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Secondary Interactions and Their Role in the Molecular Conformation of Transition Metal–Pyrimidine Complexes. Semichelation and Interligand Hydrogen Bonding Involving O(2) of Cytosine in the Complex [(*N*-Salicylidene-*N'*-methylethylenediamine)(cytosine)copper(II)] Nitrate Monohydrate

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The preparation and structure of the complex (*N*-salicylidene-*N'*-methylethylenediamine)(cytosine)copper(II) nitrate are reported. The complex crystallizes as the monohydrate in the monoclinic system, space group $P2_1/c$, with a = 7.453 (3) Å, b = 12.555 (2) Å, c = 20.336 (7) Å, β = 110.07 (3)°, V = 1787.0 Å^3, Z = 4, d_m = 1.59 (1) g cm^{-3} and, d_c = 1.60 g cm^{-3}. Intensities for 4130 independent reflections were collected by counter methods employing the θ–2θ scan technique and graphite-monochromatized Mo Kα radiation. The structure was solved by standard heavy-atom Patterson and Fourier methods. Full-matrix least-squares refinement has led to a final R value of 0.069; the final weighted R value and goodness of fit are 0.063 and 1.6, respectively. The primary coordination sphere about the copper is approximately square planar with the tridentate Schiff-base ligand and N(3) of cytosine occupying the four coordination sites. The coordination sphere about the copper is extended to (4 + 2)-coordination geometry via an intramolecular interaction involving O(2) of the cytosine ligand, Cu···O(2) = 2.772 (1) Å, and an intermolecular interaction with one of the oxygen atoms of the nitrate group, Cu···O = 2.806 (1) Å. The complex also exhibits a weak interligand hydrogen bond involving O(2) of cytosine and the *N*-methylethylenediamine terminus of the Schiff-base chelate. The crystal structure is dominated by columns of complexes, along the short a axis, which show significant overlap of the salicylidene rings of the Schiff base. The stability of these columns is enhanced by an intermolecular hydrogen bond between the exocyclic amine, N(4)H$_2$, of cytosine on one complex and O(2) on a translationally related complex. The interaction between the columns is primarily by hydrogen bonds involving the semicoordinated nitrate group and the water of crystallization.

Introduction

Interligand interactions play an important role in determining the selectivity of chelate complexes in the reactions of these complexes with other ligands. For example, the stereochemistry of the quinquedentate Schiff-base ligand *N,N'*-bis(salicylidene)dipropylenetriamine in a cobalt(III) complex is such as to influence sterically the coordination of monodentate ligands to the sixth coordination position.[1] Ligands which are planar in the vicinity of the donor atom (e.g., pyridine) form more stable complexes relative to nonplanar ligands (e.g., tertiary phosphines) than might otherwise be expected on the basis either of basicity or the usual affinities of these monodentate ligands toward cobalt(III).[1]

Furthermore, it is likely in multisite ligands, such as the nucleic acids and some proteins where the nucleophilicity of a site is an insufficient criterion for specificity of binding, that interligand interactions, both favorable and unfavorable, will be important factors in determining binding selectivity. The interactions between polyamine chelate ligands and the exocyclic groups on the commonly occurring nucleosides appear to impart semiquantitative differentiation among deoxythymidine, deoxyguanosine, and deoxycytidine with complete exclusion of deoxyadenosine binding.[2] In seeking a more quantitative understanding of interligand interactions we have prepared and studied the reactivity of a variety of metal chelate complexes with nucleic acid constituents.[2-10]

The tridentate Schiff-base ligand *N*-salicylidene-*N'*-methylethylenediamine occupies three of the four sites about a copper(II) ion and presents to an incoming ligand both the exocyclic oxygen atom on the salicylidene ring and the *N*-methyl terminus of the ethylenediamine chain. In copper(II) complexes, exocyclic groups on the nucleic acid heterocycles may bind to the axial positions on the metal.[7,8,11] Therefore, the interaction of the (*N*-salicylidene-*N'*-methylenediamine)copper(II) moiety with nucleic acid components is of particular interest to us, and we report here the preparation and structure of the cytosine complex.

Experimental Section

Preparation of (*N*-Salicylidene-*N'*-methylethylenediamine)(cytosine)copper(II) Nitrate. The complex (chloro)(*N*-salicylidene-*N'*-methylethylenediamine)copper(II) was prepared by the method of Sacconi and Bertini.[12] A solution of the aquated cation was obtained by the addition of $AgNO_3$ (0.31 g, 2 mmol) to an aqueous solution (25 ml) of the chloro complex (0.5 g, 2 mmol). The solution was filtered to remove the precipitated AgCl, and cytosine (0.20 g, 2 mmol) was added to the filtrate. The mixture was heated for about $^1/_2$ hr on a steam bath (75–80°); the solution was then rotoevaporated to a volume of about 12 ml. After 4–6 days, deep purple crystals of the cytosine complex were obtained. The infrared spectrum of this material contained bands attributable to cytosine, in particular bands at 1685 and 1230 cm^{-1} (KBr disk). Several attempts were made to isolate crystalline salts other than the nitrate, but these were unsuccessful.

