Preparation and Stereochemistry of an Unusual Copper(II)–Purine Complex. Axial and Equatorial Purine Ligands in the Square-Pyramidal Complex Bis(theophyllinato)(diethylenetriamine)copper(II) Dihydrate

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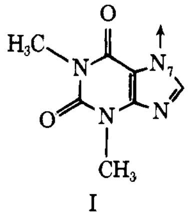
Abstract: The synthesis and crystal and molecular structure of the complex bis(theophyllinato)(diethylenetriamine)copper(II), $[(N_4O_2C_7H_7)_2(N_3C_4H_{13})Cu]$, are reported. The complex crystallizes, as the dihydrate, in the monoclinic system, space group $P2_1/c$, with: a = 18.379 (3), b = 8.263 (4), c = 15.958 (8) Å; β = 99.98 (3)°; V = 2386.8 Å^3, Z = 4; d_{measd} = 1.57 (1), d_{calcd} = 1.56 g cm^{-3}. Intensities for 4541 independent reflections were collected by counter methods on an automated diffractometer operating in the θ-2θ mode and employing Mo Kα radiation. The structure was solved by standard heavy-atom Patterson and Fourier methods. Full-matrix, least-squares refinement has led to final R, weighted R, and goodness-of-fit values of 0.074, 0.066, and 1.4, respectively. The primary coordination sphere about the copper(II) center is approximately square pyramidal. The tridentate diethylenetriamine chelate, with its terminal amino groups in trans positions, and N(7) of a strongly bound theophylline anion define the equatorial plane. A second theophylline anion, bonded to an axial position through N(7) of its purine ring system, completes the coordination sphere. The Cu-N$(7)_{\text{eq}}$ and Cu-N$(7)_{\text{ax}}$ bond lengths are 2.007 (3) and 2.397 (3) Å, respectively. This complex represents the first report of a metal-purine system where two purine ligands occupy widely divergent coordination sites. The implications of axial coordination of a nitrogen donor purine to copper(II), which has not been experimentally observed previously, are discussed in terms of the unusual influence of Cu^{2+} ions on nucleic acid structure. The crystal structure is dominated by stacking interactions of both the axial and equatorial theophylline anions about centers of symmetry; the interplanar spacings for these dimers are 3.47 Å for the equatorial ligand and 3.40 Å for the axial ligand. Appreciable molecular overlap of the pyrimidine portions of the purine ring system is noted in each dimer, with the heterobond N(1)-C(1)H_3 lying about over the centroid of the pyrimidine ring in each case. The crystal packing is completed via hydrogen bonds involving the dien chelate, the theophylline anion ligands, and the waters of crystallization.

Studies of the interaction of transition and other metal ions with nucleic acids have been aimed primarily at probing the structure and base sequence of these biopolymers. Many interesting, and as yet incompletely understood, effects have been observed, particularly with Cu^{2+} ions.[1] For example, this transition metal appears to maintain unwound complementary DNA strands in register.[1] Nuclear magnetic resonance studies involving biopolymers and their constituents have served to demonstrate that the primary metal base binding sites of Cu^{2+} are the same in both the polymer and the monomer of a given heterocyclic purine or pyrimidine base.[1]

Synthesis of solid metal-bound derivatives of such nucleic acid fragments or models of such fragments are often hampered by unsuitably small stability constants or poor solubility properties. It has been only in the last 2 or 3 years, through the efforts of many laboratories, that a body of information on the preparative and structural chemistry of such species has emerged.[2-13] Such research has gained additional momentum from the belief that the antitumor activity of coordination compounds[5] may involve interaction of these compounds with nucleic acids.

As suggested by ^{1}H NMR studies, most transition metal derivatives have the metal bonded to a heterocyclic nitrogen of the purine or pyrimidine base. The structural chemistry of these compounds has proven to be rich in variety but several recognizable patterns, many involving the exocyclic groups of the purine and pyrimidine bases, have emerged. These include: (1) direct chelation[6c,13j] in two 6-thiopurine derivatives; (2) occupation of an open axial position by the carbonyl oxygen O(2) of cytosine or cytidine in Cu-N(3) bonded complexes;[9-11,13m] (3) indirect chelation involving the carbonyl group at C(6) of the xanthine and hypoxanthine ring systems and a coordinated water molecule via a metal-OH_2···O(6)-C(6) hydrogen bond;[3,4a-c] (4) indirect chelation through the exocyclic amine group in adenine residues in a metal-H_2O···H_2N(6)-C(6) hydrogen bond system;[6,7] (5) indirect chelation involving an acceptor atom belonging to a chelated ligand and the exocyclic amine group of adenine, C(6)-N(6)H_2···O (salicylidene) hydrogen bond, in a 9-methyladenine complex of (*N*-salicylidene-*N'*-methylethylenediamine)copper(II);[8] (6) indirect chelation involving a donor group on a chelate ligand and the carbonyl group at C(6) of xanthine and hypoxanthine ring systems,[2] -N-H···O(6)-C(6) hydrogen bonding.

We detail, here, the synthesis and structure of a copper(II) complex, which unlike the previous 14 reports of transition metal complexes containing two nucleic acid derivatives,[13] has two purine ligands in completely different environments. Additionally, the structure of the compound, bis(theophyllinato)(diethylenetriamine)copper(II), reveals that one of the purine monoanions is coordinated to an axial site on copper(II). Such axial coordination has not been observed previously. The theophylline monoanion (I) has been used[2] as a model for the nucleoside guanosine (II) (R = ribose). This purine offers the same bonding potential in the N(7) region as does guanosine, but does not suffer from the poor solubility of the nucleoside.



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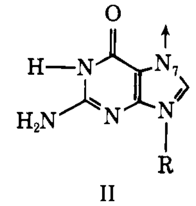

II

Table I. Crystal Data for Bis(theophyllinato)(diethylenetriamine)-copper(II) Dihydrate

a = 18.379 (3) Å	$[(N_4O_2C_7H_7)_2(N_3C_4H_{13})Cu]\cdot 2H_2O$
b = 8.263 (4) Å	Mol wt = 561.1
c = 15.958 (8) Å	Space group $P2_1/c$
β = 99.98 (3)°	d_{measd} = 1.57 (1) g cm^{-3}
V = 2386.8 Å^3	d_{calcd} = 1.56 g cm^{-3}
Z = 4	μ = 9.9 cm^{-1}

Experimental Section

Preparation of Bis(theophyllinato)(diethylenetriamine)copper(II) Dihydrate. The diethylenetriamine complex of copper(II) was prepared by combining warm aqueous solutions of $Cu(NO_3)_2$ (1.21 g, 5 mmol) and diethylenetriamine (0.52 g, 5 mmol). Solid theophylline (0.90 g, 5 mmol) was added to the dark blue reaction mixture. It was found necessary to add about 1 ml of 1 N KOH in order to dissolve the solid theophylline. Shortly after the addition of the base, a pulpy, green solid precipitated. This material was later identified, by comparative ir analysis, to be bis(theophyllinato)copper(II).[14] The solution was filtered to remove the green precipitate and 2-3 ml of 1 N KOH was added to the filtrate. Slow evaporation of the solution at room temperature (21°) yielded dark blue crystals, which were collected. The ir spectrum of the crystals contains bands attributable to the coordinated theophylline monoanion (1500-1700 and 1200-1250 cm^{-1}). Successive crops of crystals gave material suitable for elemental analysis and the crystallographic study. The magnetic moment, 1.8 μ_B, was measured on a Faraday balance and is typical of square-pyramidal copper(II) complexes.[8]

Anal. Calcd for $C_{18}CuH_{31}N_{11}O_6$: C, 38.5; H, 5.6. Found: C, 38.8; H, 5.9.

