chemical process. The copper ion evidently adds a fifth ligand upon oxidation or releases it upon reduction.

In the TET complexes, the copper ion is in a high potential environment. $[Cu^{II}(TET)](ClO_4)_2$ is reduced to the Cu(I) complex upon prolonged standing in organic solution, and the reduction is immediate on addition of a drop of H_2O_2. This high Cu(II)/Cu(I) potential cannot be due only to the presence of π-acceptor diimine type ligands, since planar complexes of the macrocyclic bis(α-diimine) ligand TIM show very low Cu(II)/Cu(I) potentials (–0.34 V vs. NHE).[33] The geometry of the complex and the actual coordination number seem to influence the potential more than the nature of the ligand system, tetrahedral complexes showing the highest potentials. The potential of $[Cu(TET)]^+$ was also found to be very sensitive to anions: if 1 equiv of tetrabutylammonium chloride is added to a TMU solution of II, the reduction wave is shifted to +0.19 V, indicating strong coordination of chloride ion to the Cu(II) complex. With an excess (5 equiv) of tetrabutylammonium chloride, the solution of II becomes colorless and the ligand reduction waves vanish; the cyclic voltammogram obtained is identical with that of a solution of Cu(I) without TET in TMU in the presence of an excess of chloride. The displacement of TET from Cu(I) by chloride may be reversed by addition of 10% water: the orange color of the solution is restored, and the voltammogram of II reappears. We presume this to be due to the greater solvation (and thus weaker nucleophilicity) of chloride ion in the presence of water.

Conclusions

Our objective in undertaking this work was to study the influence of the relatively rigid biphenyl group as a spacer between two planar nitrogen-containing heterocycles. Although the flexibility of this pacing unit is limited to three torsion angles, this appears to be sufficient to allow a considerable variation in N–Cu–N angles where the two nitrogen atoms are separated by the biphenyl spacer: in the tetradentate N_2S_2 ligand 2,2′-bis((1-phenyl-3-methyl-5-(*tert*-butylthio)pyrazol-4-ylmethylene)amino)biphenyl[7] the angle subtended at the copper atom by the nitrogen atoms separated by the biphenyl spacer is 94.7 (2)°, whereas in the complex of Cu(II) with two 2,2′-bis(2-imidazolyl)biphenyl ligands[8] the angles are close to 140°. The values found with TET lie between these two extremes.

The failure of TET to impose a tetrahedral geometry on Cu(II) is shown not only by the crystal structure of III but also by the strong solvent dependence shown in the electrochemical measurements. Although TET cannot impose a tetrahedral geometry, it nonetheless appears to favor this geometry, as shown by the crystal structure of III, in which a strong Cu–N bond is weakened rather than the weaker Cu–Cl bond, and by the ease with which the Cu(II) complexes are reduced to Cu(I).

Registry No. I, 16291-44-4; II, 112595-90-1; III, 112595-95-6; $[Cu(TET)](ClO_4)_2$, 112595-92-3; $[Ni(dppe)Cl_2]$, 14647-23-5; $[Cu(AN)_4]ClO_4$, 14057-91-1; $[Ni(bpy)_2]^+$, 36450-97-2; 2,2′-dilithiobiphenyl, 16291-32-0; zinc biphenyl, 112595-96-7; 6-chloro-2,2′-bipyridine, 13040-77-2.

Supplementary Material Available: Full tables of bond distances and angles and a listing of atomic displacement parameters (17 pages); a table of observed structure factors in the format of the Standard Crystallographic Data File[34] (50 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7,
and Chemistry Division, National Research Council, Ottawa, Ontario, Canada K1A 0R6

Binuclear Complexes of the Ligand 3,6-Bis(2-pyridylthio)pyridazine Involving Homo- and Heterodiatomic Binuclear Centers (Cu–Cu, Cu–Co, Cu–Zn). Crystal Structure of Bis[μ-3,6-bis(2-pyridylthio)pyridazine-N^1,μ-N^2,μ-N^3,N^4](μ-chloro)dicopper(II) Triperchlorate–Acetonitrile[†]

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Homo- and heterobinuclear complexes (Cu–Cu, Cu–Co, Cu–Zn) of the ligand PTP (3,6-bis(2-pyridylthio)pyridazine) can be generated by the unprecedented reaction of the mononuclear complex $[Cu(PTP)_2(H_2O)](ClO_4)_2\cdot 3H_2O$ with the appropriate metal chloride salt in acetonitrile. The binuclear complexes have a unique binuclear cation $[CuM(PTP)_2Cl]^{3+}$ (M = Cu, Co, Zn) involving a triple-bridging arrangement between the two square-pyramidal metal centers (two diazine bridges and a chlorine bridge). The dicopper complex exhibits fairly strong antiferromagnetic exchange ($-2J = 479$ cm^{-1}), and the copper–cobalt derivative exhibits variable-temperature magnetism indicative of an interacting $S = {}^1/_2$, $S = {}^3/_2$ pair with $-4J = 29 \pm 3$ cm^{-1}. The crystal and molecular structure of $[Cu_2(PTP)_2Cl](ClO_4)_3\cdot CH_3CN$ is reported. This complex crystallizes in the orthorhombic system, space group *Pmcn*, with $a = 10.325$ (3) Å, $b = 17.917$ (5) Å, $c = 22.458$ (4) Å, and eight formula units per unit cell. A preliminary report of the structure of $[CuZn(PTP)_2Cl](ClO_4)_3\cdot CH_3CN\cdot H_2O$ is also described.