Table I. Crystal Data for (*N*-Salicylidene-*N'*-methylethylenediamine)(cytosine)copper(II) Nitrate Monohydrate

a = 7.453 (3) Å	$Cu(O_3N_5C_{14}H_{18})\cdot NO_3\cdot H_2O$
b = 12.555 (2) Å	Mol wt 431.9
c = 20.336 (7) Å	d_m = 1.59 (1) g cm^{-3}
β = 110.07 (3)°	d_c = 1.60 g cm^{-3}
V = 1787.0 Å^3	Space group $P2_1/c$
μ = 13.1 cm^{-1}	Z = 4
λ(Mo K$\bar{\alpha}$) = 0.71069 Å	

Collection and Reduction of the X-Ray Data. The complex crystallizes as elongated monoclinic prisms with [010] as the prism axis. The crystal system is monoclinic with systematic absences ($0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$) consistent with the space group $P2_1/c$. Unit cell dimensions and their associated standard deviations were derived from a least-squares fit to the 2θ, ω, and χ settings for 15 carefully centered reflections; the density was measured by neutral buoyancy methods and indicated one formula unit plus one water molecule per asymmetric volume. Complete crystal data are given in Table I.

The 4947 reflections in the $h\bar{k}l$, $hk\bar{l}$ quadrant to 2θ = 55° were measured on a Syntex $P\bar{1}$ automated diffractometer; molybdenum graphite-monochromatized radiation was employed. The crystal used in data collection was a rectangular prism with dimensions 0.15 × 0.20 × 0.25 mm; the long axis was mounted approximately along the ϕ axis of the spectrometer. Intensity data were collected by the θ–2θ scan technique; individual scan speeds were determined by a rapid scan at the calculated Bragg peak, and the rate of scanning varied from 1.5° min^{-1} (less than 100 counts in the rapid scan) to 24° min^{-1} (more than 1000 counts during the rapid scan). Three standards were monitored after every 100 reflections, and their intensities showed

Table II. Final Heavy-Atom Parameters ($\times 10^4$)[a]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	7972 (0.5)	2298 (0.3)	1371 (0.2)	135 (0.7)	36 (0.2)	16 (0.1)	1 (0.4)	18 (0.2)	2 (0.1)
O(2)	5233 (3)	3892 (2)	995 (1)	120 (4)	55 (2)	31 (1)	2 (2)	24 (2)	8 (1)
O(7)	11864 (5)	1919 (3)	2092 (2)	313 (8)	88 (2)	30 (1)	18 (4)	17 (2)	0 (1)
O(8)	13059 (9)	1854 (8)	3174 (3)	615 (20)	578 (16)	44 (2)	−234 (15)	−21 (5)	101 (4)
O(9)	14137 (7)	2949 (4)	2723 (3)	403 (13)	160 (5)	96 (3)	−50 (7)	78 (5)	−50 (3)
O(10)	7980 (3)	1817 (2)	475 (1)	193 (5)	34 (1)	18 (1)	−0 (2)	26 (1)	0 (1)
O(15)	6462 (3)	3276 (2)	−587 (1)	196 (6)	47 (2)	28 (1)	16 (3)	21 (2)	4 (1)
N(1)	6566 (4)	5343 (2)	684 (2)	149 (6)	39 (2)	25 (1)	13 (3)	20 (2)	28 (1)
N(3)	8349 (3)	3791 (2)	1089 (1)	117 (5)	36 (2)	17 (1)	2 (2)	17 (2)	−1 (1)
N(4)	11494 (4)	3712 (3)	1155 (2)	147 (6)	63 (2)	34 (1)	9 (3)	37 (2)	5 (1)
N(6)	13004 (5)	2215 (4)	2675 (2)	175 (8)	150 (5)	33 (1)	30 (5)	28 (3)	18 (2)
N(17)	7367 (4)	897 (2)	1637 (1)	167 (6)	42 (2)	21 (1)	0 (3)	22 (2)	6 (1)
N(20)	7776 (5)	2738 (2)	2314 (1)	261 (8)	65 (2)	18 (1)	2 (4)	30 (2)	1 (1)
C(2)	6653 (4)	4322 (2)	928 (2)	126 (6)	38 (2)	16 (1)	4 (3)	12 (2)	−2 (1)
C(4)	9873 (4)	4254 (2)	994 (1)	124 (6)	42 (2)	15 (1)	−2 (3)	19 (2)	−4 (2)
C(5)	9766 (5)	5313 (3)	740 (2)	169 (7)	42 (2)	21 (1)	−21 (3)	26 (2)	−4 (1)
C(6)	8089 (5)	5829 (3)	598 (2)	213 (8)	35 (2)	23 (1)	−8 (3)	25 (2)	1 (1)
C(10)	7735 (4)	836 (2)	231 (2)	99 (6)	41 (2)	20 (1)	9 (3)	12 (2)	−0 (1)
C(11)	7857 (5)	639 (3)	−439 (2)	151 (7)	50 (2)	22 (1)	9 (3)	19 (2)	0 (1)
C(12)	7598 (5)	−365 (3)	−725 (2)	160 (7)	60 (3)	26 (1)	13 (3)	17 (2)	−10 (1)
C(13)	7203 (5)	−1227 (7)	−370 (2)	188 (8)	43 (2)	38 (1)	4 (4)	22 (3)	−14 (1)
C(14)	7068 (5)	−1063 (3)	279 (2)	149 (7)	38 (2)	36 (1)	4 (3)	25 (2)	1 (1)
C(15)	7352 (4)	−50 (2)	597 (2)	108 (6)	34 (2)	25 (1)	8 (3)	15 (2)	2 (1)
C(16)	7142 (5)	42 (3)	1271 (2)	129 (6)	37 (2)	27 (1)	7 (3)	18 (2)	11 (1)
C(18)	7024 (6)	877 (3)	2306 (2)	317 (11)	64 (3)	25 (1)	−3 (4)	48 (3)	12 (1)
C(19)	8013 (7)	1796 (4)	2732 (2)	351 (13)	98 (4)	24 (1)	0 (6)	46 (3)	7 (2)
C(20)	8714 (8)	3686 (4)	2673 (2)	441 (15)	86 (4)	26 (1)	−39 (6)	45 (4)	−18 (2)