X-Ray Diffraction Data. The external morphology of the dark blue crystals was that of an approximate hexagonal prism. The prism axis was identified as the a axis of a monoclinic cell by photographic methods. Further photographic analysis showed the space group to be $P2_1/c$ (systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$). Unit-cell dimensions and their associated standard deviations were derived on the basis of a least-squares fit to the 2θ, ω, and χ diffractometer setting angles for 15 reflections; the crystal density was measured by neutral buoyancy methods in a mixture of bromoform and carbon tetrachloride. Standard crystallographic data are collected in Table I.

The 5455 independent reflections in the hkl, $hk\bar{l}$ quadrant to 2θ = 55° were surveyed on a Syntex P$\bar{1}$ automated diffractometer; molybdenum graphite-monochromatized radiation was employed. The crystal used in data collection was an approximate hexagonal prism with dimensions: 0.15 × 0.20 mm (cross-sectional minimum and maximum values) × 0.30 mm (along the prism axis); the prism axis was mounted approximately parallel to 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 (2θ) varied from 1.5° min^{-1} (less than 100 counts in the rapid scan) to 12.0° min^{-1} (more than 1000 counts during the rapid scan). Four standards were monitored after every 100 reflections; three of the standards behaved in a normal manner (maximum deviation from the mean of about 5%) while the fourth standard showed a somewhat erratic behavior (deviations of up to 20% from its mean intensity). The erratic behavior of the fourth standard was attributed to a strong streak component; the other standards were normal and a survey of several reflections after the termination of data collection showed excellent agreement with their initial values. The 5455 measured intensities were reduced to a set of 4541 reflections with $I > 0.7\sigma(I)$ (counting statistics) which were subsequently used in the structure determination and refinement. These reflections were assigned observational variances based on the following equation:

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

where S and 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 ($T_B = \frac{1}{4}T_S$ for all reflections), and p was taken to be equal to 0.05 and represents the expected error proportional to the diffracted intensity.[15] Intensities and their standard deviations were corrected for Lorentz and polarization effects; no correction for absorption was applied (μ = 9.9 cm^{-1}, maximum and minimum transmission factors equal to 0.86 and 0.82, respectively). The squared structure factors were placed on an approximate absolute scale by the method of Wilson.[16]

Solution and Refinement of the Structure. The positional coordinates of the copper atom were deduced from a three-dimensional Patterson synthesis. Two subsequent structure factor-Fourier calculations allowed the positioning of the remaining 35 non-hydrogen atoms ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.30$). Two cycles of full-matrix, isotropic least-squares refinement, minimizing the quantity $\Sigma w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, reduced the R value to 0.15 for all 4541 data. A difference Fourier map based on reflections with $(\sin\theta/\lambda) \leq 0.55$ yielded positional parameters for the 23 independent hydrogen atoms; the hydrogen atoms were assigned the same isotropic temperature factor as the atom to which they were bonded.

The refinement was continued with anisotropic temperature factors being refined for all the non-hydrogen atoms; no attempt was made to vary any of the parameters associated with the hydrogen atoms. Three cycles of refinement in this mode led to a final R value of 0.074. The final weighted R value $[(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}]$ and goodness-of-fit $[(\Sigma w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV}))^{1/2}$, where NO = 4541 independent observations and NV = 325 parameters] were 0.066 and 1.4, respectively.

Neutral scattering factors for all non-hydrogen atoms were taken from the compilation of Hanson, Herman, Lea, and Skillman;[17] the scattering curve for H was that of Stewart, Davidson, and Simpson.[18] The real part of the scattering factor for Cu was corrected for anomalous dispersion effects.[19] Final heavy-atom parameters are collected in Table II, while the parameters for the hydrogen atoms are given in Table III.[20] A complete list of observed and calculated structure factor amplitudes is available.[20]

The crystallographic computations were performed with the following programs: structure factor-Fourier, X-RAY 67;[21] least-squares refinements, ORFLS;[22] best planes, MEAN PLANE;[23] illustrations, ORTEP.[24] Calculations not cited were performed with locally written programs.

Results and Discussion

As part of a program aimed at developing stereoselective metal chelate complexes which might utilize the hydrogen bonding potential of the exocyclic groups of nucleic acid derivatives, we have examined the reaction of theophylline with Cu^{2+} in the presence of diethylenetriamine. Chemical analysis indicated that the product isolated was unusual for metal chelate complexes with theophylline or with other purine or pyrimidine derivatives in that two theophylline monoanions were contained in the complex. However, the presence of at least two such bases in the same complex is not unusual for nonchelate complexes. Fourteen crystallographic studies of such metal-purine[13a-l] or metal-pyrimidine[13m,n] complexes where the derivative is coordinated to the metal via nitrogen have been reported. These complexes have involved a variety of metal centers (Cu;[13a-f,i,k,m] Co;[13g,h] Pt;[13e,l] Pd;[13j] Hg[13n]) and coordination geometries (square planar, square pyramidal, tetrahedral, octahedral). There is, however, one unifying aspect in all of the previous studies—the metal-N bond lengths, within any one complex, are all approximately equivalent (maximum difference in coordinated bond distances of about 0.04 Å); in fact, in many instances crystallographic symmetry rigorously requires the equivalence of the metal-N distances.

Description of the Molecular Structure. The molecular conformation of the bis(theophyllinato)(diethylenetriamine)copper(II) complex is illustrated in Figure 1. The primary coordination sphere about the copper(II) center is approximately square pyramidal. The tridentate chelate diethylenetriamine (dien), with its terminal amine nitrogen atoms in the commonly observed[12,25-28] trans positioning, occupies three of the four equatorial coordination sites. The coordination sphere is completed by a strongly bound, equatorial theophylline anion, Cu(II)-N(7) bond length = 2.007

