(29) C. H. Wei and L. F. Dahl, *Cryst. Struct. Commun.*, **4**, 583 (1975).

(30) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **6**, 1229 (1967).

(31) D. L. Stevenson, H. C. Wei, and L. F. Dahl, *J. Am. Chem. Soc.*, **93**, 6027 (1971).

(32) J. M. Coleman, A. Wojcicki, P. J. Pollick, and L. F. Dahl, *Inorg. Chem.*, **6**, 1236 (1967).

(33) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 493 (1965).

(34) S. Martinengo, B. T. Heaton, R. J. Goodfellow, and P. Chini, *J. Chem. Soc., Chem. Commun.*, 39 (1977).

(35) V. Albano, P. Chini, S. Martinengo, and M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 299 (1974).

(36) V. Albano, P. Chini, G. Ciani, S. Martinengo, and M. Sansoni, paper presented at the VIIth Congresso Nazionali Chimica Inorganica, Perma, 1974, and private communication.

(37) V. Albano, P. Chini, S. Martinengo, and M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 299 (1974); *J. Chem. Soc., Dalton Trans.*, 305 (1975).

(38) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, in preparation.

(39) D. T. Cromer and D. Lieberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(40) A. F. Wells, "Structural Inorganic Chemistry", 3rd ed., Clarendon Press, London, 1962.

(41) V. Albano, M. Sansoni, P. Chini, and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, 651 (1973).

(42) V. Albano, P. Bellon, and C. F. Ciani, *Chem. Commun.*, 1024 (1969).

(43) B. Heaton, A. Towl, P. Chini, A. Fumagalli, D. McCaffrey, and S. Martinengo, *J. Chem. Soc., Chem. Commun.*, 523 (1975).

(44) F. A. Cotton, L. Kruckzinski, B. Shapiro, and L. Johnson, *J. Am. Chem. Soc.*, **94**, 6191 (1972).

(45) B. Heaton, D. Toni, P. Chini, A. Fumagalli, D. McCaffrey, and S. Martinengo, *J. Chem. Soc., Chem. Commun.*, 523 (1975).

(46) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed, Interscience, New York, N.Y., 1975.

(47) The X-ray crystal structure of a rhodium-carbonyl cluster containing an encapsulated phosphorus atom is being determined and the results will be reported later.

(48) Other sulfur–rhodium–carbonyl clusters have been isolated by the reaction of $Rh_4(CO)_{12}$ with tetrahydrothiophene and other sulfur ligands under variable experimental conditions. (J. L. Vidal and Z. C. Mester).

(49) We have found that a total of 242 electrons are required by $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ to satisfy the noble gas rule as calculated by $N_3 = 18N_1 - 2N_2$.[1] Electron-counting for the anion results in 232 electrons = $(9 \times 17) + (2 \times 32) + (2 \times 6) + 3$, indicating this species is an exception to the rule. This conclusion has been reached by assuming that the encapsulated rhodium atom is equivalent to those on the surface. Applications of Wade's rules (*Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976)) in a manner similar to that reported by Chini et al., $N_3 = 14N_1 + X$, results in a total of 226 electrons if the condensed square antiprismatic structure of the cluster is considered as a closo polyhedron ($N_1 = 16$): $(14 \times 16) + 2$.

Contribution from the Department of Chemistry, The Johns Hopkins University,
Baltimore, Maryland 21218

On the N(7),O(6) Chelation Mode of 6-Oxopurines. Preparation and Structure of (*N*-Salicylidene-*N'*,*N'*-dimethylethylenediamine)(theophyllinato)copper(II)–3.5-Water