[a] Estimated standard deviations are enclosed in parentheses. The form of the anisotropic ellipsoid is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

no unusual variation over the course of the experiment (maximum deviation of any standard from its mean intensity of about 4%). The 4947 measured intensities, which included standards and systematic absences as well as some symmetry-related data, were reduced to a set of 4130 independent values. All reflections were assigned observational variances based on the equation

$$\sigma^2(I) = S + (B_1 + B_2)(T_S/2T_B)^2 + (pI)^2$$

where S, B_1, and B_2 are the scan and extremum background counts, T_S and T_B are the scan and individual background counting times ($T_B = 1/4T_S$ for all reflections), and p was taken to be equal to 0.04 and represents the expected error proportional to the diffracted intensity.[13] Intensities and their standard deviations were corrected for Lorentz and polarization effects; the amplitudes of reflections with negative intensities were set equal to zero. No correction for absorption was applied ($\mu = 13.1$ cm^{-1}); the maximum error introduced by the neglect of absorption effects was estimated to be about 5% in I. The squared structure factors were placed on an approximate absolute scale by the method of Wilson.[14]

Solution and Refinement of the Structure. The positional coordinates of the copper atom were deduced from a three-dimensional Patterson synthesis. A subsequent structure factor Fourier calculation allowed the positioning of the remaining 26 heavy atoms in the asymmetric unit (including all heavy atoms, $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.23$). Four cycles of isotropic least-squares refinement, minimizing the quantity $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, reduced the R value to 0.11. A difference Fourier map was computed at this stage, and positional parameters for all 20 independent hydrogen atoms were assigned; the hydrogen atoms were given the same isotropic temperature factor as the atom to which they were bonded. The refinement was continued with anisotropic temperature factors being refined for the heavy atoms; no attempt was made to vary any of the hydrogen atom parameters. Three cycles of refinement in this mode led to a final R value of 0.069. The final weighted R value $[(\sum w(F_o - F_c)^2/\sum wF_o^2)^{1/2}]$ and goodness of fit $[(\sum w(F_o - F_c)^2/(NO - NV))^{1/2}$, where NO = 4130 independent observations and NV = 244 parameters] were 0.063 and 1.6, respectively.

Neutral scattering factors for all the nonhydrogen atoms were taken from the compilation of Hanson, Herman, Lea, and Skillman;[15] the scattering curve for H was that of Stewart, Davidson, and Simpson.[16] The real part of the scattering factor for Cu was corrected for anomalous dispersion effects.[17] Final heavy-atom parameters are collected in Table II, while the parameters for the hydrogen atoms are given in Table III.[18] A complete list of observed and calculated structure factor amplitudes is available.[18]

The crystallographic computations were performed with the following programs: structure factor Fourier, X-RAY 67;[19] least-squares refinements, ORFLS;[20] best planes, MEAN PLANE;[21] illustrations, ORTEP.[22] Calculations not cited were done with locally written programs.

Discussion

Examination[7] of the several recent crystallographic studies of copper(II)–cytosine or copper(II)–cytidine complexes clearly shows two principal features common to all of the complexes: (1) binding of the pyrimidine or pyrimidine nucleoside through the N(3) position of the ring; (2) an axial, intramolecular Cu···O(2) interaction with essentially constant geometrical features. In fact, the ubiquity and constancy of the geometrical parameters of this Cu···O(2) intramolecular interaction has prompted us[7] to suggest that its occurrence may play some role in the recognition of cytosine residues in nucleic acids by copper(II). We have suggested[7] that there is some theoretical justification for this semichelation of cytosine (cytidine) by square-planar copper(II). Square-planar copper(II) has a decided tendency to extend its coordination sphere to five, the so-called (4 + 1)-coordination geometry, and even to six, the (4 + 2)- and (4 + 1 + 1)-coordination geometries.[23] Moreover, a molecular electrostatic potential calculation[24] for cytosine shows that the presence of the carbonyl group, C(2)–O(2), adjacent to the pyrimidine nitrogen N(3) establishes a wide attractive region for electrophilic agents. The calculation[24] shows two deep minima, one in the direction of the lone pair at N(3) and one at an angle of 55° to the C(2)–O(2) bond. The minima at N(3) and O(2) are significantly deeper than at similar sites in adenine or thymine, respectively. Thus, the simultaneous binding of copper(II) to N(3) and O(2) may be a consequence of the tendency of copper(II) to extend its coordination sphere and the electrostatic potential distribution inherent to the cytosine (cytidine) molecular framework.