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	2777 (0.2)	1998 (0.6)	1306 (0.3)	17 (0.1)	88 (0.7)	29 (0.2)	10 (0.3)	8 (0.1)	2 (0.4)
O(2)	6353 (1)	-1104 (3)	997 (2)	16 (1)	117 (4)	42 (1)	5 (2)	10 (1)	-3 (2)
O(6)	4670 (1)	2976 (3)	1005 (2)	22 (1)	76 (4)	68 (2)	-1 (2)	14 (1)	-1 (2)
O(22)	-582 (1)	-3319 (4)	-124 (2)	16 (1)	166 (6)	46 (1)	-14 (2)	1 (1)	-1 (2)
O(26)	895 (2)	-103 (4)	1798 (2)	26 (1)	187 (6)	30 (1)	-7 (2)	7 (1)	-23 (2)
O(30)	3819 (2)	4473 (4)	2102 (2)	31 (1)	123 (5)	42 (1)	-5 (2)	13 (1)	8 (2)
O(31)	2132 (2)	-1535 (4)	2940 (2)	28 (1)	191 (6)	46 (2)	-11 (2)	8 (1)	26 (3)
N(1)	5495 (2)	908 (4)	997 (2)	13 (1)	81 (5)	38 (2)	-2 (2)	8 (1)	1 (2)
N(3)	5215 (2)	-1824 (4)	1234 (2)	14 (1)	78 (5)	40 (2)	4 (2)	8 (1)	-2 (2)
N(7)	3596 (2)	360 (4)	1460 (2)	14 (1)	88 (5)	37 (2)	4 (2)	9 (1)	3 (2)
N(9)	4002 (2)	-2255 (4)	1613 (2)	18 (1)	83 (5)	47 (2)	-1 (2)	9 (1)	10 (2)
N(10)	3058 (2)	3125 (4)	265 (2)	24 (1)	104 (5)	32 (1)	-5 (2)	8 (1)	-3 (3)
N(11)	2013 (2)	3774 (4)	1225 (2)	16 (1)	105 (5)	39 (2)	8 (2)	3 (1)	-7 (2)
N(12)	2629 (2)	1907 (4)	2543 (2)	22 (1)	127 (6)	32 (2)	-7 (2)	8 (1)	-8 (3)
N(21)	162 (2)	-1677 (4)	807 (2)	15 (1)	124 (6)	29 (1)	-2 (2)	5 (1)	2 (2)
N(23)	495 (2)	-2466 (4)	-493 (2)	18 (1)	109 (5)	28 (1)	-7 (2)	4 (1)	-6 (2)
N(27)	1965 (2)	70 (4)	503 (2)	16 (1)	102 (5)	35 (2)	-3 (2)	4 (1)	-6 (2)
N(29)	1679 (2)	-1427 (4)	-729 (2)	21 (1)	105 (5)	31 (1)	-1 (2)	8 (1)	-6 (2)
C(1)	6065 (2)	2097 (5)	879 (3)	21 (1)	99 (7)	66 (3)	-7 (3)	18 (2)	-7 (4)
C(2)	5717 (2)	-710 (5)	1073 (2)	15 (1)	95 (6)	29 (2)	2 (2)	5 (1)	-3 (3)
C(3)	5407 (2)	-3542 (5)	1292 (3)	21 (1)	72 (6)	62 (3)	1 (2)	15 (2)	11 (3)
C(4)	4532 (2)	-1307 (4)	1375 (2)	15 (1)	69 (5)	32 (2)	-1 (2)	4 (1)	1 (3)
C(5)	4308 (2)	288 (4)	1285 (2)	15 (1)	82 (6)	30 (2)	0 (2)	7 (1)	-4 (3)
C(6)	4796 (2)	1505 (4)	1086 (3)	17 (1)	82 (6)	34 (2)	1 (2)	7 (1)	-2 (3)
C(8)	3462 (2)	-1171 (5)	1651 (3)	17 (1)	100 (6)	42 (2)	1 (2)	10 (1)	7 (3)
C(10)	2454 (3)	4234 (6)	-86 (3)	32 (2)	161 (8)	35 (2)	13 (3)	2 (1)	18 (4)
C(11)	2187 (3)	5053 (5)	642 (3)	31 (2)	99 (7)	51 (2)	16 (3)	4 (2)	11 (3)
C(12)	1954 (2)	4346 (5)	2086 (3)	23 (1)	127 (7)	48 (2)	8 (3)	11 (1)	-27 (3)
C(13)	1980 (2)	2892 (6)	2658 (3)	23 (1)	159 (8)	35 (2)	-7 (3)	12 (1)	-25 (3)
C(21)	-382 (2)	-1799 (6)	1373 (3)	21 (1)	193 (9)	36 (2)	2 (3)	10 (1)	7 (4)
C(22)	-4 (2)	-2535 (5)	43 (3)	17 (1)	107 (6)	31 (2)	3 (2)	0 (1)	12 (3)
C(23)	347 (3)	-3331 (6)	-1302 (3)	32 (2)	173 (9)	38 (2)	-26 (3)	5 (2)	-21 (4)
C(24)	1132 (2)	-1566 (4)	-269 (2)	16 (1)	83 (6)	26 (2)	4 (2)	2 (1)	1 (2)
C(25)	1280 (2)	-687 (5)	472 (2)	14 (1)	86 (6)	28 (2)	-0 (2)	2 (1)	-1 (3)
C(26)	806 (2)	-737 (5)	1087 (3)	16 (1)	99 (6)	28 (2)	4 (2)	2 (1)	5 (3)
C(28)	2159 (2)	-428 (5)	-215 (3)	16 (1)	94 (6)	39 (2)	-4 (2)	8 (1)	-11 (3)

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

(3) Å, and a loosely bound, axial theophylline anion, Cu(II)-N(27) bond length = 2.397 (3) Å. The binding of both purine anions through the imidazole ring nitrogen atom N(7) (labeled N(27) for the axial theophylline anion) is of particular interest as this site is available for coordination in nucleosides and nucleotides.[29-32]

There do not seem to be any unusual interactions between the equatorial and axial theophylline anions. The equatorial theophyllinato framework is tilted at an angle of 50.7 (3)° to the plane defined by the four nitrogen atoms of the equatorial plane, see Figure 1. The tipping of the equatorial theophyllinato plane, presumed to be in response to the formation of an interligand hydrogen bond, see below, leaves an open fifth coordination site. In fact, the relative orientation of the axial theophylline anion seems to be primarily dictated by interactions with the dien chelate. We cite, for example, the following interligand contacts: C(13)-H(17)···O(26), H···O distance = 2.42 Å; N(10)-H(8)···C(28), H···C distance = 2.90 Å. The H(17)···O(26) contact, in particular, seems determinative of the molecular orientation and is very near to the expected sum of the van der Waals radii for H and O (2.4 Å assuming van der Waals radii of 1.0 for H[34] and 1.4 Å for O[35]).

In support of these arguments, we note that the Cu-N(27) bond is significantly off axis, with the largest N-Cu-N(27) angular deviation from 90° being 18.5 (3)° (N(12)-Cu-N(27), 108.5 (3)°, see Table IV). That the largest deviation from ideality occurs in the N(12)-Cu-N(27) bond angle is not surprising in light of the O(26)···H(17)-C(13) interligand contact noted above.

