N\alpha \quad (1)$$

$-2J\hat{S}_1 \cdot \hat{S}_2$) is the singlet-triplet splitting or exchange integral and other symbols have their usual meaning. The temperature-independent paramagnetism for a binuclear copper(II) complex, $N\alpha$, was taken as $120 \times 10^{-6} \text{ cgsu/mol}$. The pa-

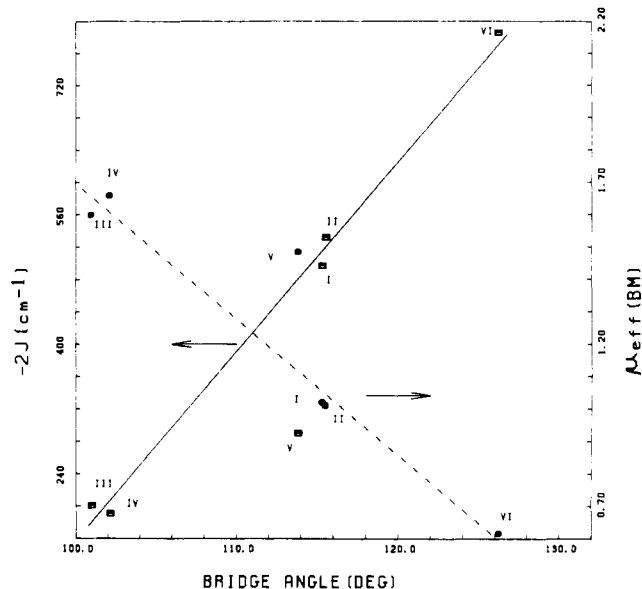


Figure 7. $-2J \text{ (cm}^{-1}\text{)}$ (half-filled boxes) and $\mu_{\text{eff}} \text{ (}\mu_{\text{B}}\text{)}$ (octagons) vs. oxygen bridge angle for the μ -hydroxo-bridged complexes I–VI.

rameters giving the best fit were obtained by minimizing the function

$$E = \sum_i W_i (\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})^2$$

where

$$W_i = (\chi_i^{\text{obsd}})^{-1}$$

with use of a Simplex nonlinear fitting routine.^{41,42}

The exchange integral, $-2J$, is much larger in compounds I and II than values observed for related complexes (Table VI) with single hydroxide bridges and triply bridged binuclear centers, and the increased exchange can be related to the larger metal-metal separation and oxygen bridge angle.

While, in a series of bis(μ -hydroxo)-bridged copper(II) complexes, a linear variation of exchange integral with oxygen bridge angle was observed,¹³ this is certainly not the case with the few systems involving single hydroxide bridges that have been reported recently.^{9,10,12,43} These systems are structurally unrelated, with $d_{x^2-y^2}$ copper ion ground states in three cases^{9,10,12} and a d_{z^2} ground state in the other.⁴³ No systematic evaluation of the relationship between oxygen bridge angle and exchange has been reported so far for systems with a single hydroxide bridge.

The results of our present study allow the structural and magnetic data of five closely related pyridylphthalazine complexes to be compared (Table VI). A common structural feature in this series includes the hydroxide bridge and the phthalazine diazine bridge, and the systematic structural variation is developed by changing the third anionic bridge. The order of increasing oxygen bridge angle ($\text{Cl}^- \approx \text{Br}^- < \text{IO}_3^- < \text{NO}_3^- < \text{SO}_4^{2-}$) is matched by the trend in increasing exchange. Figure 7 illustrates plots of both $-2J$ and room-temperature magnetic moment (μ_{eff}) vs. oxygen bridge angle for these complexes. A reasonable straight-line relationship exists for both $-2J$ and μ_{eff} as a function of oxygen bridge angle for compounds I–IV. However the iodate complex, V, does not relate exchange or magnetic moment with bridge angle in the same way. Structurally compounds I–IV have copper stereochemistries that are best represented as distorted

(41) Spendley, W.; Hext, G. R.; Himsworth, F. R. *Technometrics* **1962**, *4*, 441.

(42) Nelder, J. A.; Mead, R. *Comput. J.* **1965**, *7*, 308.

(43) Haddad, M. S.; Wilson, S. R.; Hodgson, D. R.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1981**, *103*, 384.

(40) Van Vleck, J. H. "The Theory of Electric and Magnetic Susceptibilities"; Oxford University Press: London, 1932; Chapter IX.

square pyramidal or octahedral with $d_{x^2-y^2}$ ground states. In V the stereochemistry at copper is between a square pyramid and a trigonal bipyramid and so the ground-state representation for this system may not be $d_{x^2-y^2}$. Such a situation may lead to a different relationship between exchange and bridge angle.