In this respect, a recent structure determination of a copper(II) N(1)-bonded thymine complex[25] shows no meaningful Cu···O(2) interaction, Cu···O(2) = 3.159 (4) Å. This is to be expected since, as noted above, the electrostatic

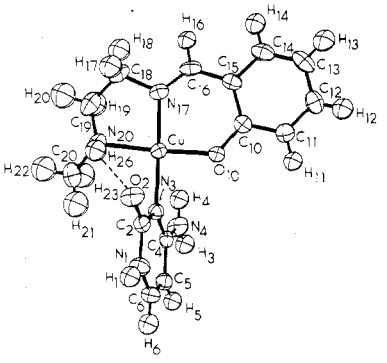

Figure 1. Perspective view of the (*N*-salicylidene-*N'*-methylethylenediamine)(cytosine)copper(II)$^+$ cation. The thermal ellipsoids are drawn at the 50% probability level. The dashed line indicates the weak interligand hydrogen bond. The atomic numbering scheme is also given in this figure.

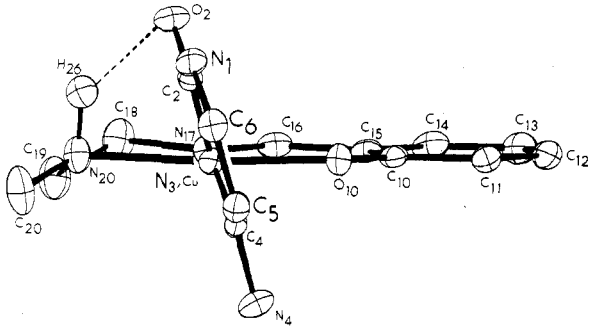

Figure 2. Projection of the complex cation down the N(3)–Cu bond. The thermal ellipsoids are drawn at the 25% probability scale. Note in particular the disposition of the cytosine ring relative to the Schiff base and the weak interligand hydrogen bond (dashed line).

potential[24] at O(2) of thymine is considerably less nucleophilic than at O(2) of cytosine.

The cytosine complex reported here fits the general pattern exhibited by the other known cytosine complexes of copper(II).[7,8,11] The binding of the copper atom has taken place through N(3), Figure 1, with a Cu–N(3) distance of 2.008 (1) Å, which is comparable to those found in (dichloro)(bis(cytosine))copper(II),[11] 1.95 (1) and 1.97 (1) Å, and the cytosine,[8] 1.979 (3) Å, and cytidine[7] complexes of glycylglycinatocopper(II), 1.97 (1) and 2.04 (1) Å for the two independent molecules in the asymmetric unit for this structure.

The parameters in the Cu···O(2) intramolecular interaction in the Schiff base–cytosine complex [Cu···O(2) = 2.772 (1) Å; Cu···C(2) = 2.762 (1) Å; Cu···O(2)–C(2) = 76.7 (3)°] are in good agreement with the average values in the other three copper(II)–cytosine complexes noted above [Cu···O(2) = 2.78 Å; Cu···C(2) = 2.76 Å; angle Cu···O(2)–C(2) = 76°]. The stability of the binding of the cytosine ligand appears to be enhanced by the formation of a weak,[26] interligand hydrogen bond between O(2) and the hydrogen atom off the secondary amine nitrogen, N(20), of the Schiff base [H(26)···O(2) = 2.30 Å; N(20)–H(26)···O(2) = 134°; see Figures 1 and 2].

We have recently reported the synthesis and structure of a complex of this Schiff base–copper(II) system with theophylline, 1,3-dimethyl-2,6-dioxopurine.[10] In this complex, bonding occurs at N(7) with a strong interligand hydrogen bond formed between the carbonyl group at C(6) and the hydrogen atom on the *N*-methylethylenediamine terminus of the Schiff base, but there is no Cu···O(6) interaction, Cu···O(6) = 3.730 (1) Å.

These differences in the two complexes are probably directly related to the fact that the carbonyl function in theophylline is one more bond removed from the site of the Cu–N bond than in cytosine, leading then to a larger "bite" distance between the exocyclic oxygen and the nitrogen binding site and a reduction in the nucleophilicity of O(6) of theophylline relative to O(2) of cytosine [see the above discussion on the influence of the adjacent nitrogen atom on the electrostatic potential distribution at the O(2) oxygen of cytosine]. This conclusion is supported by a lack of evidence of chelate formation involving the O(6) oxygen of a hypoxanthine derivative when coordination takes place at N(7).[27] The existence of such a chelate in bis(6-mercapto-9-benzylpurine)palladium(II)[28] is probably a consequence of the greater versatility of sulfur in comparison to oxygen in forming bonds to metals.

The copper atom in the Schiff base–cytosine complex extends its coordination geometry to (4 + 2)[23] via a Cu···O(7)$_{nitrate}$ interaction, Cu···O(7) = 2.806 (1) Å. The nitrate oxygen O(7) is considerably more "on axis" than O(2) of the cytosine ligand. The largest angular deviation from 90° involving O(7) is 5.9° [O(10)–Cu···O(7) = 95.9 (1)°], while O(2) has a necessarily acute angle with N(3), N(3)–Cu···O(2) = 53.8 (1)°, and a very obtuse angle with N(17), N(17)–Cu···O(2) = 120.8 (1)°. The angle between the axial substituents, O(2)···Cu···O(7), is 142.9 (1)°.

The bond lengths and angles in the primary coordination sphere about the copper are collected in Table IV. Comparison of the values in the cytosine vs. the theophylline complex[10] shows a slight contraction in the Cu–N(17) distance, 0.009 Å, while significant elongations have occurred in the Cu–N(20) distance, 2.048 (1) vs. 2.020 (1) Å, and the Cu–O(10) bond length, 1.922 (1) vs. 1.902 (1) Å. These elongations are accompanied by a substantial increase in the N(20)–Cu–O(10) bond angle, 175.5 (1) vs. 171.9 (1)°.

