reported study. D.K.L. wishes to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and gratefully acknowledges the PSC-BHE grant program of the City University of New York, for partial support of this work.

Registry No. Fe(*N*-MeTPP)Cl, 64813-94-1; Fe(TPP)Cl, 16456-81-8; Mn(*N*-MeTPP)Cl, 59765-80-9; Co(*N*-MeTPP)Cl, 51552-52-4; Zn(*N*-MeTPP)Cl, 59765-81-0.

Supplementary Material Available: Table VII listing the calculated hydrogen atom positions, Table VIII listing the anisotropic thermal parameters for the nonhydrogen atoms and Table IX listing observed and calculated structure factor amplitudes (×10) (21 pages). Ordering information is given on any current masthead page.

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Reactions of Metal Ions with Vitamins. 2. Crystal Structures of Copper Complexes with Anionic and with Neutral Pyridoxamine[1]

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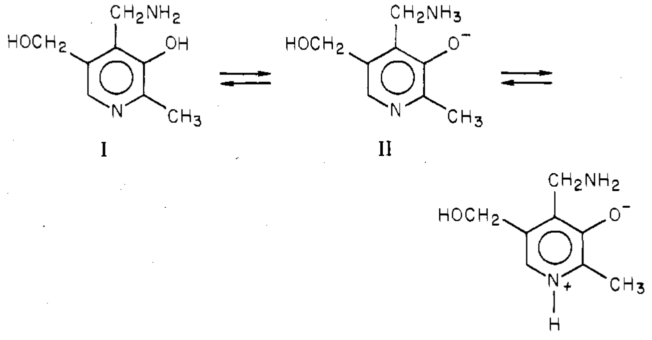
Received January 30, 1980

The crystal structures of the two pyridoxamine (PM) complexes $Cu(PM)_2(NO_3)_2 \cdot H_2O$ ($CuC_{16}H_{26}N_6O_{11}$) and $Cu(PM\text{-}H)_2 \cdot 2H_2O$ ($CuC_{16}H_{26}N_4O_6$) have been determined from three-dimensional X-ray data collected by counter methods. $Cu(PM)_2(NO_3)_2 \cdot H_2O$ crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ and cell dimensions $a = 14.248$ (2) Å, $b = 8.568$ (1) Å, $c = 9.319$ (1) Å, $\alpha = 94.08$ (1)°, $\beta = 89.73$ (1)°, and $\gamma = 99.13$ (1)°. The observed and calculated densities are both 1.61 g/cm^3. The structure was refined to a final R factor of 0.041 for 2390 observed reflections. The copper atoms lie on centers of symmetry and are chelated to the PM ligands through the 4-(aminomethyl) and phenolate groups of a PM zwitterion. Six-coordination is completed by nitrate groups, which bridge adjacent copper chelates through a single oxygen atom. $Cu(PM\text{-}H)_2 \cdot 2H_2O$ crystallizes in the orthorhombic space group *Pbca*, with cell dimensions $a = 10.982$ (1), $b = 13.918$ (1), and $c = 12.095$ (1) Å. The observed and calculated densities are 1.56 (1) and 1.57 g/cm^3, respectively, for $Z = 4$. The copper ions in this structure are also located on centers of symmetry and are chelated to the PM anions. Six-coordination of copper is completed by hydroxymethyl groups from neighboring molecules.

Introduction

Metal complexes of the B_6 vitamins and the Schiff bases derived from them have been an interesting area of study for the bioinorganic chemist.[2] Much research has been concerned with the liganding sites in these compounds.[3-14] In PM and PN, chelation though the 4-(aminomethyl) or 4-(hydroxymethyl) and phenolic groups has been suggested, whereas other experimental evidence points to bonding though the pyridine nitrogen or the side chains in the 5-position.[9-14] Chelation is always observed in the Schiff-base compounds.[15-22]

The question of binding site is complicated by the possibilities for tautomerism in the B_6 vitamins. For example, neutral PM has three tautomeric forms:



I II III

Tautomer II, which is the one actually found in crystalline PM and PM solutions,[23] is incapable of chelation because the amino group is protonated. Thus if chelation is to occur, one of the other two tautomers must be generated.

The two crystal structures reported herein for copper complexes of neutral and anionic PM show that chelation does in fact occur through the aminomethyl and phenolate groups of tautomer III and its anion. In addition, the hydroxymethyl

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(1) For part 1 see M. F. Richardson, K. Franklin, and D. M. Thompson, *J. Am. Chem. Soc.*, **97**, 3204 (1975).
(2) R. H. Holm, *Inorg. Biochem.*, **2**, 1137-1167 (1973).
(3) R. L. Gustafson and A. E. Martell, *Arch. Biochem. Biophys.*, **68**, 485 (1957).
(4) M. E. Farago, M. M. McMillan, and S. S. Sabir, *Inorg. Chim. Acta*, **14**, 207 (1975).
(5) M. S. El-Ezaby and F. R. El-Eziri, *J. Inorg. Nucl. Chem.*, **38**, 1901 (1976).
(6) F. Gaillais, R. Haran, J. P. Laurent, and F. Nepveu-Juras, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **284**, 29 (1977).
(7) K. J. Franklin and M. F. Richardson, *J. Chem. Soc., Chem. Commun.*, 97 (1978).
(8) A. Mosset, F. Nepveu-Juras, R. Haran, and J. J. Bonnet, *J. Inorg. Nucl. Chem.*, **40**, 1259 (1978).
(9) E. C. Kelusky and J. S. Hartman, *Can. J. Chem.*, **57**, 2118 (1979).
(10) T. S. Viswanathan and T. J. Swift, *Can. J. Chem.*, **57**, 1050 (1979).
(11) M. S. El-Ezaby and N. Gayed, *J. Inorg. Nucl. Chem.*, **37**, 1065 (1975).
(12) Ya. D. Fridman and M. G. Levina, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **19**, 1324 (1974).
(13) M. S. El-Ezaby, M. Rashad, and N. M. Moussa, *J. Inorg. Nucl. Chem.*, **39**, 175 (1977).
(14) L. Asso, M. Asso, J. Mossoyan, and D. Benlian, *J. Chim. Phys. Phys.-Chim. Biol.*, **75**, 561 (1978).
(15) E. Willstadter, T. A. Hamor, and J. L. Hoard, *J. Am. Chem. Soc.*, **85**, 1205 (1963).
(16) J. F. Cutfield, D. Hall, and T. N. Waters, *Chem. Commun.*, 785 (1967).
(17) G. A. Bentley, J. M. Waters, and T. N. Waters, *Chem. Commun.*, 988 (1968).
(18) S. Yamada, Y. Kuge, T. Yamayoshi, and H. Kuma, *Inorg. Chim. Acta*, **11**, 253 (1974).
(19) S. Capasso, F. Giordano, C. Mattia, L. Mazzarella, and A. Ripamonti, *J. Chem. Soc., Dalton Trans.*, 2228 (1974).
(20) J. T. Wrobleski and G. L. Long, *Inorg. Chem.*, **16**, 2752 (1977).
(21) M. Nardelli, C. Pelizzi, and G. Predieri, *Transition Met. Chem.*, **3**, 233 (1978).
(22) M. Darriet, A. Cassaigne, J. Darriet, and N. Neuzil, *Acta Crystallogr., Sect. B*, **34**, 2105 (1978).
(23) O. A. Gansow and R. H. Holm, *Tetrahedron*, **24**, 4477 (1968).

0020-1669/80/1319-2107$01.00/0

groups are bonded to copper in the anionic PM complex.