THOMAS J. KISTENMACHER,* DAVID J. SZALDA, CHIAN C. CHIANG, MIRIAM ROSSI,
and LUIGI G. MARZILLI*

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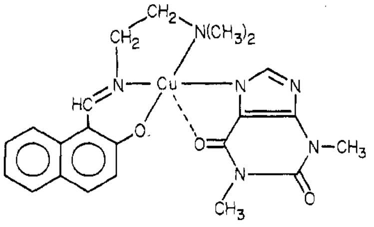
(*N*-Salicylidene-*N'*,*N'*-dimethylethylenediamine)(theophyllinato)copper(II)–3.5-water is orthorhombic, with $a = 12.570$ (4) Å, $b = 14.983$ (5) Å, $c = 23.249$ (8) Å, $V = 4378.6$ Å^3, $CuO_3N_6C_{18}H_{22}\cdot 3.5H_2O$, $Z = 8$, $d_{measd} = 1.496$ (5) g cm^{-3}, and $d_{calcd} = 1.508$ g cm^{-3}. A model in space group *Pnna* has been refined by full-matrix least-squares techniques (nonhydrogen atoms anisotropic with the inclusion, but no refinement, of the hydrogen atoms associated with the complex) based on 3028 counter-collected F_o's to a final R index of 0.130 and a final weighted R index of 0.088. The waters of crystallization (hence the structure) appear to deviate slightly from space group *Pnna*. The primary coordination sphere about the copper is approximately square planar with the tridentate Schiff base and N(7) of the theophylline monoanion occupying the four coordination sites. Weak axial interactions involving O(6) of the theophylline monoanion and a water molecule are also observed. Crystal data are reported for the trihydrate and the monohydrate as well as the title compound.

Introduction

The title complex is a close analogue of (*N*-3,4-benzosalicylidene-*N'*,*N'*-dimethylethylenediamine)(theophyllinato)copper(II), I.[1] I is unique among 6-oxopurine complexes in that in addition to the common metal–N(7) bond[1,2] a direct, *but weak*, bond is formed between the exocyclic oxygen atom at position 6 of the purine ring and an axial site on the Cu(II) center.[1]



I

Coordination of 6-oxopurines by such an N(7),O(6) chelation mode has been frequently postulated in the literature,[3] most recently[4–6] in connection with the mechanism of action of *cis*-$Pt^{II}(NH_3)_2Cl_2$, a wide-spectrum antineoplastic agent. Except for I, crystallographic studies of 6-oxopurine complexes have failed to reveal any direct interaction between O(6) and the metal.[1,2] Very frequently, the exocyclic oxygen O(6) interacts with hydrogen-bond donors either within the metal complex or with other species in the crystalline lattice.[2,7] For example, in complexes analogous to I but containing only one methyl group (and hence one hydrogen atom) on the terminal nitrogen atom of the Schiff base ligand, O(6) does not interact with the Cu(II) but accepts a hydrogen bond from the terminal N–H group.[8,9]

In order to determine whether the weak N(7),O(6) chelate mode found in I would survive other crystalline environments, we have prepared and studied the crystal structure of the title complex.

Experimental Section

The complex (*N*-salicylidene-*N'*,*N'*-dimethylethylenediamine)(theophyllinato)copper(II) was prepared in a very similar fashion to I.[1] Recrystallization from a variety of solvents yielded three crystalline hydrates: the monohydrate from 95% EtOH, the trihydrate from H_2O, and the 3.5 hydrate from MeOH.

Preliminary oscillation and Weissenberg photographs on all modifications gave crystal systems, rough cell constants, and space groups. Accurate cell dimensions and their associated standard deviations were obtained in each case from a least-squares fit of the setting angles for 15 reflections measured on a Syntex $P\bar{1}$ automated diffractometer. Crystal densities were obtained by neutral buoyancy methods. Complete crystal data for all three hydrates are collected in Table I.

The 3.5 hydrate was chosen for a complete structural investigation as it formed crystals of the highest quality. A crystal with the following faces and mean dimensions was subsequently chosen for data collection: (010)–(0$\bar{1}$0), 0.27 mm; (100)–($\bar{1}$00), 0.16 mm; (001)–(00$\bar{1}$), 0.066