There are also significant differences in the geometrical parameters in the *N*-salicylidene-*N'*-methylethylenediamine chelate. The salicylidene portion of the Schiff base is nearly identical in the cytosine and theophylline complexes (maximum deviation of 0.012 Å in the C(13)–C(14) benzenoid ring bond with an average difference of 0.007 Å). However, the *N*-methylethylenediamine portion of the chelate shows marked differences. In particular, we find significant contractions in the C(18)–C(19), 0.03 Å, C(19)–N(20), 0.05 Å, and N(20)–C(20), 0.03 Å, bond lengths in the cytosine vs. the theophylline complex. These bond length contractions are accompanied by rather dramatic differences in some bond angles [C(18)–C(19)–N(20), +4.1 (4)°, Cu–N(20)–C(20), +8.0 (2)°, and C(19)–N(20)–C(20), +4.6 (4)° for the cytosine vs. the theophylline complex] and in the conformational torsion angles in the five-membered *N*-methylethylenediamine chelate ring, Table V. It is also evident, Table II, that the thermal parameters on C(18), C(19), and N(20) are somewhat larger than expected, all of which suggests that there is somewhat more strain in the *N*-methylethylenediamine portion of the Schiff base in the cytosine complex than in the theophylline complex. Some strain in such a tridentate complex is expected.[29] We have concluded, for example, that the substantial tetrahedral component to the basic square-planar geometry in the theophylline complex[10] was a consequence of the concurrent steric requirement of the five- and six-membered chelate rings. In contrast, the cytosine complex is nominally planar, Table VI, part a. The distribution of the steric strain to the *N*-methylethylenediamine ring as opposed to the equatorial plane in the cytosine complex may, in part at least, be due to the simultaneous requirements of the Cu···O(2) intramolecular interaction and the N(20)–H(26)···O(2) interligand hydrogen bond. As expected, the salicylidene ring is reasonably planar (Table VI, part b).

Comparison of the bond lengths in the coordinated cytosine ligand to those in cytosine[30,31] and cytosine monohydrate[31,32] reveals no significant changes in bond lengths upon coordi-

Table IV. Heavy-Atom Interatomic Distances (Å) and Angles (deg)[a]

(a) Primary Coordination Sphere about the Copper Atom

Bond Lengths			
Cu-N(3)	2.008	Cu-N(20)	2.048
Cu-N(17)	1.938	Cu-O(10)	1.922

Bond Angles			
N(3)-Cu-N(17)	174.6	N(17)-Cu-N(20)	83.4
N(3)-Cu-N(20)	94.4	N(17)-Cu-O(10)	93.2
N(3)-Cu-O(10)	88.6	N(20)-Cu-O(10)	175.5

(b) *N*-Salicylidene-*N'*-methylethylenediamine Chelate Ligand

Bond Lengths			
O(10)-C(10)	1.317	C(15)-C(10)	1.421
C(10)-C(11)	1.418	C(15)-C(16)	1.437
C(11)-C(12)	1.374	C(16)-N(17)	1.284
C(12)-C(13)	1.387	N(17)-C(18)	1.468
C(13)-C(14)	1.373	C(18)-C(19)	1.479
C(14)-C(15)	1.409	C(19)-N(20)	1.432
		N(20)-C(20)	1.445

Bond Angles			
Cu-O(10)-C(10)	127.3	C(14)-C(15)-C(16)	117.5
O(10)-C(10)-C(11)	118.6	C(15)-C(16)-N(17)	125.8
O(10)-C(10)-C(15)	124.2	C(16)-N(17)-C(18)	119.6
C(11)-C(10)-C(15)	117.2	Cu-N(17)-C(16)	126.4
C(10)-C(11)-C(12)	121.4	Cu-N(17)-C(18)	113.9
C(11)-C(12)-C(13)	121.3	N(17)-C(18)-C(19)	108.6
C(12)-C(13)-C(14)	118.8	C(18)-C(19)-N(20)	111.2
C(13)-C(14)-C(15)	121.8	Cu-N(20)-C(19)	107.4
C(10)-C(15)-C(14)	119.4	Cu-N(20)-C(20)	121.2
C(10)-C(15)-C(16)	123.0	C(19)-N(20)-C(20)	116.2

(c) Cytosine Ligand

Bond Lengths			
N(1)-C(2)	1.368	N(4)-C(4)	1.326
N(1)-C(6)	1.352	C(2)-O(2)	1.237
N(3)-C(2)	1.366	C(4)-C(5)	1.419
N(3)-C(4)	1.348	C(5)-C(6)	1.348

Bond Angles			
C(2)-N(1)-C(6)	122.2	N(1)-C(2)-N(3)	118.0
C(2)-N(3)-C(4)	120.8	N(3)-C(4)-N(4)	119.0
Cu-N(3)-C(2)	108.4	N(3)-C(4)-C(5)	120.8
Cu-N(3)-C(4)	130.6	N(4)-C(4)-C(5)	120.2
N(1)-C(2)-O(2)	120.9	C(4)-C(5)-C(6)	117.4
N(3)-C(2)-O(2)	121.1	N(1)-C(6)-C(5)	120.9

(d) Nitrate Anion

Bond Lengths			
N(6)-O(7)	1.26	N(6)-O(9)	1.23
N(6)-O(8)	1.10		

Bond Angles			
O(7)-N(6)-O(8)	123	O(8)-N(6)-O(9)	115
O(7)-N(6)-O(9)	121		

[a] Bond length esd's: Cu-N(O), 0.001 Å; C-C, 0.006 Å; C-N, 0.006 Å; C-O, 0.006 Å; N-O (nitrate), 0.01 Å. Bond angle esd's: N-Cu-N(O), 0.1°; C-C-N(O), 0.4°; N-C-N, 0.4°; O-N-O (nitrate), 1.0°.