Experimental Section

Triclinic crystals of $Cu(PM)_2(NO_3)_2 \cdot H_2O$ were prepared by evaporation of an aqueous solution containing equimolar amounts of $Cu(NO_3)_2 \cdot 3H_2O$ and PM.[24] A perfectly shaped green parallelepiped, 0.43 × 0.15 × 0.03 mm, was mounted on a glass fiber with epoxy cement and aligned about the b^* axis on the Picker manual four-circle diffractometer. Cell dimensions were determined from scans of the axial reflections as well as certain $0kl$, $h0l$, and $hk0$ reflections (chosen to optimize the determinations of α, β, and γ). Scans were taken out to $2\theta = 60°$ with Mo Kα radiation ($\lambda = 0.709\,26$ Å for Mo Kα_1). The cell parameters are $a = 14.248$ (2) Å, $b = 8.568$ (1) Å, $c = 9.319$ (1) Å, $\alpha = 94.08$ (1)°, $\beta = 89.73$ (1)°, and $\gamma = 99.13$ (1)°, with space group $P1$ or $P\bar{1}$ (successfully refined in $P\bar{1}$), $Z = 2$ units of $CuC_{16}H_{26}N_6O_{11}$, $d_{obsd} = 1.61$ g/cm^3 (flotation), $d_{calcd} = 1.61$ g/cm^3, and μ(Mo Kα) = 10.90 cm^{-1}.

Orthorhombic crystals of $Cu(PM\text{-}H)_2 \cdot 2H_2O$ were synthesized by recrystallization of the brown hexahydrate, which was prepared by cooling a hot aqueous solution of $Cu(NO_3)_2$ and PM (1:2 mole ratio).[24] Repeated attempts to get good crystals were frustrating because of coprecipitation of the brown hexahydrate. One large, dark green, chunky crystal with well-developed faces was eventually chosen for the X-ray study. Its dimensions were 0.54 × 0.51 × 0.40 mm. After alignment about the b^* axis on the diffractometer, cell dimensions were determined as described above: $a = 10.982$ (1), $b = 13.918$ (1), $c = 12.095$ (1) Å; space group $Pbca$; $Z = 4$ units of $CuC_{16}H_{26}N_4O_6$; $d_{obsd} = 1.56$ (1) g/cm^3 (flotation), $d_{calcd} = 1.57$ g/cm^3; μ(Mo Kα) = 11.60 cm^{-1}.

Data were collected by ω–2θ scans on a manual Picker four-circle diffractometer with Zr-filtered Mo Kα radiation. Scans were made over a 2θ range of 1.333° at a rate of 1°/min. Ten-second backgrounds were counted at each end of the scan range. A standard reflection was measured after every 25–30 reflections and did not vary significantly during the data collection for either crystal. The reflection intensities were corrected for background effects and converted to structure factors by applying Lorentz and polarization corrections. Standard deviations, $\sigma(F)$, based on counting statistics were calculated by using

$$\sigma(F) = 0.5(Lp)^{-1/2}\left(\frac{N_T + 16N_B}{N_T - N_B}\right)^{1/2}$$

where Lp is the Lorentz–polarization factor and N_T and N_B are the total scan intensity and the sum of the two background intensities. The weighting scheme used in the least-squares refinements was

$$w = k/[\sigma^2(F) + gF^2]$$

where w is the weight and k and g are refinable parameters in the SHELX programs.[25] The final values of k and g were 1.6762 and 0.001 062 for $Cu(PM)_2(NO_3)_2 \cdot H_2O$ and 2.3146 and 0.000 696 for $Cu(PM\text{-}H)_2 \cdot 2H_2O$, respectively.

A total of 2931 independent reflections with $2\theta < 45°$ were collected for $Cu(PM)_2(NO_3)_2 \cdot H_2O$. Of these, 2390 had $F > 3\sigma(F)$ and were classified as observed. For $Cu(PM\text{-}H)_2 \cdot 2H_2O$, 2067 reflections with $2\theta < 50°$ were measured in the independent octant: 1587 had $F > 3\sigma(F)$ and were classified as observed.

Shedrick's SHELX-76 programs[25] were used for structure solution and refinement by full-matrix least-squares methods. Scattering factors for neutral Cu, C, H, N, and O atoms were taken from the International Tables for X-ray Crystallography,[26] as were the real and imaginary parts of the anomalous scattering. Unweighted and weighted residuals, R and R_w, respectively, were calculated after each refinement:

$$R = \sum\Delta/\sum|F_o| \qquad R_w = [\sum w\Delta^2/\sum wF_o^2]^{1/2}$$

where

$$\Delta = ||F_o| - |F_c||$$

Three-dimensional Patterson function maps were calculated for both crystals. Although the copper atoms could be located, structure solution was not straightforward because of pseudosymmetry problems. Eventually, the nitrate groups in $Cu(PM)_2(NO_3)_2 \cdot H_2O$ were correctly located from analysis of the Patterson map, whereupon the remaining atoms of the structure were easily found on a difference map. Experience with this structure facilitated solution of the structure of $Cu(PM\text{-}H)_2 \cdot 2H_2O$. Refinement proceeded smoothly with all nonhydrogen atoms being treated anisotropically. Difference maps at this stage clearly revealed the hydrogen atoms in both structures. Their positional parameters were refined (except as noted below) with isotropic temperature factors fixed at values 20% greater than the temperature factor of the atom to which the hydrogen was bonded. The methyl groups in $Cu(PM)_2(NO_3)_2 \cdot H_2O$ were refined as rigid rotors.

The hydroxymethyl group was disordered in one of the independent $Cu(PM)_2$ units in the structure of $Cu(PM)_2(NO_3)_2 \cdot H_2O$. The two possible positions for O(2A) and O(2B) correspond to a rotation of ~100° about the C(6)–C(7) bond; the occupancy factors for O(2A) and O(2B) are 0.569 (11) and 0.431 (11), respectively.

In the final least-squares cycle, the average shift:σ ratio was 0.35 for $Cu(PM)_2(NO_3)_2 \cdot H_2O$ and 0.21 for $Cu(PM\text{-}H)_2 \cdot 2H_2O$. The R and R_w values were 0.041 and 0.043 for $Cu(PM)_2(NO_3)_2 \cdot H_2O$, respectively, and 0.042 and 0.045 for $Cu(PM\text{-}H)_2 \cdot 2H_2O$. In neither structure were there any unusual features in the final difference maps. The observed and calculated structure factors are given in the supplementary material. Final coordinates and thermal parameters are presented in Tables I–IV.

Results and Discussion

The structures and atom-numbering schemes of $Cu(PM)_2(NO_3)_2 \cdot H_2O$ and $Cu(PM\text{-}H)_2 \cdot 2H_2O$ are shown in Figures 1 and 2, respectively. Bond distances and angles for both compounds are presented in Table V.

In both compounds, the six-coordinate copper ions lie at crystallographic centers of symmetry and are chelated to two pyridoxamine ligands through the amino and phenolate groups. Further, both compounds are polymeric. In $Cu(PM)_2(NO_3)_2 \cdot H_2O$, the $Cu(PM)_2$ units are linked into infinite columns parallel to the y axis by nitrate groups which bridge adjacent copper atoms through a single oxygen (Figure 1). In $Cu(PM\text{-}H)_2 \cdot 2H_2O$, infinite sheets perpendicular to the z axis are formed because the CH_2OH groups of pyridoxamine in the $Cu(PM\text{-}H)_2$ units are coordinated to adjoining copper atoms (Figure 2).