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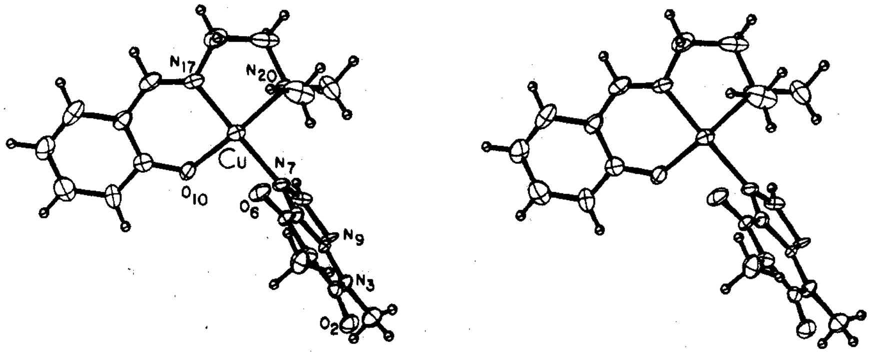

Figure 1. Stereoview of the (*N*-salicylidene-*N'*,*N'*-dimethylenediamine)(theophyllinato)copper(II)–3.5-water complex. The thermal ellipsoids of the nonhydrogen atoms are drawn at the 40% probability level. The isotropic thermal parameters for the hydrogen atoms have been artificially set to 1 Å^2.

Table I. Crystal Data for Various Hydrates of (*N*-Salicylidene-*N'*,*N'*-dimethylethylenediamine)-(theophyllinato)copper(II)

	$3.5H_2O$	$3H_2O$	H_2O
a, Å	12.570 (4)	12.744 (8)	14.547 (6)
b, Å	14.983 (5)	13.846 (12)	22.530 (9)
c, Å	23.249 (8)	25.260 (16)	12.498 (3)
α, deg	90.00	90.00	90.00
β, deg	90.00	92.52 (5)	90.00
γ, deg	90.00	90.00	90.00
V, Å^3	4378.6	4452.9	4096.1
space group	*Pnna*	*P*2/*c*	*Pbcm*
formula	$CuO_3N_6C_{18}H_{22}\cdot 3.5H_2O$	$CuO_3N_6C_{18}H_{22}\cdot 3H_2O$	$CuO_3N_6C_{18}H_{22}\cdot H_2O$
mol wt	497.0	487.9	452.0
Z	8	8	8
d_{measd}, g cm^{-1}	1.496 (5)	1.456 (7)	1.48 (1)
d_{calcd}, g cm^{-1}	1.508	1.456	1.47
solvent	MeOH	H_2O	95% EtOH

mm. The crystal was mounted with the *b* axis inclined at an angle of about 7° to the ϕ axis of the four-circle diffractometer. The intensities of 7780 reflections in the complete *hkl* octant and the $hk\bar{l}$ octant (to $h = 8$ after which the crystal was lost) to $2\theta = 50°$ were collected in the θ–2θ scan mode employing graphite-monochromatized Mo Kα radiation. Individual scan speeds were determined by a rapid scan at the calculated Bragg peak, and the rate of scanning (2θ) varied from 1.5 to 12.0° min^{-1}. The intensities of three standards were monitored after every 100 reflections and they showed no significant variation before the crystal was lost.

The 7780 measured intensities were assigned observational variances based on counting statistics plus a term $(pI)^2$, where p was taken to be 0.03 and represents the expected error proportional to the diffracted intensity.[10] The intensities and their standard deviations were corrected for Lorentz, polarization, and absorption [μ(Mo K$\bar{\alpha}$) = 1.08 mm^{-1}, maximum and minimum transmission factors on F^2 of 0.93 and 0.85, respectively] effects. The data were subsequently symmetry averaged and reduced to a set of 3028 independent reflections with $I > \sigma(I)$. Careful scrutiny of the measured intensities showed that 20 *h*0*l* reflections with $h + l = 2n + 1$ had significant intensities above background [$21 \geq I/\sigma(I) \geq 5$] indicating that the *n* glide normal to *b* was not rigorous. However, we initiated the structural analysis in *Pnna* with the realization that such an analysis might not be completely correct. An approximate absolute scale was determined by the method of Wilson.[11]