Table V. Torsion Angles (deg) in the Five-Membered *N*-Methylethylenediamine Chelate Ring[a]

Torsion angle	Cytosine complex[b]	Theophylline complex[c]
C(18)-N(17)-Cu-N(20)	2.3 (3)	10.6 (2)
C(19)-C(18)-N(17)-Cu	−24.1 (3)	−36.3 (2)
N(20)-C(19)-C(18)-N(17)	42.2 (4)	50.8 (3)
Cu-N(20)-C(19)-C(18)	−39.6 (3)	−41.8 (2)
N(17)-Cu-N(20)-C(19)	20.5 (3)	17.9 (2)

[a] A positive torsion angle corresponds to a right-handed screw. [b] This study. [c] Reference 10.

nation to N(3). There are, however, a few minor changes in bond angles, mainly those involving N(3); for example, C(2)–N(3)–C(4) is 120.8 (4)° in the complex and 119.4 (2) and 119.1 (2)° in cytosine and cytosine monohydrate; N(3)–C(4)–N(4) is 119.0 (4) vs. 117.1 (2) and 118.1 (2)°; and N(3)–C(4)–C(5) is 120.8 (4)° vs. 122.7 (2) and 121.7 (2)°.

Table VI. Least-Squares Planes and the Deviations of Individual Atoms from These Planes[a]

(a) Copper and Its Four Ligated Atoms
$(-0.8957X + 0.1542Y - 0.4171Z = -5.0556$ Å)

Cu	−0.056	N(3)	0.029
O(10)	−0.001	N(17)	0.030
		N(20)	−0.002

(b) Salicylidene Ring
$(-0.8874X + 0.1779Y - 0.4253Z = -4.9692$ Å)

C(10)	−0.004	C(15)	−0.020
C(11)	0.000	C(16)	0.010
C(12)	0.003	O(10)	0.006
C(13)	0.003	N(17)	−0.019*
C(14)	0.003	C(18)	0.074*
		Cu	−0.055*

(c) Cytosine Ring $(0.0375X - 0.3454Y - 0.9377Z = -3.3804$ Å)

N(1)	0.004	C(5)	0.004
N(3)	−0.010	C(6)	−0.008
C(2)	0.005	O(2)	0.031*
C(4)	0.005	N(4)	−0.008*
		Cu	0.115*

(d) Nitrate Anion $(0.7501X - 0.6571Y - 0.0752Z = -3.6548$ Å)

N(6)	0.003	O(8)	−0.001
O(7)	−0.001	O(9)	−0.001

[a] In each of the equations of the planes, the X, Y, and Z are coordinates (Å) referred to the orthogonal axes a, b, and c^*. Atoms indicated by an asterisk were given zero weight in calculating the planes; other atoms were equally weighted.

We have noted a considerable variability[2,4,6-8,10] in the exocylic bond angles at the coordinated nitrogen atom in response to interligand hydrogen bonding or chelation in metal–purine and metal–pyrimidine complexes. This structural feature is also evident in this cytosine complex; Cu–N(3)–C(2) = 108.4 (4)° and Cu–N(3)–C(4) = 130.6 (4)°, as one might expect from the presence of the intramolecular Cu···O(2) interaction and the N(20)–H(26) interligand hydrogen bond.

The six-atom framework of the cytosine ligand is quite planar, Table VI, with only minor deviations of the exocyclic groups out of the plane. The copper lies 0.115 Å out of the plane on the same side as O(2), 0.031 Å.

The derived parameters in the nitrate group, Table IV, are marginal at best. The environment about the nitrate ion is illustrated in Figure 3.[18] As might be expected, O(7) which is involved in the intermolecular interaction with the copper atom shows a reasonable N–O distance[33] and restricted thermal motion. The other two oxygen atoms of the nitrate ion are involved in only weak hydrogen bonds or intermolecular contacts; consequently, these atoms show large thermal anisotropy approximately consistent with a librational motion about the O(7)–N(6) bond. The mean positions of the atoms in the nitrate ion as determined from our analysis do, however, lead to a coplanar arrangement of the atoms in the nitrate group, Table VI.

Crystal Packing. An important feature in the structure of the (*N*-salicylidene-*N'*-methylethylenediamine)(theophyllinato)copper(II) complex[10] was the significant overlap of the salicylidene rings of the Schiff base with the pyrimidine portion of the coordinated purine monoanion to form helical arrays of self-stacked complexes. The mean separation between theophylline planes is 6.92 Å with the salicylidene ring asymmetrically intercalated with mean distances of 3.29 and 3.62 Å to the facially stacked theophylline moieties.