Introduction

Symmetrical, tetradentate (N_4) phthalazine and pyridazine ligands have been shown to form predominantly binuclear complexes, in which the diazine nitrogen pair is the binucleating focus of the ligand itself.[2-24] In a few cases, however, the ligands behave in a bidentate fashion with the formation of both mononuclear and binuclear derivatives.[9,25-27] The ligand 3,6-bis(2-pyridylthio)pyridazine (PTP, Figure 1) forms binuclear complexes $[Cu_2(PTP)(OH)X_3]$ (X = Cl, Br, NO_3), involving antiferro-

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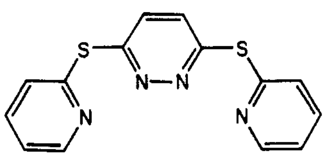

Figure 1. Structure of PTP.

magnetically coupled binuclear copper(II) centers, but with copper perchlorate only the mononuclear derivative, $[Cu(PTP)_2(H_2O)](ClO_4)_2\cdot 3H_2O$, could be obtained.[24] This complex is characterized by having an unusually high and positive reduction potential ($E_{1/2}$ = +0.57 V vs SCE in acetonitrile), which results in the formation of a copper(I) derivative on reaction with aqueous iodide.[27] The reduction product is, however, a rearranged binuclear copper(I) species, $[Cu_2(PTP)_2](I_3)_2$, involving two pseudotetrahedral copper(I) ions sandwiched between two tetradentate PTP ligands. The same binuclear copper(I) cations can be generated by simply refluxing $[Cu(PTP)_2(H_2O)](ClO_4)_2\cdot 3H_2O$ in methanol or acetonitrile, by reaction with triphenylphosphine in acetonitrile or sulfite in aqueous acetonitrile, or by coulometric reduction in acetonitrile.[27] The unusual rearrangement reactions from the mononuclear copper(II) complex to the binuclear copper(I) species are not just restricted to these redox processes. In this study we report the synthesis and characterization of binuclear derivatives of the type $[MM'(PTP)_2X]^{3+}$ (M = M' = Cu, X = Cl, OH; M = Cu, M' = Co, X = Cl; M = Cu, M' = Zn, X = Cl), which can be generated by reacting $[Cu(PTP)_2(H_2O)](ClO_4)_2\cdot 3H_2O$ with appropriate copper(II), cobalt(II), and zinc(II) salts.

Table I. Crystal Data for $Cu_2C_{30}H_{23}Cl_4N_9O_{12}S_4$

cryst syst	orthorhombic
space group	*Pmcn*
a, Å	10.325 (3)
b, Å	17.917 (5)
c, Å	22.458 (4)
V, Å^3	4154.54
Z	8
ρ(calcd), g cm^{-3}	1.757
μ, mm^{-1}	1.55
radiation (λ), Å (Mo Kα)	0.709 30
temp for data collcn, °C	22

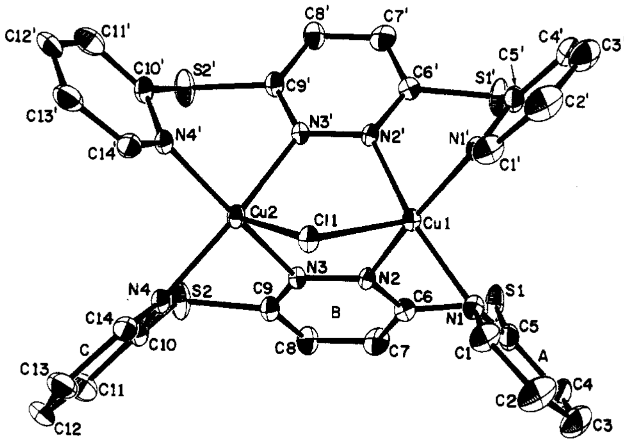

Figure 2. Structural representation of the cation in $[Cu_2(PTP)_2Cl](ClO_4)_3\cdot CH_3CN$ (I) with hydrogen atoms omitted (40% probability thermal ellipsoids).