Copper Coordination and Chelate Rings. The copper atoms in both compounds display tetragonally distorted octahedral coordination. The equatorial planes are formed by two amino nitrogen atoms and two phenolate oxygen atoms from the PM ligands. The Cu–N distances in the two independent molecules of $Cu(PM)_2(NO_3)_2 \cdot H_2O$ are 1.990 (3) and 1.978 (3) Å, with corresponding Cu–O(phenolate) distances of 1.977 (3) and 1.970 (3) Å. These values compare to 1.995 (3) Å for Cu–N and 1.951 (2) Å for Cu–O(phenolate) in $Cu(PM\text{-}H)_2 \cdot 2H_2O$. All of these distances are somewhat longer than those observed in pyridoxylidene Schiff-base complexes of copper,[16,17,22] probably because the copper atoms in the present structures are six-coordinate whereas those of the Schiff-base complexes are five-coordinate.[27]

The axial positions of the Cu(1) octahedron in $Cu(PM)_2(NO_3)_2 \cdot H_2O$ are occupied by the centrosymmetrically related nitrate oxygen atoms O(5) and O(5)^{i} (Figure 1). The Cu(2) octahedron is completed by O(5) and O(5)^{ii}. The Cu(1)–O(5) and Cu(2)–O(5) distances are 2.466 (3) and 2.549 (3) Å, respectively. Bridging by a single oxygen atom from a nitrate group is unusual and has been discussed in more detail in a previous paper.[7] The axial positions of the copper octahedron in $Cu(PM\text{-}H)_2 \cdot 2H_2O$ are occupied by oxygen atoms from

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(24) T. A. Franklin, M.S. Thesis, Brock University, St. Catharines, Ontario, Canada, 1978.

(25) G. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University Chemical Laboratory, Cambridge, England, 1976.

(26) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, pp 99–100, 149.

(27) J. Gage, I. N. Bersuker, J. Garaj, M. Kabesova, J. Kahout, H. Langfelderova, M. Melnick, M. Serator, and F. Valach, *Coord. Chem. Rev.*, **19**, 253 (1976).

Table I. Positional and Thermal Parameters (×10^4) for the Nonhydrogen Atoms in $\mathrm{Cu(C_8H_{12}N_2O_2)_2(NO_3)_2{\cdot}H_2O}$[a, b]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	0	0	0	276 (4)	290 (4)	312 (4)	72 (3)	32 (3)	102 (3)
Cu(2)	0	5000	0	235 (4)	303 (4)	388 (4)	−28 (3)	4 (3)	91 (3)
N(1)	2912 (2)	−440 (4)	−3162 (4)	339 (21)	509 (23)	345 (21)	38 (18)	97 (17)	122 (18)
C(1)	2112 (3)	152 (5)	−2944 (4)	326 (25)	386 (25)	380 (25)	47 (20)	24 (19)	60 (20)
C(2)	1610 (4)	622 (7)	−4235 (5)	557 (32)	826 (39)	353 (28)	200 (26)	23 (23)	264 (28)
C(3)	1770 (3)	350 (5)	−1541 (4)	299 (23)	265 (21)	346 (24)	27 (18)	58 (18)	81 (18)
O(1)	981 (2)	931 (3)	−1336 (3)	342 (16)	294 (15)	391 (17)	116 (13)	50 (13)	136 (13)
C(4)	2301 (3)	80 (4)	411 (4)	243 (21)	263 (21)	347 (23)	19 (18)	4 (17)	26 (17)
C(5)	1959 (3)	223 (6)	1097 (5)	306 (24)	421 (27)	323 (25)	−31 (20)	−26 (18)	56 (20)
N(2)	972 (2)	591 (4)	1297 (4)	334 (20)	294 (19)	302 (20)	24 (16)	39 (16)	91 (16)
C(6)	3136 (3)	−705 (5)	−702 (5)	268 (23)	281 (23)	451 (28)	46 (20)	−14 (20)	25 (18)
C(7)	3740 (4)	−1195 (7)	481 (6)	289 (28)	460 (35)	481 (32)	53 (25)	−59 (24)	67 (25)
O(2A)[c]	4522 (4)	−1903 (7)	−155 (8)	330 (35)	480 (38)	502 (44)	47 (29)	−23 (26)	124 (28)
O(2B)[c]	4077 (6)	65 (11)	1546 (8)	393 (49)	577 (56)	355 (45)	64 (42)	−91 (38)	−51 (38)
C(8)	3430 (3)	−873 (5)	−2102 (5)	295 (24)	472 (28)	431 (28)	−16 (21)	38 (20)	148 (21)
N(3)	3061 (3)	4585 (5)	2682 (4)	314 (22)	583 (26)	325 (23)	35 (20)	−37 (17)	86 (19)
C(9)	2256 (3)	5199 (5)	2666 (4)	281 (24)	475 (27)	315 (26)	−17 (20)	16 (19)	40 (21)
C(10)	1829 (4)	5677 (7)	4065 (5)	505 (32)	710 (36)	410 (30)	−71 (26)	9 (24)	155 (27)
C(11)	1842 (3)	5336 (5)	1320 (4)	242 (23)	283 (23)	375 (26)	9 (19)	9 (19)	59 (18)
O(3)	1054 (2)	5979 (3)	1292 (3)	254 (16)	340 (16)	439 (18)	−54 (13)	10 (13)	98 (13)
C(12)	2310 (3)	4909 (5)	75 (4)	253 (23)	300 (23)	329 (25)	37 (19)	13 (18)	5 (18)
C(13)	1866 (3)	5132 (6)	−1365 (5)	246 (24)	374 (26)	384 (26)	73 (21)	−11 (19)	38 (20)
N(4)	877 (3)	4278 (4)	−1464 (4)	249 (20)	292 (20)	337 (21)	43 (17)	−32 (16)	58 (16)
C(14)	3160 (3)	4311 (5)	164 (5)	242 (24)	392 (26)	376 (29)	72 (21)	8 (20)	59 (20)
C(15)	3622 (3)	3907 (6)	−1146 (5)	312 (26)	498 (30)	366 (26)	26 (22)	74 (20)	132 (22)
O(4)	4067 (2)	5346 (4)	−1790 (4)	470 (20)	560 (22)	406 (19)	27 (17)	156 (16)	50 (16)
C(16)	3528 (3)	4168 (6)	1482 (5)	285 (25)	566 (32)	407 (29)	32 (23)	0 (21)	190 (23)
N(5)	22 (3)	2613 (4)	2751 (4)	461 (23)	372 (21)	354 (23)	40 (18)	1 (18)	143 (18)
O(5)	9 (2)	2554 (3)	1402 (3)	685 (22)	363 (17)	285 (18)	19 (13)	−4 (15)	142 (15)
O(6)	567 (3)	1900 (4)	3385 (4)	907 (27)	643 (23)	484 (20)	−89 (17)	−247 (19)	498 (21)
O(7)	−513 (3)	3373 (4)	3445 (3)	822 (26)	757 (24)	422 (19)	128 (17)	210 (18)	507 (22)
N(6)	4480 (4)	3118 (5)	5116 (5)	797 (34)	607 (29)	386 (28)	52 (22)	2 (24)	153 (26)
O(8)	4933 (3)	2844 (6)	6177 (4)	1250 (39)	1324 (42)	440 (25)	52 (24)	−43 (24)	802 (34)
O(9)	4618 (4)	2539 (5)	3908 (4)	1553 (46)	915 (33)	369 (24)	−59 (22)	122 (25)	498 (31)
O(10)	3880 (3)	4031 (5)	5312 (4)	760 (28)	1053 (33)	440 (22)	27 (21)	−39 (19)	437 (26)
O(11)	3967 (3)	−879 (6)	4195 (4)	732 (28)	877 (32)	508 (23)	79 (21)	236 (20)	293 (23)

[a] Estimated standard deviations given in parentheses. [b] The form of the anisotropic temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* \cos \gamma^* + 2U_{13}hla^*c^* \cos \beta^* + 2U_{23}klb^*c^* \cos \alpha^*)]$. [c] Disordered atoms. The site occupation factor for O(2A) is 0.569 (11); that for O(2B) is 0.431 (11).