This result is not repeated in the cytosine complex, primarily owing to the differences in the molecular conformations of the two Schiff-base complexes. In the theophylline complex, the strong interligand hydrogen-bonding geometry is accomplished

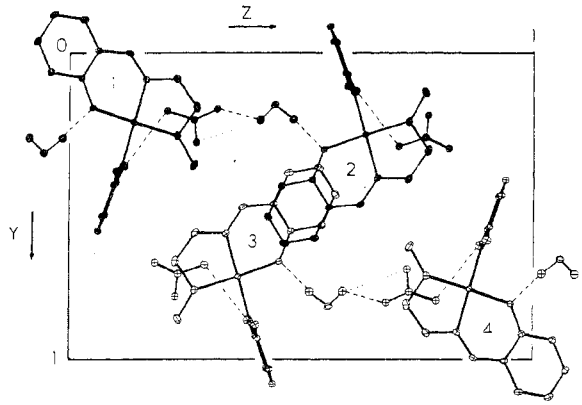

Figure 4. Projection view of the crystal packing down the a^* axis. The thermal ellipsoids are drawn at the 10% probability level. Dashed lines indicate hydrogen bonds; dotted lines indicate D-H · · ·A interactions. The four labeled complex cations have the following symmetry transforms relative to Table II: (1) x, y, z; (2) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (3) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (4) $1-x, 1-y, 1-z$. The four atoms of the nitrate anion have been arbitrarily assigned isotropic temperature factors of 3.0 Å^2 for this figure.

by tilting the theophylline plane at an angle of 33.8 (3)° to the mean equatorial plane; the net result being a roughly planar complex. In contrast, in the cytosine complex the dihedral angle between the six-atom plane of the cytosine ligand and the equatorial plane is 72.3 (4)°; see Figure 2. This nonplanarity of the complex effectively precludes intercalation of the cytosine and salicylidene rings.

This larger dihedral angle in the cytosine complex is surely due to the requirements for the formation of the intramolecular Cu···O(2) interaction and the interligand hydrogen bond involving the terminal *N*-methylamino group of the Schiff base. Similar, or larger, dihedral angles have been observed in the other known complexes of copper(II) and cytosine or cytidine: (dichloro)(bis(cytosine)copper(II)),[11] 90.6 (6) and 84.3 (6)°; (glycylglycinato)(cytosine)copper(II),[8] 63.0 (4)°; (glycylglycinato)(cytidine)copper(II),[7] 105 (1) and 104 (1)°.

A projection of the unit cell contents onto the *bc* plane, Figure 4, does show a columnar stacking of the salicylidene rings of the Schiff base. The molecular overlaps in these columns are shown in detail in Figure 5A and 5B. In each case, the two molecular fragments shown are symmetry related about centers of symmetry and significant overlap of the molecular π systems is observed. The molecular overlap and stacking distances, 3.29 Å in Figure 5A and 3.32 Å in Figure 5B, are similar to those found in molecular systems with extensive π networks.[34,35] The stability of these columnar stacks is further enhanced by the formation of an intermolecular hydrogen bond between the exocyclic amine group, $N(4)H_2$, on cytosine of one complex and O(2) on a translationally equivalent complex, Figure 6[18] and Table VII. The interaction between the columnar stacks is accomplished via intermolecular hydrogen bonds involving the semicoordinated nitrate anion and the water of crystallization, Figures 4 and 6.[18]

Details of both the intramolecular and intermolecular hydrogen bonds, as well as other close contacts of the type D–H···A, are given in Table VII.

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Registry No. [(*N*-Salicylidene-*N'*-methylethylenediamine)(cytosine)copper(II)] nitrate monohydrate, 55660-51-0; [(chloro)(*N*-salicylidene-*N'*-methylethylenediamine)copper(II)], 14242-78-5.

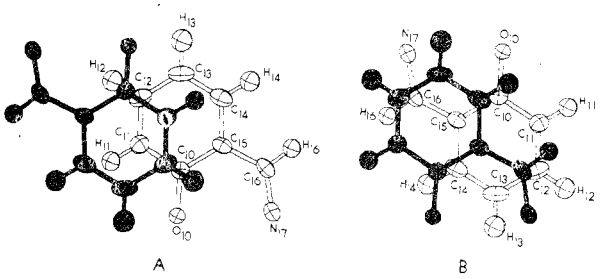

Figure 5. Molecular overlap in the columnar stacking of the salicylidene fragments of the complex cations. The view direction in each case is normal to the least-squares plane of the molecular fragment at x, y, z. The ellipsoids are drawn at the 40% probability level. (A) The overlap between the molecular fragments at x, y, z (unshaded) and $2-x, -y, -z$ (shaded); the mean separation between molecular planes is 3.29 Å. (B) The overlap between the molecular fragments at x, y, z (shaded) and $1-x, -y, -z$ (unshaded). The mean separation between molecular planes is 3.32 Å.

Table VII. Distances and Angles in Interactions of the Type D–H· · ·A

D	H	A	D–H, Å	D· · ·A, Å	H· · ·A, Å	D–H· · ·A, deg
		Hydrogen Bonds				
N(1)	H(1)	O(15)[a]	0.88	2.799	1.94	164
N(4)	H(3)	O(2)[b]	0.96	2.923	2.05	152
N(4)	H(4)	O(7)[c]	0.96	2.901	2.01	153
O(15)	H(8)	O(8)[d]	0.93	2.902	2.24	127
O(15)	H(9)	O(10)[c]	1.04	2.761	1.76	159
N(20)	H(26)	O(2)[c]	0.99	3.065	2.30	134
		Others				
N(1)	H(1)	O(8)[e]	0.88	2.937	2.79	91
C(5)	H(5)	O(15)[f]	0.97	3.426	2.46	171
O(15)	H(8)	O(9)[d]	0.93	3.618	2.80	147
C(12)	H(12)	O(7)[g]	0.96	3.530	2.69	147
C(16)	H(16)	O(9)[h]	0.96	3.652	2.72	165
C(19)	H(19)	O(8)[c]	0.97	3.555	2.65	155
C(19)	H(20)	O(9)[i]	0.97	3.226	2.74	112
N(20)	H(26)	O(9)[i]	0.99	3.109	2.58	114