Experimental Section

Synthesis of PTP and Its Complexes. The synthesis of PTP has already been reported.[24]

$[Cu_2(PTP)_2Cl](ClO_4)_3\cdot CH_3CN$ (I). $[Cu(PTP)_2(H_2O)](ClO_4)_2\cdot 3H_2O$[24] (0.46 g, 0.5 mmol) was dissolved in cold acetonitrile (25 mL) and added quickly to a solution of $CuCl_2\cdot 2H_2O$ (0.17 g, 1.0 mmol) dissolved in cold acetonitrile (50 mL). The resulting mixture was allowed to stand at room temperature until green crystals formed. The product (0.28 g) was filtered off, washed with cold acetonitrile, and dried in air. The mixed metal complexes (III, IV) were prepared in a similar manner by using hydrated chloride salts of the appropriate metal. In all cases only the first fraction of the crystallized product produced was used. Anal. Calcd for $[Cu_2(C_{14}H_{10}N_4S_2)_2Cl](ClO_4)_3\cdot CH_3CN$ (I): C, 32.76; H, 2.09; N, 11.47. Found: C, 32.56; H, 2.11; N, 11.42. Anal. Calcd for $[CuCo(C_{14}H_{10}N_4S_2)_2Cl](ClO_4)_3\cdot(CH_3CN)_2\cdot 0.5H_2O$ (III): C, 33.59; H, 2.36; N, 12.25; Co, 5.15; Cu, 5.55. Found: C, 33.56; H, 2.31; N, 12.12; Co, 5.01; Cu, 5.96. Anal. Calcd for $[CuZn(C_{14}H_{10}N_4S_2)_2Cl](ClO_4)_3\cdot 2CH_3CN$ (IV): C, 33.67; H, 2.27; N, 12.26. Found: C, 33.86; H, 2.29; N, 12.19. The X-ray sample of this compound had the formula $[CuZn(PTP)_2Cl](ClO_4)_3\cdot CH_3CN\cdot H_2O$.

$[Cu_2(PTP)_2(OH)](ClO_4)_3\cdot CH_3CN\cdot 1.5H_2O$ (II). A cold solution of $[Cu(PTP)_2(H_2O)](ClO_4)_2\cdot 3H_2O$[24] (0.46 g, 0.5 mmol) in acetonitrile (20 mL) was added to a cold solution of $CuCl_2\cdot 2H_2O$ (0.17 g, 1.0 mmol) in acetonitrile (50 mL). Triethylamine (0.10 g, 0.50 mmol) dissolved in acetonitrile (10 mL) was then added, and the mixture was stirred for 20 m, the solution filtered, and the filtrate allowed to stand at room temperature until green crystals formed. The product was filtered off, washed with ethanol, and air-dried. Anal. Calcd for $[Cu_2(C_{14}H_{10}N_4S_2)_2(OH)](ClO_4)_3\cdot CH_3CN\cdot 1.5\text{-}H_2O$ (II): C, 32.54; H, 2.44; N, 11.39. Found: C, 32.61; H, 2.27; N, 11.41.

C, H, and N analyses were carried out by Canadian Microanalytical Service, Vancouver, Canada, and metal analyses were obtained on a Varian Techtron AA-5 instrument after sample digestion in concentrated HNO_3.

Magnetic Measurements. Room-temperature magnetic moments were measured by the Faraday method using a Cahn 7600 Faraday magnetic susceptibility system. Variable-temperature magnetic susceptibility data were obtained in the range 5–300 K (compounds I, III) by using an Oxford Instruments superconducting Faraday magnetic susceptibility system with a Sartorius 4432 microbalance. A main solenoid field of 1.5 T and a gradient field of 10 T m^{-1} were employed.

Infrared and Electronic Spectra. Infrared spectra were recorded as Nujol mulls with a Perkin-Elmer 283 instrument and electronic spectra with a Cary 17 instrument.

Crystallographic Data Collection and Refinement of the Structure of $[Cu_2(PTP)_2Cl](ClO_4)_3\cdot CH_3CN$ (I). Crystals of I are green. The diffraction intensities of an approximately 0.20 × 0.20 × 0.20 mm crystal were collected with graphite-monochromatized Mo Kα radiation by using the $\theta/2\theta$ scan technique with profile analysis[28] to $2\theta_{max}$ = 45° on a Picker

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Table II. Final Atomic Positional Parameters and Equivalent Isotropic Debye–Waller Temperature Factors (Esd's) for $[Cu_2(PTP)_2Cl](ClO_4)_3\cdot CH_3CN$ (I)