Table II. Positional Parameters (×10^3) for Hydrogen Atoms in $\mathrm{Cu(C_8H_{12}N_2O_2)_2(NO_3)_2{\cdot}H_2O}$[a]

atom	x	y	z
H(1)	321 (3)	−48 (6)	−401 (5)
H(2)*	98	114	−397
H(3)*	142	−44	−493
H(4)*	211	144	−478
H(5)	199 (3)	140 (5)	133 (4)
H(6)	236 (3)	−14 (5)	179 (4)
H(7)	100 (4)	−159 (6)	130 (5)
H(8)	83 (4)	−27 (6)	209 (6)
H(9A)	337 (16)	−205 (21)	102 (20)
H(9B)	328 (19)	−170 (26)	112 (25)
H(10A)	409 (9)	5 (18)	87 (14)
H(10B)	422 (14)	−161 (22)	56 (18)
H(11A)	432 (7)	−260 (11)	−73 (10)
H(11B)	463 (9)	69 (14)	128 (13)
H(12)	397 (3)	−135 (5)	−238 (4)
H(13)	331 (4)	446 (7)	354 (6)
H(14)*	121	622	392
H(15)*	236	650	468
H(16)*	164	462	464
H(17)	188 (3)	625 (5)	−139 (4)
H(18)	232 (2)	468 (5)	−209 (4)
H(19)	62 (4)	443 (7)	−233 (6)
H(20)	83 (4)	326 (6)	−149 (5)
H(21)	331 (4)	314 (6)	−182 (6)
H(22)	426 (4)	335 (6)	−90 (5)
H(23)	422 (4)	520 (6)	−266 (6)
H(24)	409 (3)	377 (5)	160 (4)
H(25)	416 (4)	−143 (7)	418 (6)
H(26)	393 (4)	−7 (7)	381 (6)

[a] The asterisks indicate hydrogen atoms refined as part of a rigid methyl group.

centrosymmetrically related hydroxymethyl groups, with a Cu–O(2)$^{\mathrm{ii}}$ distance of 2.688 (3) Å. The tetragonal elongation observed for the copper octahedra in both compounds is characteristic of copper complexes.[27]

The chelate ring bites are 2.858 and 2.853 Å in the two independent molecules of $\mathrm{Cu(PM)_2(NO_3)_2{\cdot}H_2O}$ and 2.840 Å in $\mathrm{Cu(PM\text{-}H)_2{\cdot}2H_2O}$. These distances are greater than the corresponding nonbite distances in each octahedron by ~0.1 Å. The intra-ring bond angles at copper range from 92.1 (1)° in $\mathrm{Cu(PM\text{-}H)_2{\cdot}2H_2O}$ to 92.6 (1)° for the Cu(2) atom in $\mathrm{Cu(PM)_2(NO_3)_2{\cdot}H_2O}$. Other bond angles at the copper atoms are not far from 90° (Table V).

The chelate rings are all in very similar boat conformations. Four atoms define a plane in each chelate ring: Cu(1)–N(2)–C(3)–C(4) and Cu(2)–N(4)–C(11)–C(12) in $\mathrm{Cu(PM)_2(NO_3)_2{\cdot}H_2O}$ and Cu–N(2)–C(3)–C(4) in $\mathrm{Cu(PM\text{-}H)_2{\cdot}2H_2O}$. In each ring, the phenolate oxygen atom and the methylene carbon atom lie well out of the plane defined by the other four atoms, with the carbon atom displaced further than the oxygen atom. This kind of boat conformation is also found in $\mathrm{Cd(PN)Cl_2}$[8] but is different from the boat observed in metal chelates of 2-(2-aminoethyl)pyridine,[28] in which the metal atoms occupy one of the "flagpole" positions. Boat conformations are generally not favored in saturated six-membered chelate rings,[29] but the introduction of trigonally bonded atoms into the ring apparently changes the preferred conformation.

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(28) R. B. Wilson, J. R. Wasson, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **17**, 641 (1978).

(29) L. J. DeHayes and D. H. Busch, *Inorg. Chem.*, **12**, 1505 (1973).

Table III. Positional and Thermal Parameters ($\times 10^4$) for the Nonhydrogen Atoms in $Cu(C_8H_{11}N_2O_2)_2 \cdot 2H_2O$[a, b]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	0	0	0	427 (4)	209 (3)	232 (3)	1 (2)	−41 (2)	−28 (2)
N(1)	−386 (3)	3191 (2)	1942 (3)	388 (15)	260 (14)	406 (17)	−86 (12)	53 (14)	−12 (13)
C(1)	−352 (3)	2231 (2)	2002 (3)	305 (16)	293 (17)	303 (17)	−35 (13)	−14 (14)	−48 (14)
C(2)	−1091 (4)	1740 (3)	2879 (4)	513 (24)	435 (23)	384 (20)	−49 (18)	89 (19)	−104 (19)
C(3)	355 (3)	1683 (2)	1262 (3)	284 (14)	242 (15)	257 (16)	−29 (12)	−49 (12)	−20 (12)
O(1)	363 (2)	729 (1)	1337 (2)	452 (13)	197 (10)	263 (11)	4 (9)	−42 (10)	−8 (10)
C(4)	1050 (3)	2164 (2)	458 (3)	276 (15)	273 (16)	279 (16)	−31 (13)	−23 (13)	−25 (13)
C(5)	1785 (3)	1560 (3)	−320 (3)	302 (17)	344 (18)	373 (18)	−66 (16)	45 (15)	−32 (15)
N(2)	979 (3)	893 (2)	−936 (2)	343 (14)	293 (14)	274 (14)	−51 (11)	25 (12)	15 (12)
C(6)	1028 (3)	3166 (2)	423 (3)	367 (18)	283 (17)	315 (16)	2 (13)	−11 (15)	−67 (15)
C(7)	1824 (5)	3776 (3)	−321 (4)	671 (28)	315 (20)	413 (21)	52 (17)	81 (20)	−144 (19)
O(2)	2979 (3)	3919 (3)	149 (3)	522 (18)	659 (23)	640 (21)	18 (16)	184 (16)	−183 (16)
C(8)	286 (3)	3640 (2)	1173 (3)	448 (19)	233 (16)	379 (20)	−46 (14)	−7 (15)	−29 (14)
O(3)	2057 (3)	−423 (2)	2323 (3)	337 (13)	435 (16)	566 (17)	137 (13)	−13 (13)	−24 (13)

[a] Estimated standard deviations given in parentheses. [b] The form of the anisotropic temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* \cos \gamma^* + 2U_{13}hla^*c^* \cos \beta^* + 2U_{23}klb^*c^* \cos \alpha^*)]$.