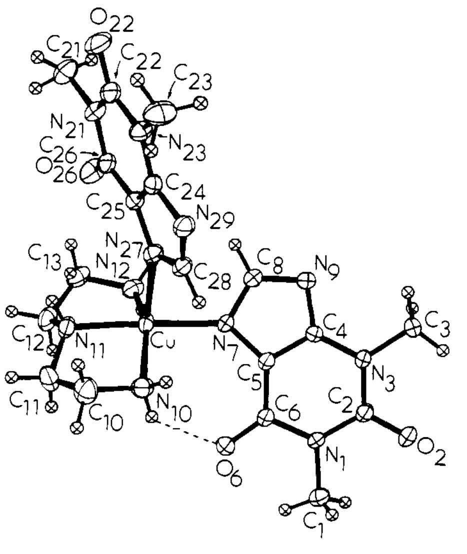

Figure 1. A perspective view of the bis(theophyllinato)(diethylenetriamine)copper(II) complex. The interligand hydrogen bond between the carbonyl group C(6)-O(6) of the equatorial theophylline monoanion and the primary amine group N(10)H_2 of the diethylenetriamine chelate is denoted by the dashed line. The thermal ellipsoids are drawn at the 40% probability level.

The typically[36,37] long axial Cu-N bond distance appears to limit steric interaction between the two purines. Although the complexes of Cu^{2+} are normally labile, this metal ion can delay rewinding under conditions where the

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

(a) Primary Coordination Sphere about the Copper Atom

Bond Lengths

Cu–N(7)	2.007 (3)	Cu–N(12)	2.040 (3)
Cu–N(10)	2.047 (3)	Cu–N(27)	2.397 (3)
Cu–N(11)	2.020 (3)		

Bond Angles

N(7)–Cu–N(10)	96.7 (2)	N(10)–Cu–N(12)	153.7 (2)
N(7)–Cu–N(11)	174.9 (2)	N(10)–Cu–N(27)	95.2 (2)
N(7)–Cu–N(12)	94.6 (2)	N(11)–Cu–N(12)	83.2 (2)
N(7)–Cu–N(27)	90.1 (2)	N(11)–Cu–N(27)	95.0 (2)
N(10)–Cu–N(11)	83.6 (2)	N(12)–Cu–N(27)	108.5 (2)

(b) Diethylenetriamine Chelate Ring

Bond Lengths

N(10)–C(10)	1.473 (6)	N(12)–C(13)	1.481 (6)
C(10)–C(11)	1.499 (7)	C(13)–C(12)	1.505 (7)
C(11)–N(11)	1.479 (6)	C(12)–N(11)	1.475 (6)

Bond Angles

Cu–N(10)–C(10)	108.2 (3)	Cu–N(12)–C(13)	110.2 (3)
N(10)–C(10)–C(11)	108.2 (4)	N(12)–C(13)–C(12)	107.8 (4)
C(10)–C(11)–N(11)	107.5 (4)	C(13)–C(12)–N(11)	108.0 (4)
Cu–N(11)–C(11)	109.6 (3)	Cu–N(11)–C(12)	109.6 (3)
C(11)–N(11)–C(12)	114.6 (3)		

(c) Theophylline Monoanion Ligands

Bond Lengths

Equatorial		Axial	
N(1)–C(1)	1.472 (6)	N(21)–C(21)	1.462 (6)
N(1)–C(2)	1.397 (5)	N(21)–C(22)	1.398 (5)
N(1)–C(6)	1.406 (5)	N(21)–C(26)	1.421 (5)
N(3)–C(2)	1.359 (5)	N(23)–C(22)	1.359 (5)
N(3)–C(3)	1.462 (6)	N(23)–C(23)	1.459 (6)
N(3)–C(4)	1.381 (5)	N(23)–C(24)	1.381 (5)
N(7)–C(5)	1.386 (5)	N(27)–C(25)	1.399 (5)
N(7)–C(8)	1.334 (6)	N(27)–C(28)	1.323 (5)
N(9)–C(4)	1.355 (5)	N(29)–C(24)	1.349 (5)
N(9)–C(8)	1.346 (5)	N(29)–C(28)	1.372 (5)
C(2)–O(2)	1.239 (5)	C(22)–O(22)	1.233 (5)
C(4)–C(5)	1.381 (6)	C(24)–C(25)	1.374 (6)
C(5)–C(6)	1.420 (6)	C(25)–C(26)	1.421 (6)
C(6)–O(6)	1.240 (5)	C(26)–O(26)	1.235 (5)

Bond Angles

Equatorial		Axial	
C(1)–N(1)–C(2)	116.5 (3)	C(21)–N(21)–C(22)	115.8 (3)
C(1)–N(1)–C(6)	117.5 (3)	C(21)–N(21)–C(26)	117.7 (3)
C(2)–N(1)–C(6)	125.8 (3)	C(22)–N(21)–C(26)	126.5 (3)
C(2)–N(3)–C(3)	120.4 (3)	C(22)–N(23)–C(23)	119.6 (3)
C(2)–N(3)–C(4)	119.2 (3)	C(22)–N(23)–C(24)	119.6 (3)
C(3)–N(3)–C(4)	120.4 (3)	C(23)–N(23)–C(24)	120.8 (3)
Cu–N(7)–C(5)	135.9 (3)	Cu–N(27)–C(25)	142.1 (3)
Cu–N(7)–C(8)	120.2 (3)	Cu–N(27)–C(28)	115.7 (3)
C(5)–N(7)–C(8)	102.9 (3)	C(25)–N(27)–C(28)	101.9 (3)
C(4)–N(9)–C(8)	101.5 (3)	C(24)–N(29)–C(28)	100.9 (3)
N(1)–C(2)–O(2)	120.6 (4)	N(21)–C(22)–O(22)	120.3 (4)
N(3)–C(2)–O(2)	121.6 (4)	N(23)–C(22)–O(22)	122.4 (4)
N(1)–C(2)–N(3)	117.8 (4)	N(21)–C(22)–N(23)	117.3 (4)
N(3)–C(4)–N(9)	125.8 (4)	N(23)–C(24)–N(29)	125.7 (4)
N(3)–C(4)–C(5)	122.8 (4)	N(23)–C(24)–C(25)	122.7 (4)
N(9)–C(4)–C(5)	111.4 (4)	N(29)–C(24)–C(25)	111.6 (4)
N(7)–C(5)–C(4)	107.2 (4)	N(27)–C(25)–C(24)	108.0 (4)
N(7)–C(5)–C(6)	132.1 (4)	N(27)–C(25)–C(26)	130.1 (4)
C(4)–C(5)–C(6)	120.7 (4)	C(24)–C(25)–C(26)	121.7 (4)
N(1)–C(6)–O(6)	119.4 (4)	N(21)–C(26)–O(26)	119.4 (4)
N(1)–C(6)–C(5)	113.4 (4)	N(21)–C(26)–C(25)	112.o (4)
C(5)–C(6)–O(6)	127.2 (4)	C(25)–C(26)–O(26)	128.5 (4)
N(7)–C(8)–N(9)	117.0 (4)	N(27)–C(28)–N(29)	117.7 (4)

[a] Estimated standard deviations in the least significant figure are contained in parentheses.

double helix is stable.[1] No complete explanation for this effect has been advanced, although it is believed that the Cu^{2+} ions bind simultaneously to bases on both strands.[1] Such binding keeps the complementary strands in register. Zinc(II) ions will also facilitate rewinding, but the helix is re-formed rapidly when the solution is brought to conditions where the double helix is stable.[1] From this study it appears that the presence of an axially bound and an equatorially bound purine is sterically feasible for copper(II). In its interaction with the nucleic acid the copper may be bound to two bases, one on each nucleic acid strand and simultaneously bound to another base of one strand by using the axial position. The absence of long axial bonds in zinc(II) might prevent the zinc from binding to more than one base on each strand. Certainly more studies are needed to test this hypothesis; particularly, as it is still not clear why copper decreases the rate of rewinding of the helix.