atom	*x*	*y*	*z*	B_{iso}, Å^2
Cu(1)	0.75000 (0)	0.24937 (8)	0.11223 (6)	2.18 (6)
Cu(2)	0.75000 (0)	0.42960 (7)	0.13491 (6)	2.30 (6)
Cl(1)	0.75000 (0)	0.35448 (14)	0.04385 (11)	2.48 (13)
Cl(2)	0.25000 (0)	0.37149 (30)	0.10332 (19)	6.51 (26)
Cl(3)	0.75000 (0)	0.29715 (29)	0.34252 (17)	7.09 (28)
Cl(4)	0.25000 (0)	0.47004 (20)	0.37686 (14)	4.24 (21)
S(1)	0.9454 (3)	0.15275 (11)	0.19019 (9)	4.54 (13)
S(2)	0.9504 (3)	0.49231 (11)	0.23206 (9)	4.58 (13)
O(1)	0.2500 (0)	0.4081 (7)	0.1586 (5)	13.1 (11)
O(2)	0.2500 (0)	0.4205 (9)	0.0555 (6)	18.9 (15)
O(3)	0.1428 (10)	0.3341 (6)	0.0981 (4)	17.3 (8)
O(4)	0.7500 (0)	0.2346 (8)	0.3024 (4)	11.4 (9)
O(5)	0.7500 (0)	0.3634 (7)	0.3143 (6)	12.3 (9)
O(6)	0.8601 (10)	0.2896 (4)	0.3756 (3)	13.7 (7)
O(7)	0.2500 (0)	0.5124 (5)	0.4311 (4)	6.3 (6)
O(8)	0.1059 (15)	0.4615 (10)	0.3659 (7)	7.8 (10)
O(9)	0.2867 (31)	0.5082 (7)	0.3280 (5)	8.6 (16)
O(10)	0.2978 (35)	0.4032 (6)	0.3799 (7)	12.0 (28)
N(1)	0.8901 (6)	0.1866 (3)	0.07634 (28)	2.8 (3)
N(2)	0.8825 (6)	0.2928 (3)	0.16844 (22)	2.0 (3)
N(3)	0.8831 (6)	0.3666 (3)	0.17737 (22)	1.9 (3)
N(4)	0.8901 (6)	0.5028 (3)	0.11706 (26)	2.5 (3)
N(5)	0.2500 (0)	0.1828 (11)	0.33907 (59)	7.7 (9)
C(1)	0.9098 (10)	0.1804 (5)	0.0172 (4)	3.9 (5)
C(2)	0.9955 (13)	0.1299 (7)	−0.0051 (5)	5.7 (7)
C(3)	1.0673 (11)	0.0851 (6)	0.0291 (5)	5.3 (6)
C(4)	1.0573 (9)	0.0925 (5)	0.0908 (5)	5.0 (6)
C(5)	0.9658 (8)	0.1452 (4)	0.1128 (3)	3.2 (4)
C(6)	0.9591 (7)	0.2502 (4)	0.1993 (3)	2.7 (4)
C(7)	1.0428 (10)	0.2784 (5)	0.2433 (4)	3.9 (5)
C(8)	1.0439 (9)	0.3542 (4)	0.2539 (3)	3.6 (4)
C(9)	0.9614 (8)	0.3955 (4)	0.2171 (3)	2.8 (4)
C(10)	0.9690 (8)	0.5280 (4)	0.1594 (3)	2.9 (4)
C(11)	1.0585 (9)	0.5827 (5)	0.1506 (4)	4.1 (5)
C(12)	1.0674 (11)	0.6131 (6)	0.0933 (6)	5.3 (6)
C(13)	0.9907 (9)	0.5873 (5)	0.0468 (4)	4.3 (5)
C(14)	0.9053 (8)	0.5308 (4)	0.0596 (4)	3.3 (4)
C(15)	0.2500 (0)	0.2074 (12)	0.3879 (11)	9.6 (16)
C(16)	0.2500 (0)	0.2372 (11)	0.4494 (8)	11.2 (14)
H(1)	0.849 (6)	0.211 (3)	−0.0031 (25)	2.2 (18)
H(2)	0.992 (7)	0.125 (4)	−0.0344 (24)	0.5 (18)
H(3)	1.143 (8)	0.044 (4)	0.0110 (36)	9.8 (30)
H(4)	1.113 (11)	0.067 (6)	0.1282 (47)	17.4 (47)
H(5)	1.094 (7)	0.251 (4)	0.2671 (31)	5.3 (24)
H(6)	1.101 (11)	0.379 (6)	0.2866 (52)	16.1 (45)
H(7)	1.123 (5)	0.594 (3)	0.1775 (24)	1.0 (15)
H(8)	1.125 (8)	0.642 (4)	0.0891 (36)	5.8 (29)
H(9)	1.034 (9)	0.617 (4)	0.0002 (36)	9.7 (27)
H(10)	0.845 (6)	0.504 (3)	0.0197 (26)	4.2 (19)

four-circle diffractometer. A total of 2916 reflections were measured, of which 2916 were unique and 1984 reflections were considered significant with $I_{net} > 2.5\sigma(I_{net})$. Lorentz and polarization factors were applied, but no correction was made for absorption. The cell parameters were obtained by the least-squares refinement of the setting angles of 54 reflections with 2θ in the range 40–42° (λ(Mo Kα_1) = 0.70930 Å).