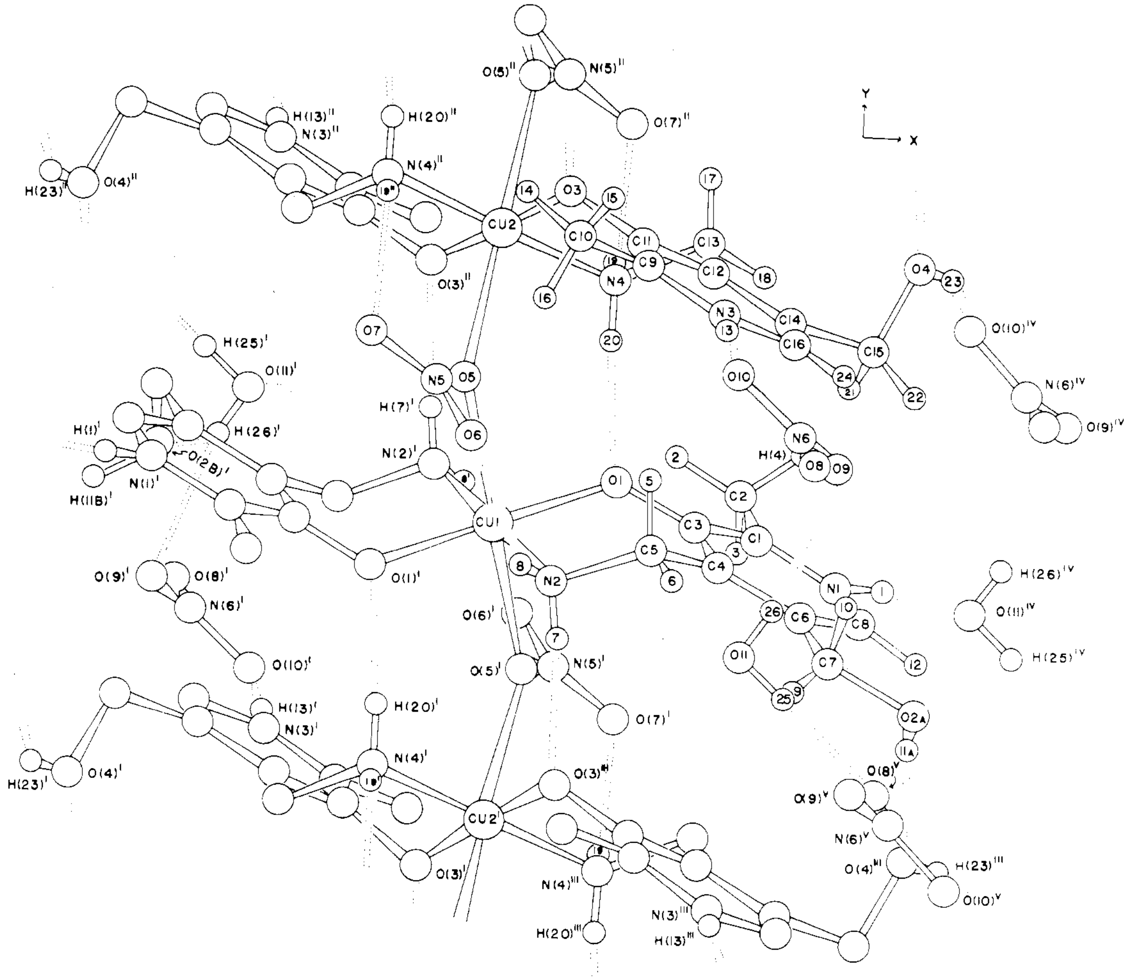
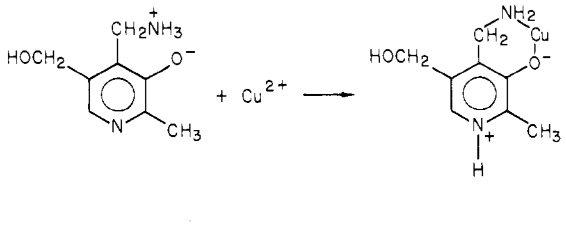


Figure 1. Structure of $Cu(PM)_2(NO_3)_2 \cdot H_2O$. The smallest circles are hydrogen atoms. Many of the symmetry-related hydrogens have been omitted for clarity. Both positions of the disordered CH_2OH group are shown: O(2A) on the right of Cu(I); O(2B) on the left. Hydrogen bonds are indicated by dotted lines. The symmetry transformations are as follows: x, y, z (no superscript); $-x, -y, -z$ (i); $-x, 1 - y, -z$ (ii); $x, -1 + y, z$ (iii); $x, y, -1 + z$ (iv); $1 - x, -y, 1 - z$ (v).

Pyridoxamine Ligands. The hydrogen atom locations in $Cu(PM)_2(NO_3)_2 \cdot H_2O$ show that the PM ligands occur as tautomer III in the complex. Complex formation thus involves a change in tautomeric form (eq 1). Loss of the pyridinium protons from the $Cu(PM)_2^{2+}$ ions produced in eq 1 formally yields $Cu(PM\text{-}H)_2$ molecules.



(1)

The bond angles and distances in the PM and PM-H ligands (Figure 3) are generally similar to those found in other structures.[8,15,19,22,30-34] There are variations which can be

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(30) F. Hanic, *Acta Crystallogr.*, **21**, 332 (1966).

(31) A. N. Barrett and R. A. Palmer, *Acta Crystallogr., Sect. B*, **25**, 688 (1969).

(32) F. Giordano and L. Mazzarella, *Acta Crystallogr., Sect. B*, **27**, 128 (1971).

Table IV. Positional Parameters ($\times 10^3$) for Hydrogen Atoms in $Cu(C_8H_{11}N_2O_2)_2 \cdot 2H_2O$[a,b]

atom	x	y	z
H(1)	−113 (5)	119 (4)	272 (5)
H(2)	−187 (5)	209 (3)	297 (4)
H(3)	−84 (5)	175 (3)	356 (5)
H(4)	228 (4)	189 (3)	−83 (3)
H(5)	235 (4)	130 (3)	5 (3)
H(6)	47 (4)	125 (3)	−142 (3)
H(7)	138 (4)	53 (3)	−134 (3)
H(8)	194 (4)	352 (3)	−110 (4)
H(9)	146 (4)	435 (3)	−44 (4)
H(10)	290 (4)	410 (4)	85 (4)
H(11)	21 (3)	438 (3)	125 (3)
H(12)	156 (4)	6 (3)	212 (4)
H(13)	154 (4)	−85 (3)	254 (4)

[a] Estimated standard deviations given in parentheses. [b] Temperature factors fixed at values 20% greater than the temperature factor of the atom to which the hydrogen is attached.

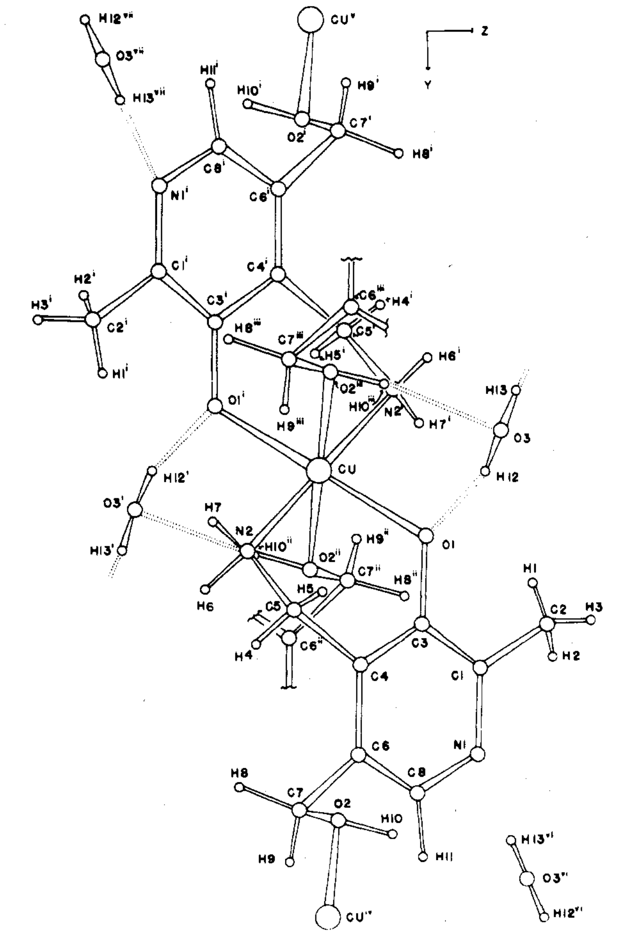


Figure 2. The structure of $Cu(PM\text{-}H)_2 \cdot 2H_2O$. Hydrogen bonds are indicated by dotted lines. The symmetry transformations are as follows: x, y, z (no superscript); $-x, -y, -z$ (i); $-^1/_2 + x, ^1/_2 - y, -z$ (ii); $^1/_2 - x, -^1/_2 + y, z$ (iii); $^1/_2 + x, ^1/_2 - y, -z$ (iv); $-^1/_2 - x, -^1/_2 + y, z$ (v); $-x, ^1/_2 + y, ^1/_2 - z$ (vi); $x, ^1/_2 - y, ^1/_2 + z$ (vii); $^1/_2 - x, -y, ^1/_2 + z$ (viii); $^1/_2 - x, ^1/_2 + y, z$ (ix).