A Patterson synthesis allowed the positioning of the copper atom, and two subsequent structure factor Fourier cycles yielded positions for all nonhydrogen atoms in the asymmetric volume. Three cycles of isotropic refinement, minimizing the quantity $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, plus three cycles in which the nonhydrogen atoms were allowed to vary anisotropically gave an *R* value $[\sum||F_o| - |F_c||/\sum|F_o|]$ of 0.15. A difference-Fourier map was calculated and positions for the hydrogen atoms attached to the complex were obtained. The hydrogen atoms bound to the waters of crystallization were only weakly in evidence in a few cases. Our ability to locate the hydrogen atoms attached to the complex was reasonable assurance that the complex obeyed the packing requirements of space group *Pnna*; our inability to locate the hydrogen atoms on the solvent molecules (nor is there any semblance of a strong hydrogen-bonding network involving the solvents; see below) suggests that the solvent molecules probably cause the deviation from *Pnna* as evidenced by the "nonsystematically absent" reflections noted above. [In the absence of the *n* glide normal to *b*, and considering the symmetry of the molecule, the correct space group would be $Pn2_1a$. Attempts to refine models in $Pn2_1a$ failed because of convergence problems.]

Two further cycles of anisotropic refinement produced convergence (no shift per error greater than 0.7) to a final *R* value of 0.130. The final weighted *R* value $[\{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}]$ and goodness-of-fit index $[\{\sum w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV})\}^{1/2}$, where NO = 3028 observations and NV = 285 variables] were 0.088 and 2.6, respectively. A final difference-Fourier map showed no features exceeding ±0.9 e/Å^3. The scattering curves for the nonhydrogen atoms[12] and the scattering curve for H[13] were taken from common sources. The real part of the scattering curves was corrected for anomalous dispersion effects.[14] Final nonhydrogen atom positional parameters are collected in Table II. The crystallographic computations were performed with standard programs.[15] Anisotropic thermal parameters, hydrogen atom parameters, nonhydrogen atom distances and angles, and a list of calculated and observed structure factor amplitudes are available.[16]

Results

The molecular conformation of the (*N*-salicylidene-*N'*,*N'*-dimethylethylenediamine)(theophyllinato)copper(II) complex is illustrated in the stereoview of Figure 1. The coordination sphere is pseudo square planar with the tridentate Schiff base and N(7) of the theophylline monoanion occupying the four equatorial coordination sites, Table III. Two weak axial interactions involving a water molecule (Cu–O(32) = 3.271 (8) Å) and O(6) of the theophylline base (Cu–O(6) = 3.340 (8) Å) are also present.

The present complex, like its close analogue I,[1] was designed to allow for the possibility of maximum axial interaction between the copper center and the exocyclic oxygen O(6) of the theophylline base. While the molecular conformations of the two complexes are virtually identical, the very long Cu–O(6) distance found here [Cu–O(6) = 3.340 (8) Å compared to the value of 2.919 (3) Å in I] clearly suggests that the energetics associated with such an interaction can be only on the order of the crystal packing forces operative in forming the solid. The present system is again in accord with the proposition that Cu–N(7),O(6) chelate formation is not a primary mode of metal–ligand bonding in Cu(II) complexes of 6-oxopurines.[1,17]

The binding of the theophylline monoanion to the copper center is strong, however, with a Cu–N(7) distance of 1.969 (7) Å that is the second shortest of the values we have observed in such complexes being only slightly longer than the Cu–N(7) distance of 1.956 (3) Å found in I,[1] where the weak Cu···O(6) interaction may add some stability to the complex. In the absence of either an interligand hydrogen bond involving O(6) or a significant Cu–O(6) interaction,[7,18-19] the exocyclic bond