The structure was solved by direct methods using MULTAN[29] and refined by full-matrix least-squares methods to final residuals of $R = 0.046$ and $R_W = 0.037$ for all data with weights based on counting statistics. The hydrogen atoms on the ligand, PTP, were located from a *D* map and refined. One perchlorate anion shows disorder over two positions that are related by mirror symmetry. All calculations were performed with the NRCVAX system of programs.[30] Scattering factors were taken from ref 31. Crystal data are given in Table I, and final atomic positional parameters and equivalent isotropic temperature factors are given in Table II. Anisotropic thermal parameters (Table SI) and a listing of structure factors (Table SII) are included as supplementary material.

Table III. Interatomic Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in $[Cu_2(PTP)_2Cl](ClO_4)_2\cdot CH_3CN$ (I)

Cu(1)–Cu(2)	3.269 (2)	Cu(2)–Cl(1)	2.448 (3)
Cu(1)–Cl(1)	2.430 (3)	Cu(2)–N(3)	2.018 (5)
Cu(1)–N(1)	2.002 (6)	Cu(2)–N(3)′	2.018 (5)
Cu(1)–N(1)′	2.002 (6)	Cu(2)–N(4)	1.994 (6)
Cu(1)–N(2)	2.018 (6)	Cu(2)–N(4)′	1.994 (6)
Cu(1)–N(2)′	2.018 (6)		
Cl(1)–Cu(1)–N(1)	100.4 (2)	Cl(1)–Cu(2)–N(3)′	95.0 (2)
Cl(1)–Cu(1)–N(1)′	100.4 (2)	Cl(1)–Cu(2)–N(4)	101.2 (2)
Cl(1)–Cu(1)–N(2)	95.5 (2)	Cl(1)–Cu(2)–N(4)′	101.2 (2)
Cl(1)–Cu(1)–N(2)′	95.5 (2)	N(3)–Cu(2)–N(3)′	85.8 (2)
N(1)–Cu(1)–N(1)′	92.5 (3)	N(3)–Cu(2)–N(4)	88.2 (2)
N(1)–Cu(1)–N(2)	88.8 (2)	N(3)–Cu(2)–N(4)′	163.2 (2)
N(1)–Cu(1)–N(2)′	163.4 (2)	N(3)′–Cu(2)–N(4)	163.2 (2)
N(1)′–Cu(1)–N(2)	163.4 (2)	N(3)′–Cu(2)–N(4)′	88.2 (2)
N(1)′–Cu(1)–N(2)′	88.8 (2)	N(4)–Cu(2)–N(4)′	93.0 (2)
N(2)–Cu(1)–N(2)′	85.4 (2)	Cu(1)–Cl(1)–Cu(2)	84.2 (1)
Cl(1)–Cu(2)–N(3)	95.0 (2)		

Results and Discussion

Description of the Structure of $[Cu_2(PTP)_2Cl](ClO_4)_3\cdot CH_3CN$ (I). The structure of I is shown in Figure 2, and distances and angles relevant to the copper coordination spheres are given in Table III. The binuclear cation consists of two distorted square-pyramidal copper(II) atoms sandwiched between two adjacent ligands and bridged equatorially by two diazine groups and apically by a chlorine. The in-plane copper–nitrogen contacts are relatively short (2.002, 2.018 Å) and typical of systems of this sort, but the apical copper–chlorine distances are long (Cu(1)–Cl(1) = 2.430, Cu(2)–Cl(1) = 2.448 Å). Intramolecular copper–sulfur contacts are too large to consider any significant Cu–S bonding interactions (Cu(1)–S(1) = 3.183 (2), Cu(2)–S(2) = 3.210 (3) Å), and intermolecular contacts exceed 5 Å. The two copper square pyramids are canted toward each other as a result of the bridging function of the apical chlorine atom and the two ligands adopt a symmetrical "butterfly" twist. The pyridine rings (A and C, Figure 2) are mutually inclined by 89.2° and inclined by 124.8 and 124.9°, respectively, to the pyridazine plane, B. Each copper center is raised by above the mean plane of the four equatorial nitrogen donors (Cu(1) +0.282 Å; Cu(2) +0.286 Å). The angle at the chlorine bridge is 84.2°, and the copper atoms are separated by 3.269 Å. The metal–metal separation is significantly larger than that observed for the complex $[Cu_2(PTP)Cl_4]\cdot CH_3CH_2OH$ (3.198 Å), which involves a single diazine and two chlorine bridges,[11] and for the complex $[Cu_2(PAP)(OH)Cl_3]\cdot 1.5H_2O$ (3.001, 2.972 Å), which has a diazine (phthalazine), chlorine and a hydroxide bridge.[3] The expansion of the binuclear center in I can be seen as a direct result of interposing a second diazine bridge in between the two copper atoms. In fact this copper–copper separation is larger than that found in related complexes involving the bidentate bridging anions IO_3^-, SO_4^{2-}, and NO_3^-.[4,6]

A preliminary X-ray structural investigation of the copper–zinc complex (IV) shows that this complex has a structure essentially identical with that of I with a five-coordinate square-pyramidal copper(II) center and a five-coordinate square-pyramidal zinc(II) center bound between the two tetradentate ligands and apically bridged by a chlorine atom.[32] The poor current refinement of this structure (12.3%), due to disordered perchlorates and the water molecule and possible Cu–Zn disorder, limits the accuracy of bond length and angle data, but the binuclear center dimensions are comparable with those of I.[33]

Synthesis, Spectroscopic, and Magnetic Properties. The common synthetic route to the homobimetallic and heterobimetallic

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(31) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B, p 99.