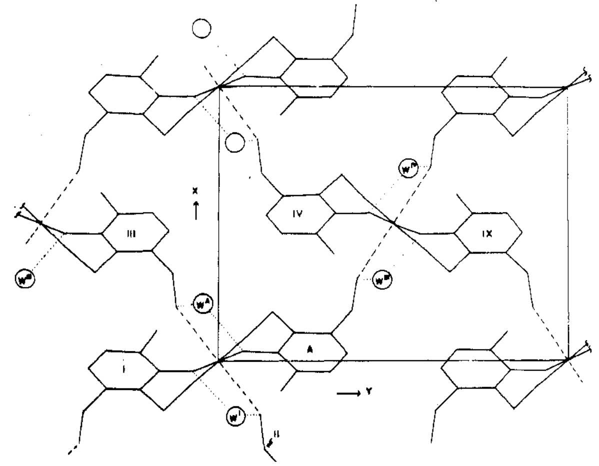
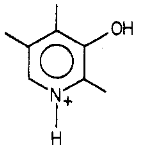
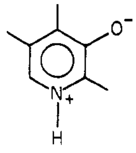
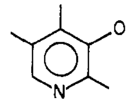


Figure 3. One layer in the structure of $Cu(PM\text{-}H)_2 \cdot 2H_2O$. Dotted lines represent hydrogen bonds. Molecule A is the starting set of coordinates; other symmetry designations may be found in Figure 2.

related to the protonation state of the ligand. The known structures of vitamin B_6 compounds can be divided into three categories: those containing cation IV as a structural moiety, those containing the neutral zwitterion V, and those containing the anion VI. Structures containing cation IV have a C–O(phenol) distance of ~1.34 Å.[30–34] Deprotonation to give zwitterion V results in shortening the C–O(phenolate) bond by ~0.04 Å, while the angle at nitrogen remains unchanged.[8,15,19] The only compound having VI as a structural unit, other than $Cu(PM\text{-}H)_2 \cdot 2H_2O$, is a Schiff-base derivative[22] whose C–O distance is 1.30 Å and whose angle at the pyridine nitrogen is 119°.


IV


V


VI

The C(3)–O(1) and C(11)–O(3) distances in $Cu(PM)_2(NO_3)_2 \cdot H_2O$ are 1.307 (4) and 1.314 (4) Å, respectively, and the C(8)–N(1)–C(1) and C(16)–N(3)–C(9) angles are both 123.7 (4)°. These values are in good agreement with the ones quoted above for structures containing moiety V. In $Cu(PM\text{-}H)_2$, the C(3)–O(1) distance increases (to 1.331 (3) Å), while the C(1)–N(1)–C(8) angle decreases, to 119.1 (3)°. Narrowing of this angle is normally observed when a pyridine nitrogen is deprotonated.[35]

The pyridine rings are planar. Substituents on the rings deviate from the planes by up to 0.1 Å, which is not unusual and is probably due to the molecular packing.

Nitrate Groups in $Cu(PM)_2(NO_3)_2 \cdot H_2O$. The distances and angles in the two independent nitrate groups are normal (Table V), and both nitrate groups are planar. The N(5)–O(7) nitrate group, which is coordinated to both Cu(1) and Cu(2) through the O(5) atom, is twisted about the O(5)–N(5) bond so that the Cu(1) and Cu(2) atoms are located more than 1.5 Å from the nitrate plane, on opposite sides. This twisting is quite surprising for two reasons. First, maximum orbital overlap between the lone pairs on O(5) and the orbitals on the copper atoms is achieved when the copper atoms are in the same plane as the nitrate group. Second, coplanarity would minimize any steric crowding of the nitrate group by the $Cu(PM)_2$ moieties. However, these considerations seem to have been overshadowed by the formation of hydrogen bonds between O(6) and O(7)

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(33) F. E. Cole, B. Lachmann, and W. Korytnyk, *J. Heterocycl. Chem.*, **9**, 1129 (1972).

(34) T. Fujiwara, *Bull. Chem. Soc. Jpn.*, **46**, 863 (1973).

(35) C. Singh, *Acta Crystallogr.*, **19**, 861 (1965).

Table V. Selected Distances (Å) and Angles (Deg) in $\mathrm{Cu(PM)_2(NO_3)_2{\cdot}H_2O}$ and $\mathrm{Cu(PM\text{-}H)_2{\cdot}2H_2O}^a$