Molecular Interactions and Dimensions. Usually, in N(7)-bonded theophylline complexes,[2,30-32] the carbonyl group C(6)–O(6) forms interligand hydrogen bonds with chelate ligands containing good hydrogen-bond donor groups. Such a hydrogen bond is present between the O(6) of the equatorial theophyllinato ligand and the terminal primary amino group $-N(10)H_2$ (Figure 1) (N(10)···O(6), 2.996 (5) Å; H(9)···O(6), 2.31 Å; N(10)–H(9)···O(6) angle = 136°). These parameters indicate a somewhat weaker hydrogen bond[33] than observed in other theophyllinato complexes,[2,30-32] probably due to the relatively low hydrogen bond donor affinity of the dien amine hydrogen atoms.[12,26,27]

There is considerable variability in the exocyclic bond angles at N(7) in N(7)-bonded purine complexes.[2,7,8,30-32] The dissymmetry in the Cu–N(7) exocyclic bond angles for the equatorial theophylline anion, Cu–N(7)–C(5) 135.9 (3)° and Cu–N(7)–C(8) 120.2 (3)°, is probably related to the interligand hydrogen bond requirements. The dissymmetry in the exocyclic bond angles at N(27) of the axial theophylline anion, Cu–N(27)–C(25) 142.1 (3)° and Cu–N(27)–C(28) 115.7 (3)°, is likely due to the steric interactions with the dien chelate, with the opening of the Cu–N(27)–C(25) angle being necessary to minimize the O(26)···H(17)–C(13) interaction described above.

The bond length and angles in the primary coordination sphere are given in Table IV. The Cu–N(7) equatorial theophylline anion bond length, 2.007 (3) Å, is measurably, but not dramatically, longer than that we have found in the complex (*N*-salicylidene-*N'*-methylethylenediamine)(theophyllinato)copper(II), 1.986 (1) Å.[32] The Schiff base complex also exhibits an interligand hydrogen bond involving the exocyclic carbonyl group C(6)–O(6). The axial Cu–N(27) theophylline anion bond length, 2.397 (3) Å, is some 0.390 (3) Å longer than for the equatorial Cu–N(7) bond. Such differences are typical for the (4 + 1) copper(II) geometry.[36,37] It has been found, for example, in the complex [(cyano)(diethylenetriamine)copper(II)] perchlorate[28] that the axial Cu–N bond length is 2.348 (4) Å, a value which is quite comparable to that observed in the present system.

As is typical of $(dien)Cu^{II}$ systems,[12,25-28] the conformation of the dien chelate is such that the terminal, primary amine nitrogen atoms, N(10) and N(12), occupy trans positions in the primary coordination sphere. The conformations for each half of the tridentate system are λ for the ethylenediamine ring N(10)–C(10)–C(11)–N(11) and δ for the ring N(12)–C(13)–C(12)–N(11); the $\delta\lambda$ conformation also exists in the crystal (50% $\lambda\delta$, 50% $\delta\lambda$) owing to the centrosymmetric nature of the space group.

The methylene carbon atoms C(11) and C(12) bonded to the secondary amine nitrogen N(11) show substantial deviations, 0.68 and 0.76 Å, respectively, from the three-atom plane N(10)- -N(11)- -N(12), while the methylene carbon atoms, C(10) and C(13), bonded to the terminal primary amine nitrogens N(10) and N(12) are more nearly in the three-atom plane with deviations of 0.01 and 0.13 Å, re-

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

(a) Equatorial Plane About the Copper Atom ($-0.6132X - 0.6625Y - 0.4303Z = -5.1328$ Å)			
N(7)	0.143	N(12)	−0.162
N(10)	−0.158	Cu	0.248*
N(11)	0.178	N(27)	2.625*
(b) Equatorial Theophylline Monoanion Planes:			
(1) Nine-Atom Framework ($-0.1905X - 0.1488Y - 0.9703Z = -3.4682$ Å)			
N(1)	−0.035	C(5)	0.033
N(3)	0.050	C(6)	0.005
N(7)	0.016	C(8)	−0.030
N(9)	−0.030	O(2)	−0.088*
C(2)	−0.026	O(6)	−0.012*
C(4)	0.018	C(1)	−0.207*
		C(3)	0.109*
(2) Imidazole Ring ($-0.2104X - 0.1728Y - 0.9622Z = -3.5699$ Å)			
N(7)	0.005	C(4)	0.004
N(9)	−0.001	C(5)	−0.006
		C(8)	−0.002
(3) Pyrimidine Ring ($-0.1704X - 0.1337Y - 0.9763Z = -3.2957$ Å)			
N(1)	−0.008	C(6)	0.012
N(3)	0.029	O(2)	−0.055*
C(2)	−0.012	O(6)	0.010*
C(4)	−0.024	C(1)	−0.143*
C(5)	0.004	C(3)	0.072*
(c) Axial Theophylline Monoanion Planes:			
(1) Nine-Atom Framework ($-0.3947X + 0.7992Y - 0.4533Z = -1.7009$ Å)			
N(21)	−0.011	C(25)	0.034
N(23)	0.011	C(26)	−0.026
N(27)	0.018	C(28)	−0.018
N(29)	−0.020	O(22)	0.006*
C(22)	0.004	O(26)	−0.101*
C(24)	0.008	C(21)	−0.038*
		C(23)	0.035*
(2) Imidazole Ring ($-0.3786X + 0.7957Y - 0.4727Z = -1.6440$ Å)			
N(27)	0.002	C(24)	−0.002
N(29)	0.003	C(25)	0.000
		C(28)	−0.003
(3) Pyrimidine Ring ($-0.4041X + 0.7997Y - 0.4441Z = -1.7048$ Å)			
N(21)	0.003	C(26)	−0.018
N(23)	−0.003	O(22)	0.017*
C(22)	0.008	O(26)	−0.082*
C(24)	−0.013	C(21)	−0.005*
C(25)	0.024	C(23)	0.009*

[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 designated by an asterisk (*) were given zero weight in calculating the planes; all other atoms were equally weighted.

spectively. As can be seen in Figure 1, the axial theophylline anion and the secondary amine hydrogen atom at N(11) of the dien chelate are cis to each other with respect to the equatorial plane of the complex. These conformation features are in good agreement with those in [(thyminato)(aquo)(dien)copper(II)] bromide,[12] where a water molecule occupies the axial position.