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(33) Crystal Data for $[CuZn(PTP)_2Cl](ClO_4)_3\cdot CH_3CN\cdot H_2O$ (IV): monoclinic, $C2/m$, $a = 37.560$ (5) Å, $b = 10.389$ (3) Å, $c = 12.1342$ (13) Å, $\beta = 108.900$ (10)°, $V = 4479.60$ Å^3, $Z = 4$, ρ(calcd) = 1.597 g cm^{-3}, $\mu = 2.97$ mm^{-1} for 3077 unique reflections and 1549 with $I_{net} > 2.5\sigma(I_{net})$.

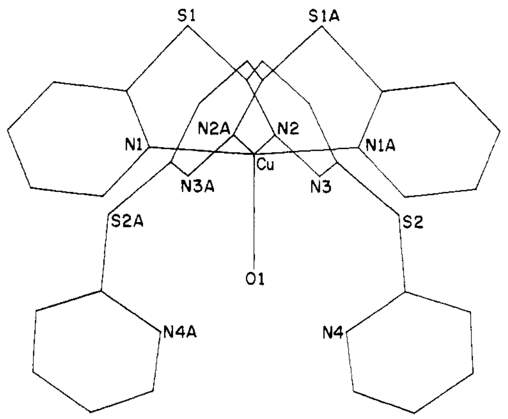

Figure 3. Structural representation of the cation in $[Cu(PTP)_2(H_2O)](ClO_4)_2 \cdot 3H_2O$.

chloro complexes of PTP involves the reaction of the relatively stable mononuclear derivative $[Cu(PTP)_2(H_2O)](ClO_4)_2 \cdot 3H_2O$ with the appropriate metal chloride in acetonitrile. The formation of a mononuclear complex by the ligand PTP, which, by virtue of the juxtaposition of the four nitrogen donor groups, would be expected to preferentially form binuclear derivatives, is somewhat surprising but can be related to the poor donor characteristics of other potential ligand groups that would otherwise occupy vacant coordination sites in generating a binuclear structural arrangement. Reaction of copper chloride and copper bromide with PTP produces binuclear complexes $[Cu_2(PTP)X_4]$ and $[Cu_2(PTP)(OH)X_3]$ (X = Cl, Br), which involve five-coordinate copper(II) centers[11,24,34] and bridging and terminal halogens bound to each copper center.

The structure of $[Cu(PTP)_2(H_2O)](ClO_4)_2 \cdot 3H_2O$ (Figure 3) involves a five-coordinate distorted-square-pyramidal copper(II) ion with two bidentate ligands bound by a diazine nitrogen and a pyridine nitrogen in a trans fashion and an axially bound water. In-plane copper–nitrogen distances are relatively short (Cu–N(1) = 2.016, Cu–N(2) = 1.993 Å) and the axial water molecule is quite tightly bound (Cu–O(1) = 2.136 Å).[27] The trans nature of the two bidentate PTP ligands necessitates a major molecular rearrangement in order to allow the formation of binuclear derivatives, in which the metal centers have a cis arrangement of nitrogen donors, in reactions involving the formation of mixed-metal and binuclear copper(II) derivatives and also the formation of binuclear copper(I) derivatives.[27] Although the complex $[Cu(PTP)_2(H_2O)](ClO_4)_2 \cdot 3H_2O$ has been formally described as having a square-pyramidal structure, the distortions around the copper center give it a structure intermediate between the five-coordinate extremes of a square pyramid and a trigonal bipyramid. Assuming the structure to be that of a distorted trigonal bipyramid (rather than a square pyramid), axial donors can be defined by nitrogen atoms N(1) and equatorial donors by nitrogen atoms N(2) and the water molecule (Figure 3). The stereochemical nonrigidity of five-coordinate complexes allows the interchange of axial and equatorial donors (Berry pseudorotation[35]), and if the water molecule were to retain its equatorial status, such a rearrangement of the nitrogen donors would allow the formation of a cis intermediate, thus presenting four nitrogen donors in a suitable group to attract an incoming metal ion in the formation of a binuclear cis derivative (Figure 4). Simultaneous attack by a chlorine atom, in displacing the coordinated water molecule, would form the chloro bridge between the two metal centers.