A. Coordination Polyhedron, $\mathrm{Cu(PM)_2(NO_3)_2{\cdot}H_2O}$			
Cu(1)–N(2)	1.990 (3)	O(1)–Cu(1)–N(2)	92.2 (1)
Cu(1)–O(1)	1.977 (3)	O(1)–Cu(1)–O(5)	92.6 (1)
Cu(1)–O(5)	2.466 (3)	N(2)–Cu(1)–O(5)	91.4 (1)
O(1)· · ·N(2)	2.858 (3)		
O(1)· · ·N(2)^{i}	2.752 (3)		
Cu(2)–N(4)	1.978 (3)	O(3)–Cu(2)–N(4)	92.6 (1)
Cu(2)–O(3)	1.970 (3)	O(3)–Cu(2)–O(5)	84.9 (1)
Cu(2)–O(5)	2.549 (3)	N(4)–Cu(2)–O(5)	92.2 (1)
O(3)· · ·N(4)	2.853 (3)		
O(3)· · ·N(4)^{i}	2.729 (3)		
B. Coordination Polyhedron, $\mathrm{Cu(PM\text{-}H)_2{\cdot}2H_2O}$			
Cu–N(2)	1.995 (3)	O(1)–Cu–N(2)	92.1 (1)
Cu–O(1)	1.951 (2)	O(1)–Cu–O(2)^{iii}	86.2 (2)
Cu–O(2)^{iii}	2.688 (3)	N(2)–Cu–O(2)^{iii}	86.7 (2)
O(1)· · ·N(2)	2.840 (3)		
O(1)· · ·N(2)^{i}	2.741 (3)		
C. Nitrate Groups, $\mathrm{Cu(PM)_2(NO_3)_2{\cdot}H_2O}$			
N(5)–O(5)	1.255 (4)	O(5)–N(5)–O(6)	120.1 (4)
N(5)–O(6)	1.237 (4)	O(5)–N(5)–O(7)	119.9 (4)
N(5)–O(7)	1.232 (4)	O(6)–N(5)–O(7)	120.0 (4)
N(6)–O(8)	1.240 (5)	O(8)–N(6)–O(9)	121.7 (5)
N(6)–O(9)	1.225 (5)	O(8)–N(6)–O(10)	117.8 (4)
N(6)–O(10)	1.251 (5)	O(9)–N(6)–O(10)	120.6 (4)
D. PM Ligands, $\mathrm{Cu(PM)_2(NO_3)_2{\cdot}H_2O}$			
O(1)–C(3)	1.307 (4)	Cu(1)–O(1)–C(3)	121.2 (2)
C(3)–C(1)	1.401 (6)	O(1)–C(3)–C(1)	119.2 (4)
C(1)–C(2)	1.513 (6)	O(1)–C(3)–C(4)	122.8 (3)
C(1)–N(1)	1.329 (5)	C(1)–C(3)–C(4)	117.9 (4)
N(1)–C(8)	1.343 (6)	C(3)–C(1)–C(2)	122.2 (4)
C(8)–C(6)	1.373 (6)	C(3)–C(1)–N(1)	119.6 (4)
C(6)–C(7)	1.524 (6)	C(2)–C(1)–N(1)	118.2 (4)
C(7)–O(2A)	1.453 (8)	C(1)–N(1)–C(8)	123.7 (4)
C(7)–O(2B)	1.438 (10)	N(1)–C(8)–C(6)	119.6 (4)
C(6)–C(4)	1.399 (5)	C(8)–C(6)–C(7)	118.6 (4)
C(4)–C(5)	1.504 (6)	C(8)–C(6)–C(4)	119.0 (4)
C(5)–N(2)	1.484 (5)	C(7)–C(6)–C(4)	122.4 (4)
C(4)–C(3)	1.403 (5)	C(6)–C(7)–O(2A)	109.8 (4)
		C(6)–C(7)–O(2B)	113.9 (5)
		C(6)–C(4)–C(5)	122.3 (4)
		C(6)–C(4)–C(3)	120.1 (4)
		C(3)–C(4)–C(5)	117.5 (3)
		C(4)–C(5)–N(2)	111.7 (3)
		C(5)–N(2)–Cu(1)	115.4 (3)
D. PM Ligands, $\mathrm{Cu(PM)_2(NO_3)_2{\cdot}H_2O}$			
O(3)–C(11)	1.314 (4)	Cu(2)–O(3)–C(11)	120.2 (2)
C(11)–C(9)	1.415 (6)	O(3)–C(11)–C(9)	119.0 (4)
C(9)–C(10)	1.494 (6)	O(3)–C(11)–C(12)	123.0 (4)
C(9)–N(3)	1.336 (5)	C(9)–C(11)–C(12)	118.0 (4)
N(3)–C(16)	1.354 (6)	C(11)–C(9)–C(10)	122.7 (4)
C(16)–C(14)	1.359 (6)	C(11)–C(9)–N(3)	118.5 (4)
C(14)–C(15)	1.507 (6)	C(10)–C(9)–N(3)	118.8 (4)
C(15)–O(4)	1.426 (6)	C(9)–N(3)–C(16)	123.8 (4)
C(14)–C(12)	1.393 (5)	N(3)–C(16)–C(14)	119.9 (4)
C(12)–C(13)	1.523 (6)	C(16)–C(14)–C(15)	118.3 (4)
C(13)–N(4)	1.481 (5)	C(15)–C(14)–C(12)	122.5 (4)
C(12)–C(11)	1.398 (5)	C(16)–C(14)–C(12)	119.0 (4)
		C(14)–C(15)–O(4)	107.8 (3)
		C(14)–C(12)–C(13)	121.9 (4)
		C(14)–C(12)–C(11)	120.7 (4)
		C(11)–C(12)–C(13)	117.3 (4)
		C(12)–C(13)–N(4)	110.4 (3)
		C(13)–N(4)–Cu(2)	115.1 (3)
E. PM Ligands, $\mathrm{Cu(PM\text{-}N)_2{\cdot}H_2O}$			
O(1)–C(3)	1.330 (3)	Cu–O(1)–C(3)	117.5 (2)
C(3)–C(1)	1.408 (4)	O(1)–C(3)–C(1)	120.1 (3)
C(1)–C(2)	1.495 (5)	O(1)–C(3)–C(4)	121.1 (3)
C(1)–N(1)	1.339 (4)	C(1)–C(3)–C(4)	118.8 (3)
N(1)–C(8)	1.342 (4)	C(3)–C(1)–C(2)	120.5 (3)
C(8)–C(6)	1.386 (4)	C(3)–C(1)–N(1)	121.5 (3)
C(6)–C(7)	1.516 (5)	C(2)–C(1)–N(1)	118.0 (3)
C(7)–O(2)	1.403 (5)	C(1)–N(1)–C(8)	119.1 (3)
C(6)–C(4)	1.395 (4)	N(1)–C(8)–C(6)	123.7 (3)
C(4)–C(5)	1.497 (5)	C(8)–C(6)–C(7)	117.5 (3)
C(5)–N(2)	1.483 (4)	C(8)–C(6)–C(4)	117.8 (3)
C(4)–C(3)	1.406 (4)	C(7)–C(6)–C(4)	124.5 (3)
		C(6)–C(7)–O(2)	111.1 (3)
		C(6)–C(4)–C(5)	123.5 (3)
		C(6)–C(4)–C(3)	119.1 (3)
		C(3)–C(4)–C(5)	117.4 (3)
		C(4)–C(5)–N(2)	110.2 (3)
		C(5)–N(2)–Cu	115.2 (2)

[a] Estimated standard deviations in parentheses.

and the amino groups of pyridoxamine (Figure 1; see also below).

Molecular Packing and Hydrogen Bonding. The basic packing units in $\mathrm{Cu(PM)_2(NO_3)_2{\cdot}H_2O}$ are the columns formed by linking the Cu(1) and Cu(2) chelates with the bridging nitrate groups, as shown in Figure 1. A series of hydrogen bonds further stabilizes the columns. The N(2) amino group is hydrogen bonded to O(3)^{iii}, to a phenolate oxygen coordinated to Cu(2)^{i}, and to the O(6) atom of the bridging nitrate group. The N(4) amino group undergoes similar interactions, being linked to the O(7)^{ii} atom of a bridging nitrate and to an O(1) phenolate oxygen atom coordinated to Cu(1). These hydrogen bonds are not very strong, as the N···O and H···O distances are all >2.9 and >2.0 Å, respectively (Table VI). However, they appear to be the reason that the nitrate group is twisted away from coplanarity with the copper atoms, which points to the weakness of the long Cu(1)–O(5) and Cu(2)–O(5) axial bonds.

The intercolumn linkages are complex (Table VI). A key role is played by the water molecules and the uncoordinated nitrate groups. Water molecule O(11) forms hydrogen bonds to two centrosymmetrically related nitrate groups, N(6)–O(10) and N(6)^{v}–O(10)^{v}. Its centrosymmetric equivalent, O(11)^{v}, also is hydrogen bonded to the same two nitrate groups. The O(10) atom of the uncoordinated nitrate group acts as a hydrogen-bond acceptor from the N(3)–H(13) pyridinium group and from an O(4)–H(23) hydroxymethyl group from an adjoining Cu(2) chelate. In addition, the O(11) water molecule acts as a hydrogen-bond acceptor from a pyridinium N(1)–H(1) group. The picture is further complicated by the disordered hydroxymethyl group of Cu(1). In the "A" position it is a hydrogen-bond donor (O(2A)–H(11A)···O(4)^{iii}), whereas in the "B" position it may be a hydrogen-bond acceptor (O(11)^{i}–H(26)···O(2B)^{i}). Note that O(2B)^{i} is in competition with O(9)^{i} as an acceptor site.

Table VI. Hydrogen Bonding in $\mathrm{Cu(C_8H_{12}N_2O_2)_2(NO_3)_2{\cdot}H_2O}^a$

atoms a–b· · ·c	ac, Å	bc, Å	abc, deg
N(1)–H(1)· · ·O(11)^{iv}	2.727	1.84	171
N(3)–H(13)· · ·O(10)	2.833	1.93	175
O(11)–H(25)· · ·O(8)^{v}	2.778	1.92	169
O(11)–H(26)· · ·O(9)	3.043	2.29	152
O(11)^{i}–H(26)^{i}· · ·O(2B)^{i}	2.678	2.12	124
N(2)–H(7)· · ·O(3)^{iii}	2.959	2.09	180
N(2)–H(8)· · ·O(6)	2.910	2.23	143
N(4)–H(19)· · ·O(7)^{ii}	2.931	2.24	132
N(4)–H(20)· · ·O(1)	2.906	2.06	169
O(2A)–H(11A)· · ·O(4)^{iii}	2.706	1.94	162
O(4)–H(23)· · ·O(10)^{iv}	2.848	2.10	148

[a] See caption to Figure 1 for symmetry designations.