The bond lengths and angles for the dien ligand and the Cu-N(dien) bond lengths, Table IV, are in agreement with recent structural determinations of other (dien)Cu^{II} complexes;[12,25-28] we note, in particular, the excellent agreement of the present parameters with those for the (dien)Cu^{II}-thyminato[12] and the (dien)Cu^{II}-cyano[28] complexes (N-C$_{av}$ distance = 1.477 (4) Å in the theophyllinato complex, 1.472 (4) Å in the thyminato complex, 1.474 (4) Å in the cyano complex; C-C$_{av}$ distance = 1.502 (4), 1.499 (4), and 1.496 (4) Å; Cu-N-C$_{av}$ angle = 109.4 (3)° in the theophyllinato complex and 109.0 (3)° in the thyminato complex (bond angles have not been reported for the cyano complex); N-C-C$_{av}$ angle = 108.0 (3)° in the theophyllinato complex and 107.9 (3)° in the thyminato complex).

The only structural parameter which exhibits a significant variation is the interior C-N-C angle at the secondary amine nitrogen, 116.4 (3)° in the theophyllinato complex and 114.6 (3)° in the thyminato complex. The variation in this interior C-N-C angle is probably related to difference in the Cu-N$_{middle}$ (dien) bond length. This bond length is susceptible to the trans influence of the ligand opposite in the equatorial plane.[38] The relatively large difference, 0.027 Å, in the Cu-N$_{middle}$ (dien) bond length in the thyminato, 2.009 (3) Å, and the cyano, 2.036 (4) Å, complexes is probably attributable to trans-influence considerations.[12] The bond length in the theophyllinato complex is 2.020 (3) Å and lies about midway between the observed value for the thyminato and cyano complexes.

This analysis does not seem to be complicated by steric factors. As noted above, the conformational properties and dimensions of the dien chelate are very similar in the three complexes considered. Furthermore, each of the complexes shows approximately square pyramidal coordination geometry with the axial ligands being: (1) a theophylline monoanion in the theophyllinato complex, Cu-N(27) distance = 2.397 (3) Å; (2) a water molecule in the thyminato complex, Cu-OH$_2$ distance = 2.465 (3) Å;[12] (3) a nitrogen-bonded cyano ligand, Cu-N distance = 2.348 (4) Å, in the cyano complex.[28] It appears likely, as suggested by the bond length trend above, that the theophylline monoanion is midway between the N(1)-bonded thymine monoanion and the cyanide group in the order of trans-influence ability.[38]

The four atoms in the equatorial plane about the copper(II) center are very roughly coplanar, Table V, but a definite tetrahedral component to the square plane is evident. The deviations from planarity in the theophyllinato complex, ±0.16 Å, are significantly larger than in the thyminato complex, ±0.06 Å;[12] this is possibly due to some steric interaction between the axial theophylline anion and the dien ligand; see above. The copper lies 0.248 Å out of the equatorial "plane", Table V, toward the axial position occupied by the theophylline anion. This feature parallels the result found in other (4 + 1) copper(II) complexes.[12,36,37]

The presence of a weakly bound theophylline anion is of importance in our efforts to understand the effect of coordination on the molecular dimensions of purine and pyrimidine ligands.[7,8,12,30-32] Accurate structures are available for the coordinated theophylline monoanion in *trans*-[(theophyllinato)(chloro)bis(ethylenediamine)cobalt(III)] chloride[30] and (*N*-salicylidene-*N'*-methylethylenediamine)(theophyllinato)copper(II).[32] The theophylline anions are coordinated through the imidazole nitrogen N(7) with metal-N(7) distances of Co(III)-N(7), 1.956 (1) Å,[30] and Cu(II)-N(7), 1.986 (1) Å,[32] in good qualitative agreement with the Cu(II)-N(7)$_{eq}$ distance found in the present structure, 2.007 (3) Å. A quantitative comparison of the bond lengths and angles in the equatorial theophylline anion, Table IV, with those in the Schiff base-copper(II) and the bis(ethylenediamine)cobalt(III) theophyllinato complexes shows no noteworthy trends and the root mean square differences in bond lengths and bond angles, 0.006 Å and 0.6° and 0.009 Å and 0.6°, respectively, are quite acceptable in light of the estimated standard deviations. Table IV also allows a detailed comparison of the bond lengths and bond angles in the equatorial and axial theophylline anions. Again the differences are not, in general, large with root mean square values for the bond length and bond angle differences of 0.010 Å and 0.8°. At least two of the differences are, however, worthy of comment: N(9)-C(8)$_{eq}$ = 1.346 (5) Å,

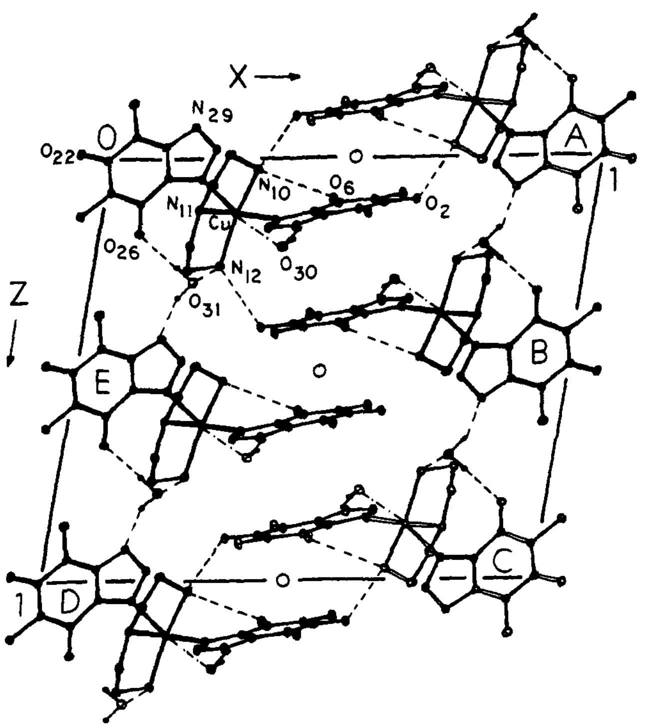

Figure 2. A projection of the unit-cell contents down the *b* axis. Dashed lines denote hydrogen bonds, while the dash-dot lines indicate the weak Cu- -O(30)H_2 interaction. The labeled complex is at *x, y, z*, while the lettered complexes have the following symmetry transforms relative to Table II: (A) $1 - x, -y, -z$; (B) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (C) $1 - x, -y, 1 - z$; (D) $x, y, 1 + z$; (E) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