[a] $1-x, 1-y, -z$. [b] $1+x, y, z$. [c] x, y, z. [d] $-1+x, \frac{1}{2}-y, -\frac{1}{2}+z$. [e] $2-x, \frac{1}{2}+y, \frac{1}{2}-z$. [f] $2-x, 1-y, -z$. [g] $2-x, -y, -z$. [h] $2-x, -\frac{1}{2}+y, \frac{1}{2}-z$. [i] $-1+x, y, z$.

Supplementary Material Available. A listing of structure factor amplitudes, Table III, showing hydrogen atom positional and isotropic thermal parameters, and Figures 3 and 6, showing the nitrate ion and its immediate environment and the crystal packing down the c^* axis, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50175B-9-75.

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Stereochemistry of Manganese Porphyrins. I. Molecular Stereochemistry of Chloro-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinato(pyridine)manganese(III)

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Chloro-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinato(pyridine)manganese(III) crystallizes in the monoclinic system, space group $P2_1/n$, as the benzene solvate. The unit cell has a = 13.149 (3) Å, b = 23.380 (6) Å, c = 14.786 (4) Å, and β = 100.50 (1)° and contains four molecules. The calculated and experimental densities are 1.277 and 1.292 g/cm^3, respectively, at 20 ± 1°. Measurement of diffracted intensities employed θ–2θ scans with graphite-monochromated Mo Kα radiation on a Syntex four-circle diffractometer. All independent reflections for $(\sin\theta)/\lambda \leq 0.626$ Å^{-1} were measured; 4980 reflections were retained as observed. These data were employed for the determination of structure using the heavy-atom method and least-squares refinement. The final conventional and weighted discrepancy factors were 0.055 and 0.075, respectively. The octahedral MnN_5Cl coordination group has an average equatorial Mn–N bond length of 2.009 Å. The axial Mn–Cl bond length is 2.467 (1) Å and the axial Mn–N bond length is 2.444 (4) Å; the elongation of the axial bonds is attributable to the unpaired electron in the d_{z^2} orbital of the high-spin manganese(III) ion.

Six-coordinate high-spin manganese(III) complexes should have a distorted coordination group resulting from the removal of the degeneracy between the d_{z^2} and the $d_{x^2-y^2}$ orbitals. With six equivalent ligands, the degeneracy is removed by a Jahn–Teller distortion. Nonequivalent ligands should also remove the degeneracy (without the necessity of invoking the Jahn–Teller theorem); the distorted octahedral complex will have (for either case) two long and four short bonds or four long and two short bonds. With nonequivalent bidentate ligands, bond length differences (two long, four short) of 0.13–0.17 Å have been observed.[1,2]

Consequently, six-coordinate high-spin manganese(III) porphyrins might be expected to have a coordination group in which the axial bonds were 0.15–0.20 Å longer than normal. However, earlier studies of low-spin six-coordinate cobalt(II) macrocycles[3-5] have shown that the tetragonal elongation resulting from the population of d_{z^2} orbital is substantially larger than 0.2 Å. For the cobalt(II) porphyrin derivatives studied,[3,4] the axial bond elongation amounted to 0.4–0.5 Å. Thus it seemed likely that the axial bonds in the six-coordinate manganese(III) porphyrins might display larger elongations than those previously observed for manganese(III) complexes utilizing bidentate ligands.[1,2]

All attempts to prepare manganese(III) porphyrin derivatives with two Lewis bases as the axial ligands failed[6] and only derivatives with an anion and a neutral Lewis base as the axial ligands could be obtained as crystalline solids. We report herein the quantitative molecular stereochemistry of one such derivative, chloro-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinato(pyridine)-manganese(III), to be written as Cl(py)MnTPP.[9] While this study was in progress, the structure of $N_3(CH_3OH)$MnTPP was reported[10] and we compare herein the pertinent stereochemical features of the two complexes.

Experimental Section

Chloro-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinato(pyridine)manganese(III). Crystals of Cl(py)MnTPP were obtained as the benzene solvate by slow evaporation of 1:1 benzene–pyridine solutions of ClMnTPP. Crystals were mounted in thin-walled capillaries to prevent loss of the solvate molecules. Preliminary X-ray photographic study established a four-molecule monoclinic unit cell. Systematic extinctions suggested $P2_1/n$ as the uniquely probable space group.[11] Precise lattice constants and diffracted intensities were derived from measurements carried out on a Syntex $P\bar{1}$ diffractometer using a crystal of dimensions 0.2 × 0.3 × 0.5 mm. The setting angles of 30 reflections, each collected at ±2θ, were determined (λ 0.71069 Å) using the automatic centering program supplied with the computer-controlled diffractometer. All measurements were made at the ambient laboratory temperature of 20 ± 1°. Least-squares refinement of these 30 reflections led to the lattice constants a = 13.149 (3) Å, b = 23.380 (6) Å, c = 14.786 (4) Å, and β = 100.50 (1)°. For a cell containing four molecules ($MnClN_5C_{49}H_{33}\cdot C_6H_6$) the density was calculated