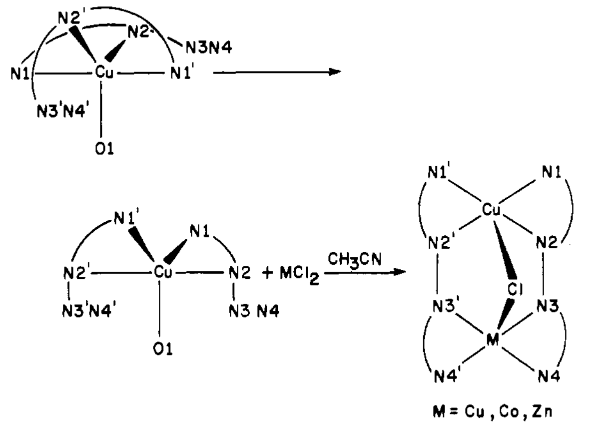

Figure 4. Proposed scheme for conversion of $[Cu(PTP)_2(H_2O)](ClO_4)_2 \cdot 3H_2O$ to binuclear products.

Table IV. Electronic Spectral, Magnetic, and Conductance Data

compd	d–d, cm^{-1}	μ_{eff},[c] μ_B	Λ_M,[d] mho mol^{-1} cm^2
$[Cu_2(PTP)_2Cl](ClO_4)_3 \cdot CH_3CN$ (I)	11 400 (243), 23 300 (543)[a] 16 900[b]	1.05	209
$[Cu_2(PTP)_2(OH)](ClO_4)_3 \cdot CH_3CN \cdot 1.5H_2O$ (II)	12 200 (161)[a] 16 400[b]	1.38	175
$[CuCo(PTP)_2Cl](ClO_4)_3 \cdot 2CH_3CN \cdot 0.5H_2O$ (III)	11 400 (164), 15 040 (175), 16 700 (90), 23 800 (273)[a] 15 050, 15 900, 16 700[b]	4.6	188
$[CuZn(PTP)_2Cl](ClO_4)_3 \cdot CH_3CN \cdot H_2O$ (IV)	11 900 (117)[a] [16 100], 17 900[b]	1.84	209

[a] Solution in DMF (ε, L mol^{-1} cm^{-1}). [b] Mull transmittance. [c] Magnetic moment per mole of copper (I, II) and per mole of complex (III, IV) at room temperature. [d] Molar conductance in DMF.

Infrared spectra on these complexes are not very informative. They are all very similar, and strong, single ν_3 perchlorate absorptions are observed in all cases in the range 1080–1100-cm^{-1}, indicative of ionic perchlorate. A weak absorption at 3480 cm^{-1} for II is associated with the hydroxide bridge. In each case a sharp absorption at approximately 1020 cm^{-1} is associated with a pyridine ring breathing vibration and indicates pyridine coordination,[2] typical of the tetradentate function of ligands of this sort. The solid-state, mull transmittance, electronic spectra of all the complexes have major absorptions in the range 15 000–18 000 cm^{-1}, which are associated with a five-coordinate, square-pyramidal copper(II) center (Table IV). For III, three major solid-state bands are observed, associated with both the cobalt(II) and the copper(II) centers. The band at 15 900 cm^{-1}, which is absent in the solution spectrum, is assigned to a five-coordinate copper(II) center, and the other bands are associated with the cobalt(II) center, which is reasonably assumed to have a square-pyramidal stereochemistry. DMF solution spectra of all the complexes exhibit a low-energy absorption (11 400–12 200 cm^{-1}), associated with the copper(II) centers, indicating a significant change in the copper chromophore in solution. Conductance data in DMF (Table IV) indicate that the solution species are 1:3 electrolytes[36] in all cases, which suggests that the chlorine and hydroxo bridge groups probably remain intact in solution. The broad, fairly intense, absorption found in the range 11 400–12 200 cm^{-1} for these compounds is therefore associated with a six-coordinate solution species involving coordinated DMF. The high-energy, much more intense band (>23 000 cm^{-1}) present in some of the spectra is associated with a charge-transfer transition. The two fairly intense DMF solution bands observed for III at 15 040 and 16 700 cm^{-1}, which are unshifted from the solid-state spectrum, suggest the presence of a five-coordinate rather than six-coordinate cobalt(II) center in solution.

The room-temperature magnetic moments of compounds I and II are significantly reduced from the spin-only value for copper(II), indicating spin-coupled copper(II) centers. A variable-temperature magnetic study on I was carried out in the range 5–300 K. The results are summarized in Figure 5. The best-fit line was cal-

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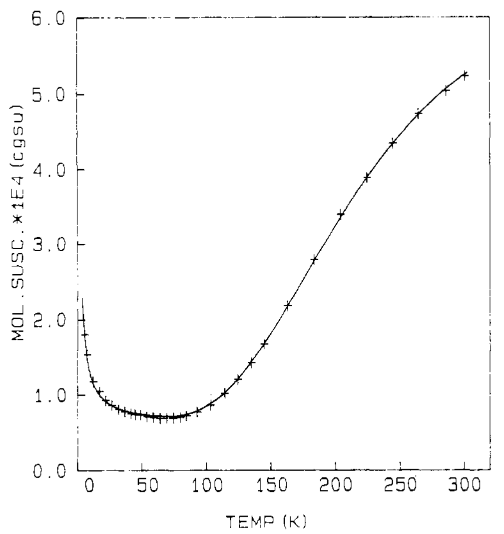