By comparison, the molecular packing in $\mathrm{Cu(PM\text{-}H)_2{\cdot}H_2O}$ is very simple. Bonding of the hydroxymethyl groups to copper ions (shown by dashed lines in Figure 3) results in a layer structure. The layer at $z = 0$ is shown in Figure 3; successive

Table VII. Hydrogen Bonding in $Cu(C_8H_{11}N_2O_2)_2 \cdot 2H_2O^a$

atoms a–b···c	ac, Å	bc, Å	abc, deg
$O(3)^{vi}$–$H(13)^{vi}$···N(1)	2.807	1.94	178
O(3)–H(12)···O(1)	2.731	1.87	161
$O(2)^{iii}$–$H(10)^{iii}$···O(3)	2.784	1.90	171
N(2)–H(7)···$O(3)^{viii}$	3.085	2.37	145
N(2)–H(6)···$N(1)^{vii}$	3.233	2.32	160

[a] See Figure 2 for symmetry superscripts.

layers are related to each other by the *a*-glide planes perpendicular to the *z* axis.

The water molecule O(3) is hydrogen bonded to two of the ligand atoms of a given copper atom. It acts as a donor to a phenolate oxygen atom O(1) and as an acceptor from the hydroxymethyl group $O(2)^{iii}$ (Figure 2). The main connection between the layers is provided by a hydrogen bond from the water molecule to a pyridine nitrogen atom in a neighboring layer. These three hydrogen bonds are of moderate strength, as indicated by the distances and the O–H···N and O–H···O angles (Table VII). Hydrogen bonding by the amino groups, which played such an important role in the structure of $Cu(PM)_2(NO_3)_2 \cdot H_2O$, appears not to occur in $Cu(PM\text{-}H)_2 \cdot 2H_2O$. The closest contacts involving the amino groups (Table VII) are essentially at van der Waals distances.

Acknowledgment. We thank the National Research Council of Canada for supporting this research. We are also grateful to Mrs. Terry Franklin for growing the crystals and to Mr. Walter Balenovich for drawing the packing diagram of $Cu(PM\text{-}H)_2 \cdot 2H_2O$.

Registry No. $Cu(PM)_2(NO_3)_2 \cdot H_2O$, 73505-56-3; $Cu(PM\text{-}H)_2 \cdot 2H_2O$, 73505-58-5.

Supplementary Material Available: Listings of structure factor amplitudes for $Cu(PM)_2(NO_3)_2 \cdot H_2O$ and $Cu(PM\text{-}H)_2 \cdot 2H_2O$ and Tables VIII and IX, distances and angles involving hydrogen atoms, and X and XI, least-squares planes (30 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Seven-Coordinate Carbonyl(5,7-dichloro-8-quinolinolato)(triphenylphosphine) Chelates of Tungsten(II)

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Received October 3, 1979

The structural complexities of seven-coordinate chelates with both hard and soft donors have been studied through a single-crystal X-ray diffraction study of tricarbonylchloro[5,7-dichloro-8-quinolinolato-*N*,*O*(1−)](triphenylphosphine)tungsten(II), $W(CO)_3Cl(dcq)(PPh_3)$, C_3, and dicarbonylbis[5,7-dichloro-8-quinolinolato-*N*,*O*(1−)](triphenylphosphine)tungsten(II), $W(CO)_2(dcq)_2(PPh_3)$, Q_2. Data for both complexes were collected on an Enraf Nonius CAD 4 diffractometer out to a maximum $2\theta_{\text{Mo K}\bar{\alpha}}$ of 43°. C_3 crystallizes in the monoclinic space group $P2_1/n$, with a = 14.623 (5) Å, b = 20.472 (9) Å, c = 9.916 (4) Å, β = 103.63 (3)°, and Z = 4. Full-matrix least-squares refinement has led to R = 0.042 and R_w = 0.055 for the 2798 reflections having $I \geq 2\sigma_I$. Q_2 crystallizes as the CH_2Cl_2 1:1 solvate in the monoclinic space group, $P2_1/c$, with a = 17.390 (5) Å, b = 15.300 (6) Å, c = 16.007 (5) Å, β = 115.50 (2) Å, and Z = 4, and has been refined to the final values of R = 0.054 and R_w = 0.067 for the 3878 reflections having $I \geq \sigma_I$. We also include for comparison some preliminary structural results for the compound $W(CO)_2(PPh_3)_2(dcq)Cl$, P_2.

Introduction

In his recent extensive review, Drew[1] summarized structural information on 161 monomeric seven-coordinate complexes; however, none of the complexes present the wide array of donor atoms available in the three seven-coordinate W(II) complexes[2] synthesized recently in our laboratory. These chelates have carbonyl and phosphine π-acceptor ligands together with phenoxy anionic π donors and aromatic heterocyclic nitrogen donors as well as chloride π-donor ions in two of the three. Thus, these chelates posed an interesting test for the π-bonding structural relationships noted recently by Hoffmann et al.[3] As discussed below, the structures follow the predicted site preferences rather well even though the structures are appreciably distorted from any of the high-symmetry seven-coordinate polytopes.

We had previously proposed a possible generalized structure for the three chelates on the basis of these site preferences and similarities between the carbonyl stretching region of their infrared spectra and that of other molybdenum(II) and tungsten(II) seven-coordinate complexes with known structures[2] and can now examine the proposal.

These chelates are specifically dicarbonylbis[5,7-dichloro-8-quinolinolato-*N*,*O*(1−)](triphenylphosphine)tungsten(II), Q_2, tricarbonylchloro[5,7-dichloro-8-quinolinolato-*N*,*O*(1−)](triphenylphosphine)tungsten(II), C_3, and dicarbonyl[5,7-dichloro-8-quinolinolato-*N*,*O*(1−)]bis(triphenylphosphine)tungsten(II), P_2, where Q_2, C_3, and P_2 have been chosen to denote the unique ligands, e.g., the two quinolinol ligands in the first chelate.

The Q_2 and C_3 structures are well refined, whereas the data for P_2 are only of a preliminary quality.[4]

Experimental Section

Reagents. Reagent grade or equivalent solvents were used exclusively. These solvents were deoxygenated with nitrogen prior to use and subsequently used without further purification unless noted.

$W(CO)_3(PPh_3)(dcq)Cl$ (C_3) and $W(CO)_2(PPh_3)_2(dcq)Cl$ (P_2) were recrystallized from a crude reaction product[2] in which both were

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(1) Drew, M. G. B. *Prog. Inorg. Chem.* **1977**, *23*, 67.

(2) Batschelet, W. H.; Archer, R. D.; Whitcomb, D. R. *Inorg. Chem.* **1979**, *18*, 48.

(3) Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* **1977**, *16*, 511.

(4) We included for comparison some preliminary results for the compound P_2 (space group $C2/c$ with a = 23.997 (10) Å, b = 12.826 (6) Å, c = 29.926 (9) Å, β = 92.46 (3)°, and Z = 8) on the basis of unit-weighted isotropic refinement using 3719 independent reflections having $I \geq 2\sigma_I$ and 2° ≤ $2\theta_{\text{Mo K}\alpha}$ ≤ 43° and giving R = 0.135. Because many of the isotropic thermal parameters seemed unreasonably small at this stage, we have abandoned further refinement until a better data set can be obtained.

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