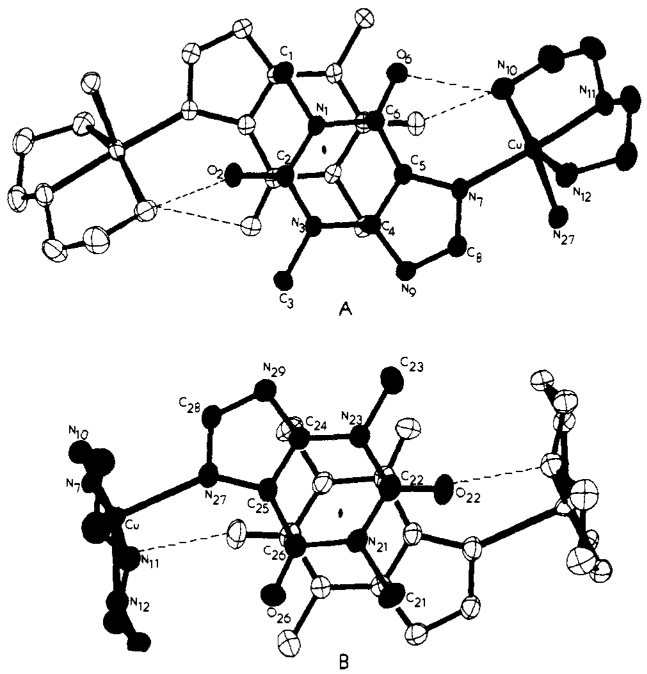

Figure 3. Molecular overlaps in the dimerization of the theophylline monoanion ligands about centers of symmetry. (A) Self stacking of the strongly coordinated, equatorial theophylline monoanion about the center of symmetry at [½, 0, 0]. The mean stacking distance is 3.47 Å. The dashed lines indicate the C(6)-O(6)···H_2N(10) intramolecular and the C(2)-O(2)···H_2N(10) intermolecular hydrogen bond systems. (B) Stacking of the weakly coordinated, axial theophylline monoanion about the center of symmetry at [0, 0, 0]. The mean stacking distance is 3.40 Å. The dashed lines denote the C(22)-O(22)···HN(11) intermolecular hydrogen bond system.

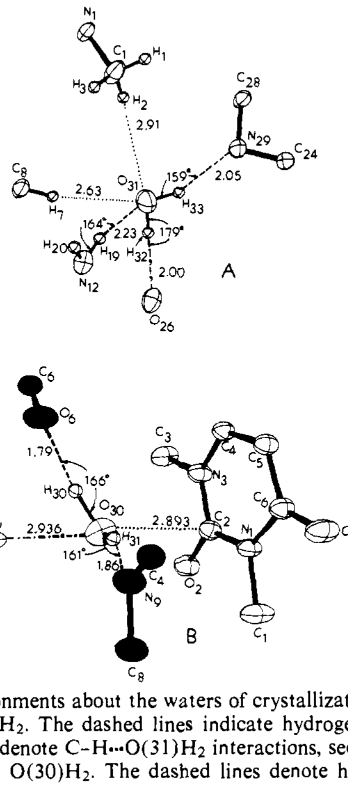

Figure 4. Environments about the waters of crystallization. (A) Water molecule O(31)H_2. The dashed lines indicate hydrogen bonds, while the dotted lines denote C-H···O(31)H_2 interactions, see Table IV. (B) Water molecule O(30)H_2. The dashed lines denote hydrogen bonds, the dotted line shows the close O(30)···C(2) interaction, and the dash-dot line indicates the weak Cu- -O(30)H_2 interaction.

N(29)-C(28)$_{ax}$ = 1.372 (5) Å; N(7)-C(5)-C(6)$_{eq}$ = 132.1 (4)°, 130.1 (4)°$_{ax}$. In each case, the axial ligand values are at variance not only with those of the equatorial ligand but also with the values obtained in the Schiff base-copper(II)[32] and the bis(ethylenediamine)cobalt(III)[30,31] systems. The length of the N(9)-C(8) imidazole ring bonds may well be related to the strength of the Cu-N(7) axial vs. equatorial bond. The closing of the N(7)-C(5)-C(6) may in part be due to either the electronic effects on the Cu-N(7) bond, or the measurably greater planarity in the axial theophylline pyrimidine ring vs. the equatorial theophylline pyrimidine ring.

As is to be expected,[39,40] the nine-atom frameworks of the axial and equatorial purine anions are significantly nonplanar, Table V. In each instance, the immidazole rings are extremely planar, while the pyrimidine portion of the equatorial ligand retains some expected nonplanarity and the pyrimidine portion of the axial ligand is surprisingly planar (Table V).[30-32,41] The folding of the purine framework about the C(4)-C(5) bond, 2.2 (4)°, for the axial anion is in about the expected range (2.3 (3)° in the *trans*-bis(ethylenediamine)cobalt(III)[30] and 2.0 (3)° in the Schiff base-copper(II) systems[32]), while the folding about the C(4)-C(5) bond in the equatorial anion, 3.3 (4)°, is at least somewhat larger than expected.

Crystal Packing and Hydrogen Bonding. The crystal packing is illustrated in Figure 2, which is a projection of the unit-cell contents along the *b* axis. The packing is dominated by stacking interactions[41,42] of the axial and equatorial theophylline anions about centers of symmetry ((0,0,0) for the axial ligands and (½,0,0) for the equatorial ligands). The molecular overlap in each of these dimers is illustrated in Figure 3. As can be seen in Figure 3A, there is an appreciable overlap of the pyrimidine portions of equatorial theophylline anions, with the heterobond N(1)-C(1)H_3 lying approximately over the centroid of the pyrimidine ring of inversion related complexes.[43] The mean separation between the nine-atom frameworks is 3.47 Å; the only short intermolecular contact is C(2)···C(6) at 3.473 (7) Å. The

Table VI. Distances (Å) and Angles (deg) in the Interactions of the Type, D–H···A

D	H	D–H	A	D···A	H···A	D–H···A
			Hydrogen Bonds			
N(10)	H(8)	0.89	O(2)[a]	2.962	2.13	157
N(10)	H(9)	0.86	O(6)[b]	2.996	2.31	136[h]
N(11)	H(14)	0.88	O(22)[c]	2.923	2.10	156
N(12)	H(19)	0.88	O(31)[b]	3.086	2.23	164
N(12)	H(20)	0.90	O(2)[d]	3.181	2.34	156
O(30)	H(30)	1.06	O(6)[b]	2.827	1.79	166
O(30)	H(31)	1.03	N(9)[e]	2.850	1.86	161
O(31)	H(32)	0.91	O(26)[b]	2.908	2.00	179
O(31)	H(33)	0.94	N(29)[f]	2.942	2.05	159
			C–H···O Interactions			
C(3)	H(6)	0.94	O(6)[g]	3.179	2.41	139
C(8)	H(7)	0.96	O(31)[b]	3.470	2.63	146
C(28)	H(27)	0.94	O(2)[a]	3.438	2.51	168

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

presence of the O(2)···H(8)–N(10) interdimer hydrogen bonds, Figure 3A, is certainly contributing to the stability of the dimers.