Table II. Final Positional Parameters

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cu[a]	10399 (8)	25135 (9)	6460 (5)	C(3)	6034 (9)	2880 (6)	1434 (4)
O(2)[b]	5611 (5)	1527 (4)	2199 (3)	C(4)	4149 (7)	2776 (5)	1190 (4)
O(6)	2106 (5)	1334 (4)	1720 (3)	C(5)	3167 (7)	2408 (6)	1240 (4)
O(10)	1484 (5)	1799 (4)	9 (3)	C(6)	2958 (7)	1734 (6)	1640 (4)
O(31)[c]	7899 (6)	1634 (6)	2264 (3)	C(8)	3150 (7)	3373 (6)	582 (4)
O(32)[c]	5727 (5)	4286 (5)	157 (3)	C(10)	924 (8)	1260 (6)	−309 (4)
O(33)[c]	$^3/_4$	$^1/_2$	741 (5)	C(11)	1415 (9)	746 (7)	−729 (5)
O(34)[c]	8582 (8)	4940 (7)	2250 (4)	C(12)	842 (12)	154 (8)	−1067 (5)
N(1)	3841 (6)	1509 (5)	1985 (3)	C(13)	−232 (11)	71 (8)	−1017 (5)
N(3)	4999 (5)	2510 (5)	1525 (3)	C(14)	−757 (8)	562 (7)	−606 (5)
N(7)	2531 (5)	2800 (4)	828 (3)	C(15)	−186 (9)	1157 (7)	−245 (4)
N(9)	4196 (5)	3396 (5)	764 (3)	C(16)	−796 (8)	1162 (7)	161 (5)
N(17)	−447 (6)	2201 (5)	537 (4)	C(18)	−1194 (8)	2662 (8)	920 (5)
N(20)	456 (6)	3371 (6)	1275 (3)	C(19)	−661 (9)	3512 (9)	1086 (5)
C(1)	3710 (8)	805 (6)	2424 (5)	C(20)	966 (10)	4238 (8)	1301 (5)
C(2)	4873 (8)	1842 (6)	1917 (4)	C(21)	500 (10)	2962 (8)	1843 (5)

[a] Cu parameters × 10^5. [b] O, N, and C parameters ×10^4. [c] Oxygen atoms of the waters of crystallization.

Table III. Bond Lengths (Å) and Angles (deg) in the Primary Coordination Sphere about the Copper

	Bond Lengths		
Cu-O(10)	1.910 (6)	Cu-N(17)	1.944 (8)
Cu-N(7)	1.969 (7)	Cu-N(20)	2.081 (8)
	Bond Angles		
O(10)-Cu-N(7)	90.6 (3)	N(7)-Cu-N(17)	175.0 (3)
O(10)-Cu-N(17)	92.6 (3)	N(7)-Cu-N(20)	92.8 (3)
O(10)-Cu-N(20)	173.7 (3)	N(17)-Cu-N(20)	84.3 (3)

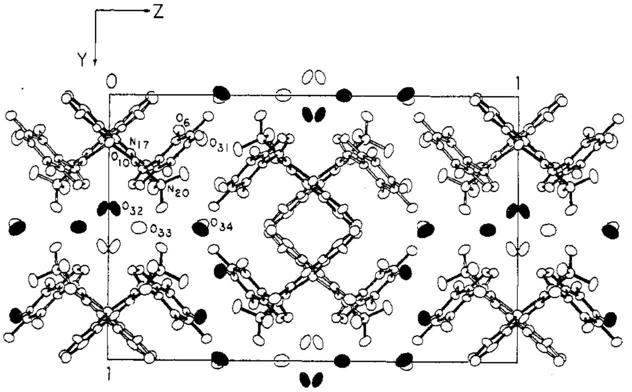

Figure 2. Projection of the structure of (*N*-salicylidene-*N′*,*N′*-dimethylethylenediamine)(theophyllinato)copper(II)–3.5-water onto the *bc* plane.

angles at N(7) are nearly symmetric with values of Cu–N(7)–C(5) = 127.5 (6)° and Cu–N(7)–C(8) = 128.6 (6)°.

The remaining bond lengths and angles in the primary coordination sphere closely resemble those we have observed in other such systems. The Cu–N(20) bond length of 2.081 (3) Å, like its analogue in I at 2.068 (3) Å, is significantly longer than in the monomethylethylenediamine systems.[8,9] The parameters in the purine ring and the Schiff base are typical.