There are few systems reported in which two small groups, of which one is hydroxide, bridge two copper(II) centers. In the macrocyclic complex reported by Lippard¹⁰ a weakly coordinated perchlorate group constitutes a second bridge (the macrocycle can perhaps be considered as a very large bridging group). A pyridazine bridge and a hydroxy bridge are found in the complex $[\text{Cu}_2\text{LCl}_3(\text{OH})(\text{H}_2\text{O})]$ ($\text{L} = 3,6\text{-bis}(2\text{-pyridyl})\text{pyridazine}$),⁴⁴ with a metal-metal separation of 3.376 Å and an oxygen bridge angle of 126.5°. No magnetic data are reported for this system. A structural investigation of the complex $[\text{Cu}_2(\text{MIP})(\text{OH})\text{Cl}_3(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ ((VI), prepared in our laboratory (MIP = 1,4-bis(1-methyl-2-imidazolyl)-phthalazine), shows a similar structure involving a diazine bridge and a hydroxide bridge with a metal-metal separation of 3.425 Å and an oxygen bridge angle of 126.2°. A room-temperature magnetic moment of 0.62 μ_B suggests a substantial exchange for this system. A variable-temperature magnetic study on VI indicates very strong exchange with $-2J = 800 \text{ cm}^{-1}$ (Table VI). The stereochemistry at each copper center in VI is close to square pyramidal, with a $d_{x^2-y^2}$ ground state, and as shown in Figure 7 this compound falls on both straight lines generated by plotting $-2J$ and room-temperature magnetic moment against oxygen bridge angle. Therefore, it is clear that for related systems involving single hydroxide bridges between copper(II) centers, with $d_{x^2-y^2}$ ground states, bound to a μ -phthalazine diazine group, both exchange and room-temperature moment are related in a systematic way to oxygen bridge angle.

The triple bridge found in I and II, and in the other related phthalazine complexes reported by us (Table VI), presents the possibility of more than one pathway for exchange. We have not been able to synthesize binuclear copper complexes involving just phthalazine bridge groups or systems with both phthalazine and anion bridges. As a result it is difficult to assess the contribution of these groups to the overall exchange. It is likely, however, that the exchange will be dominated by the hydroxide bridge. The placement of compound VI on both straight lines in Figure 7 tends to suggest that the anionic bridge group plays a minor role in the exchange process.

There are no literature reports of binuclear copper complexes involving just phthalazine bridge groups, but recent papers

dealing with systems involving just a pyrazole bridge ($-2J = 43 \text{ cm}^{-1}$)⁴⁶ and a hydrazine bridge ($-2J = 52 \text{ cm}^{-1}$)⁴⁷ indicate that diazine type bridges probably mediate relatively weak exchange. The complex $[\text{Ni}(\text{DHPH})(\text{H}_2\text{O})_2]_2\text{Cl}_4\cdot 2\text{H}_2\text{O}$ (DHPH = 1,4-dihydrazinophthalazine) has a binuclear nickel center bridged by two phthalazine diazine groups,⁴⁸ and in this and related pyridazine and pyrazole complexes of nickel(II) and cobalt(II) which are assumed to be structurally similar, exchange integrals are small.^{49,50}

It has been clearly shown, in this and other related studies, that the dimensions of the binuclear center in the pyridyl-phthalazine complexes can be systematically varied by the incorporation of anionic bridging entities of varying size. As the oxygen bridge angle and the metal-metal separation increase, exchange is enhanced. The limit of expansion of the binuclear center with phthalazine ligands like PAP, which involve six-membered chelate rings, has probably been reached with bridge groups like sulfate. However, with related ligands involving five-membered chelate rings (e.g. MIP), further expansion of the binuclear center is possible.

We are currently investigating the variable-temperature magnetism and structure of other related complexes with a view to substantiating further the exchange structure relationships in systems of this sort and also to probe the limit of expansion of the binuclear centers in diazine complexes in general. The flexibility of the oxygen bridge, e.g. as hydroxide, in accommodating changing dimensions at the binuclear centers in coordination complexes of copper and other metals lends support to the presence of such a bridge at the binuclear centers in certain copper proteins where very large spin exchange occurs.

Acknowledgment. We are indebted to the Natural Sciences and Engineering Research Council of Canada for financial support for this study. We thank Dr. F. R. Ahmed (National Research Council of Canada) for generating the ORTEP diagrams (Figures 2 and 3).

Supplementary Material Available: Listings of anisotropic thermal parameters (Tables VII and VIII), bond length and bond angle data pertaining to the ligands (Tables IX and X), angles between mean planes of the aromatic rings (Tables XI and XII), distances and angles involving H atom bridges (Table XIII), unrefined positional parameters and temperature factors for H atoms in I (Table XIV), and observed and calculated structure factors for I and II (Tables XV and XVI) (63 pages). Ordering information is given on any current masthead page.

(44) Ghedini, M.; DeMunno, G.; Denti, G.; Manotti Landfredi, A. M.; Tiripicchio, A. *Inorg. Chim. Acta* **1982**, *57*, 87.

(45) Thompson, L. K.; Hartstock, F. W.; Robichaud, P.; Hanson, A. W., submitted for publication in *Can. J. Chem.*

(46) Mori, W.; Sakurai, T.; Nakahara, A.; Nakao, Y. *Inorg. Chim. Acta* **1982**, *65*, L51.

(47) O'Connor, C. J.; Romanach, R. J.; Robertson, D. M.; Edouk, E. E.; Fronczek, F. R. *Inorg. Chem.* **1983**, *22*, 449.

(48) Andrew, J. E.; Blake, A. B. *J. Chem. Soc. A* **1969**, 1408.

(49) Ball, P. W.; Blake, A. B. *J. Chem. Soc. A* **1969**, 1415.

(50) Ball, P. W.; Blake, A. B. *J. Chem. Soc., Dalton Trans.* **1974**, 852.