Figure 3B illustrates the molecular overlap within the stacked dimers of the axial theophylline anions. The observed overlap is nearly equivalent to that found for the equatorial ligand dimers. Short interatomic contacts within these dimers are as follows: C(21)···C(24), 3.449 (7) Å; C(22)···C(26), 3.437 (7) Å. The mean separation between nine-atom frameworks is 3.40 Å, 0.07 Å less than in the equatorial dimers, and is consistent with the higher degree of planarity for the axial ligands (see above). The axial dimers also exhibit intermolecular hydrogen bonds of the type O(22)···H(14)–N(11), involving again the carbonyl group at C(2) of the pyrimidine ring and, in this case, the central nitrogen of the dien chelate.

Hydrogen bonds N(12)–H(20)···O(2) couple twofold screw related complexes, while the waters of crystallization are involved in completing the three-dimensional network, Figure 2. The environments about the two waters of crystallization are of some interest. Figure 4A illustrates the interactions about the water molecule $O(31)H_2$. The interaction geometry is approximately trigonal bipyramidal if one includes the interactions with the methyl group $C(1)H_3$ and the imidazole methine carbon, C(8)H, of the equatorial theophylline anion. It should be noted that the axial imidazole methine carbon C(28)H also shows a moderate C–H···O interaction, Table VI, and that such interactions are common for carbon-bonded hydrogens adjacent to two electronegative atoms, nitrogens in this case, and good hydrogen bond acceptor groups.[44-49]

The interaction geometry about the second water molecule, $O(30)H_2$, is shown in Figure 4B. The environment is approximately tetrahedral with two hydrogen bond donor interactions, an O(30)···C(2) contact, and a long Cu- -O(30) interaction. This Cu- -O(30) interaction qualitatively extends the coordination sphere about the copper center to six (4 + 1 + 1).[36,37]

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Supplementary Material Available: listings of structure factors and Table III, hydrogen atom positional and thermal parameters (26 pages). Ordering information is given on any current masthead page.

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Carbon Acidity. LII. Equilibrium Acidity of Cyclopentadiene in Water and in Cyclohexylamine[1]

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Abstract: Cyclopentadiene dissolves in water to form a 0.01 M solution. It is 50% ionized in 9 M NaOH, which corresponds to a pK_a of 16.0 (15.6 per hydrogen). The cesium ion pair pK in cyclohexylamine is 16.65 (16.25 per hydrogen) on a scale in which 9-phenylfluorene is assigned a pK of 18.49.

The stability of cyclopentadienyl anion is a cornerstone in modern organic and organometallic chemistry; it plays a key role, for example, in validating the Hückel $4n + 2$ rule. The pK_a value of 15 assigned to cyclopentadiene in Cram's MSAD scale[2] is indeed a rather low value for a hydrocarbon. This value has been quoted frequently, yet rests on an exceedingly tenuous experimental base, especially considering the significance of this number. In 1960, we derived a pK range of 16–20[3] on the basis of qualitative early experiments of Thiele.[4] This range was consistent with a pK of 17 deduced by a simple HMO correlation of hydrocarbon acidities available at that time.[3] In 1962, Dessy, Okuzumi, and Chen[5] found that a methanolic solution of cyclopentadiene can be carbonated in the presence of sodium methoxide but not sodium phenoxide and, accordingly, assigned a pK range of 14–15.

More recently, Bowden et al.[6] have quoted a pK of 15, apparently for aqueous dimethyl sulfoxide solutions. Breslow and Washburn[7] determined the pK_a of cyclopentadiene with lithium dicyclohexylamine and tetramethylenediamine in tetrahydrofuran relative to *tert*-butyl alcohol. They obtained a value of 18.2 in this medium at 35 °C by observing the intensity of the NMR spectrum of cyclopentadienyl anion as a function of *tert*-butyl alcohol. Bordwell et al.[8] have recently communicated a value of 18.1 for the dimethyl sulfoxide standard state.

Schaeffer[9] has reported a value of 15.3 for the pK_a of cyclopentadiene based on a comparison of chemical shift differences between carbon acids and their lithium salts in ether or THF with pK's on the MSAD scale. Finally, Butin et al.[10] have reported that the MSAD scale pK of cyclopentadiene is consistent with polarographic reduction studies of organomercury compounds. Both of the latter determinations have important limitations and cannot be regarded as reliable.

We have recently found that cyclopentadiene is soluble in water to the extent of 0.0103 mol l.$^{-1}$.[11] Spectral changes in the presence of sodium hydroxide permit assignment of a pK value for the aqueous solution. The equilibrium cesium ion pair pK of cyclopentadiene in cyclohexylamine was also determined using our standard hydrocarbon indicators in order to establish a direct comparison of cyclohexylamine and water pK scales.

Experimental Section

Materials. Cyclopentadiene was obtained from its dimer (Aldrich) by distillation onto molecular sieves. Analyses by GC showed only one peak. The cyclopentadiene was used within an hour of its preparation.

9-Phenyl-3,4-benzofluorene (7-phenyl-7*H*-benz[*c*]fluorene) (PBF) and 1,12-(*o*-phenylene)-7,12-dihydropleiadene (PDP) and their cesium ion pair pK's in cyclohexylamine have been described previously.[12] PDP was prepared from material kindly supplied by Professor P. Landsbury.

Equilibrium Acidities. Cyclopentadienylcesium does not absorb in the accessible region in cyclohexylamine solution; hence, measurements in this solvent were made by the single indicator method described previously.[13] The general method involves determination of the absorption of a known mixture of indicator hydrocarbon and its cesium salt in cyclohexylamine on addition of a known amount of cyclopentadiene. The principal change in the recorded procedure was the use of a Vacuum Atmospheres recirculating glovebox, which allowed many of the operations to be carried out readily in an argon atmosphere. Spectroscopic measurements were made with a Cary 118 spectrometer and refer to room temperature. The concentrations of cyclopentadiene added were in the range 0.02–0.16 M, but its cesium salt in equilibrium was 0.1–2.3 $\times 10^{-3}$ M. The results with the two indicators used are summarized in Table I.

Equilibrium measurements in water were made with stock solutions of concentrated carbonate-free sodium hydroxide[14] and aqueous solutions of cyclopentadiene. Freshly distilled cyclopentadiene was shaken with distilled water and centrifuged. The saturated aqueous solution was diluted by a factor of 20 for the stock solution. Various aliquots of this stock solution were added to the NaOH solution cooled in ice. Heat is evolved on mixing, and ice baths were used to minimize evaporation. The stoppered solutions were allowed to warm to room temperature and were pipetted into a 1-cm quartz spectrometer cell. Measurements were made on a Cary 118 spectrophotometer using a corresponding NaOH solution as reference. The absorbance at each wavelength was divided by the cyclopentadiene concentration added to derive an apparent extinction coefficient. The results are summarized in Figure 1.

Results and Discussion

Aqueous solutions of cyclopentadiene (CpH) show a definite λ_{max} 238 nm. As this solution is made more basic, the results in Figure 1 show that this λ_{max} tends to flatten and change to increasing absorption at shorter wavelengths. Unfortunately, the λ_{max} of cyclopentadienyl anion occurs at