The crystal packing is illustrated in the (100) projection of Figure 2. The packing is dominated by hydrogen-bonding interactions and by intermolecular overlap between the salicylidene ring and the theophylline moiety of glide-related complexes. Although the hydrogen atoms associated with the water molecules have not been located, some aspects of the hydrogen bonding are discernible. The N(9) atom on the theophylline anion accepts a hydrogen bond from water molecule atom O(32) [N(9)···O(32) = 2.73 (1) Å], which is also hydrogen bonded to water molecule atom O(33) [O(32)···O(33) = 2.82 (1) Å]. Two other hydrogen bonds appear to involve the carbonyl oxygen O(2) of the theophylline ring and the water molecule atoms O(31) and O(34) [O(2)···O(31) = 2.88 (1) Å and O(2)···O(34) = 2.86 (1) Å]. Other details of the interwater hydrogen bonding scheme are difficult to interpret, as noted above.

As in several (Schiff base)copper–theophylline complexes,[8,9] there is a significant intermolecular overlap of the salicylidene ring and the theophylline moiety. Several short contacts within these overlapped dimers, Figure 2, are on the order of 3.3–3.4 Å.

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Registry No. (*N*-salicylidene-*N′*,*N′*-dimethylethylenediamine)(theophyllinato)copper(II)·3.5H_2O, 67163-21-7; (*N*-salicylidene-*N′*,*N′*-dimethylethylenediamine)(theophyllinato)copper(II)·3H_2O, 67163-22-8; (*N*-salicylidene-*N′*,*N′*-dimethylethylenediamine)(theophyllinato)copper(II)·H_2O, 67163-20-6.

Supplementary Material Available: Tables of anisotropic thermal parameters for the nonhydrogen atoms, hydrogen atom positional parameters, nonhydrogen atom distances and angles, and observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

References and Notes

(1) D. J. Szalda, T. J. Kistenmacher, and L. G. Marzilli, *J. Am. Chem. Soc.*, **98**, 8371 (1976).
(2) D. J. Hodgson, *Prog. Inorg. Chem.*, **23**, Chapter 2 (1977).
(3) L. G. Marzilli, *Prog. Inorg. Chem.*, **23**, Chapter 3 (1977).
(4) J. Dehand and J. Jordanov, *J. Chem. Soc., Chem. Commun.*, 598 (1976).
(5) M. M. Millard, J. P. Macquet, and T. Theophanides, *Biochim. Biophys. Acta*, **402**, 166 (1975); G. Pneumatikakis, N. Hadjiliadis, and T. Theophanides, *Inorg. Chim. Acta*, **22**, L1 (1977).
(6) D. M. L. Goodgame, I. Jeeves, F. L. Phillips, and A. C. Skapski, *Biochim. Biophys. Acta*, **378**, 153 (1975).
(7) L. G. Marzilli and T. J. Kistenmacher, *Acc. Chem. Res.*, **10**, 146 (1977).
(8) T. J. Kistenmacher, D. J. Szalda, and L G. Marzilli, *Inorg. Chem.*, **14**, 1686 (1975).
(9) D. J. Szalda, T. J. Kistenmacher, and L. G. Marzilli, *Inorg. Chem.*, **15**, 2783 (1976).
(10) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).
(11) A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).
(12) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).
(13) R. F. Stewart, E. R. Davison, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(14) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(15) Crystallographic programs employed include the following: Wehe, Busing, and Levy's ORABS; Busing, Martin, and Levy's ORFLS; Zalkin's FORDAP; Pippy and Ahmed's MEAN PLANE; Johnson's ORTEP. Calculations other than those specifically noted were performed with locally written programs.
(16) Supplementary material.
(17) E. Sletten, *Acta Crystallogr., Sect. B*, **30**, 1961 (1974).
(18) T. J. Kistenmacher and L. G. Marzilli in "Metal-Ligand Interactions in Organic and Biochemistry", B. Pullman and N. Goldblum, Ed., Reidel, Dordrecht, 1977, Part I, p 7–40.
(19) B. L. Kindberg, E. A. H. Griffith, E. L. Amma, and E. R. Jones, *Cryst. Struct. Commun.*, **5**, 533 (1976).