Figure 5. Magnetic susceptibility data for $[Cu_2(PTP)_2Cl](ClO_4)_3 \cdot CH_3CN$ (I). The solid line was calculated from (1) with $g = 2.190 \pm 0.007$, $-2J = 479 \pm 1$ cm^{-1}, and $N\alpha = 60 \times 10^{-6}$ cgsu (cm^3 mol^{-1})/Cu, assuming 0.15% paramagnetic impurity ($\rho = 0.0015$).

culated from the modified Van Vleck equation[37] for exchange-coupled pairs of copper(II) ions (eq 1), where $2J$ (in the spin

$$\chi_m = \frac{N\beta^2 g^2}{3kT}\left[1 + \frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1}(1-\rho) + \left[\frac{N\beta^2 g^2}{4kT}\right]\rho + N\alpha \quad (1)$$

Hamiltonian $H = 2J\hat{S}_1 \cdot \hat{S}_2$) is the singlet–triplet splitting or exchange integral and other symbols have their usual meaning (ρ represents the fraction of a possible magnetically dilute copper(II) impurity). The temperature-independent paramagnetism for a binuclear copper(II) complex, $N\alpha$, was taken as 120×10^{-6} cgsu/mol, and the parameters giving the best fit were obtained by using a nonlinear regression analysis with ρ as a floating parameter. The exchange integral for I ($-2J$) was found to be 479 ± 1 cm^{-1} indicating quite strong exchange between the copper(II) centers.

Examples of binuclear copper(II) complexes of this sort involving two metal centers sandwiched between two tetradentate diazine ligands are rare and are restricted to ligands involving five-membered chelate rings. The ligand 3,5-bis(pyridin-2-yl)-1,2,4-triazole (bpt) forms 1:1 dimeric, and essentially planar, binuclear complexes, $[Cu(bpt)(H_2O)_2(X)_2]_2$ (X = CF_3SO_3, ClO_4, NO_3, BF_4), which have modest antiferromagnetic exchange between the copper centers, occurring via a superexchange mechanism involving the diazine bridge ($-2J$ = 204–236 cm^{-1}).[38] Considerably enhanced exchange is observed for I, indicating that the pyridazine bridge mediates exchange much more efficiently than the triazole anion. The axially bound bridging chlorine should not behave as a participant in the exchange process (orthogonal) but may influence the exchange to a minor extent due to its electronegative nature.[39]

The hydroxy-bridged compound (II) has a reduced room-temperature magnetic moment indicative of antiferromagnetic exchange, although it is clear that this system is somewhat less strongly coupled than I. It would seem reasonable to assume that a similar apically bridged structure to I would exist for this compound. If the apical hydroxide bridge does not take part in the exchange process, then the difference in the magnetic moments can be rationalized in terms of the difference in the electronegativity of the bridge groups, with the result that metal d electron density is more strongly polarized by the hydroxide bridge, thus limiting the exchange process to some extent via the diazine bridges.[39]

The relatively low room-temperature magnetic moment for III would suggest a spin-coupled situation, and preliminary variable-temperature magnetic data (5–300 K) on the copper–cobalt complex indicate this to be the case. By use of the Heisenberg model for an interacting $S = {}^1/_2$, $S = {}^3/_2$, pair the energy separation between the supposed spin-triplet ground state and the spin-quintet excited state ($-4J$) is found to be 29 ± 3 cm^{-1} for $g = 2.45 \pm 0.03$ (TIP set at 450×10^{-6} cgsu mol^{-1}). This value is much smaller than those observed for a series of planar diphenoxide-bridged copper(II)–cobalt(II) complexes derived from Schiff base adducts of 3-formylsalicylic acid and various diamines, which fall in the range 140–200 cm^{-1} ($-4J$).[40] The larger values observed for such systems are reasonable based on the ease with which such oxygen bridge groups propagate spin exchange in binuclear copper(II) systems. The copper–zinc complex IV behaves magnetically like a mononuclear system, as would be expected.

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Registry No. I, 112621-03-1; II, 112596-31-3; III, 112596-33-5; IV, 112621-05-3; IV·H_2O, 112710-06-2; $[Cu(PTP)_2(H_2O)](ClO_4)_2$, 106856-01-3.

Supplementary Material Available: Table SI, listing anisotropic thermal parameters, and Table SIII, giving a complete listing of bond lengths and angles for I along with atom coordinates and symmetry equivalents used (8 pages); Table SII, listing observed and calculated structure factors for I (39 pages). Ordering information is given on any current masthead page.

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