Reaction of Coordinated Purines. A Facile, High Yield Synthetic Route to N(7)-Alkylated Xanthines and Hypoxanthines. The Structure of [Bis(dimethylglyoximato)(xanthinato)-(tri-*n*-butylphosphine)cobalt(III)] and the Trans Influence in Cobalt(III) Chemistry

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Abstract: The synthesis and characterization of several complexes of the type $[(Bu_3P)Co(DH)_2(pur)]$, where Bu_3P = tri-*n*-butylphosphine, purH = a purine, and DH = the monoanion of dimethylglyoxime, are reported. The coordinated purine monoanions undergo facile, high yield alkylation reactions to give N(7)-alkylated derivatives. This result, in addition to consideration of steric factors influencing coordination of a series of pyrimidine and purine bases, implied coordination of the monoanions through N(9). This coordination mode was definitively established by the crystal structure of one of the complexes [bis(dimethylglyoximato)(xanthinato)(tri-*n*-butylphosphine)cobalt(III)]. The complex crystallizes in the monoclinic system, space group $C2/c$, with crystal data: $a = 16.694$ (6), $b = 14.159$ (6), $c = 30.199$ (17) Å, $\beta = 102.06$ (4)°; $Z = 8$; $d_{measd} = 1.33$ (1), $d_{calcd} = 1.35$ g cm^{-3}. The crystal contains one complex, two water molecules, and one methanol of crystallization per asymmetric unit. The structure was solved by standard heavy-atom methods and has been refined by full-matrix least squares to final residuals of $R = 0.115$ and $R_w = 0.092$. The monoanions of dimethylglyoxime are arranged about the metal center in an approximately coplanar array with the tri-*n*-butylphosphine and the purine monoanion in axial positions. Comparison of the Co–P distance in the xanthine complex (2.285 Å) and a carbon-bonded pyridine complex (2.342 Å) indicates a significant trans influence in carbon-bonded Co(III) systems.

Deprotonated purine bases offer a variety of nucleophilic sites which may not greatly differ in their electronic properties.[1] Therefore, when such heterocycles are treated with electrophiles (protons, metal ions, alkylating agents, or glycosylating agents) a number of products may result. A metal center is expected to be less effective than a proton at withdrawing negative charge from the purine, and metal complexes of purine anions can thus exceed the reactivity of the purine and approach the reactivity of the purine anion. However, most metal–purine compounds in the literature, such as [bis(theophyllinato)metal(II)] where the theophylline(1,3-dimethyl-2,6-dioxopurine) ligand is deprotonated and probably coordinated via N(7) and metal(II) is Hg(II)[2] or Cu(II),[3] are poorly soluble or have rather labile bonds. These properties limit the utility of these metal derivatives.

We have, therefore, undertaken the preparation and study of soluble, inert metal–purine complexes for several reasons. First, we hoped that these soluble derivatives would be synthetically useful under mild reaction conditions. Second, we anticipated that inert complexes could be obtained in isomerically pure form either by stereoselective synthesis or, if necessary, after fractional purification. Third, we felt that the coordination complexes would be sufficiently "bulky" to prevent reaction at more than one site. Finally, although purine compounds are relatively simple systems, characterization of purine derivatives historically has been difficult, and complete characterization of the more complex metal–purine compounds by methods other than X-ray crystallography is often not possible. We hoped, then, that alkylation reactions might prove to be a useful, albeit indirect, chemical method for characterizing the binding mode of the purine to the metal. The alternative approach, limiting the coordination sites by prior alkylation, has been useful in attempts to determine the binding sites of metal ions to polynucleotides and nucleic acids.[4]

We report here the preparation of complexes of the type $[(Bu_3P)Co(DH)_2(pur)]$, where Bu_3P = tri-*n*-butylphosphine, DH = the monoanion of dimethylglyoxime $[HONC(CH_3)C(CH_3)NO^-]$, and pur = the deprotonated forms of adenine, xanthine, or hypoxanthine. These complexes undergo facile alkylation reactions in high yield. This particular system was chosen for the known high solubility of complexes with the $[(Bu_3P)Co(DH)_2]^+$ moiety. Furthermore, an X-ray structure determination of the xanthinato complex has been undertaken. In addition to confirming the molecular stereochemistry of this class of compounds, the structure allows an assessment of the trans influence of the carbon-bonded 4-pyridinato moiety in $[(Bu_3P)CO(DH)_2(py)]$[5] which bears indirect evidence as to the possible magnitude of such an effect in the B_{12}-coenzyme 5′-deoxyadenosylcobalamin.[6] There are relatively few examples of X-ray structure determinations which allow assessment of the trans influence for complexes where only one ligand is varied.[7] Information of this type is important because a detailed knowledge of the underlying factors which determine the trans influence has yet to be obtained.[7]

Also, a trend which seems to be emerging in crystallographic studies is that the dioxime ligands are bent away from bulky axial groups such as Bu_3P and $(C_6H_5)_3P$.[8] The comparison of this structural feature in the pyridinato and the xanthinato complexes was of some interest, since we anticipated that the Co–P bond length would be different in the two complexes. This bending has been used as a basis for determining the steric size of P donor ligands.[9]

Experimental Section

Preparation of the $[(Bu_3P)Co(DH)_2(pur)]$ Complexes. A solution of silver acetate (1.67 g, 10^{-2} mol) in boiling water (75 ml) was added to a methanolic solution (100 ml) of $[(Bu_3P)Co(DH)_2Cl]$[10] (5.3 g, 10^{-2} mol). This reaction mixture was heated on a steam bath for 20 min, cooled to room temperature, and filtered through Celite. The precipitated silver chloride was triply washed with

Table I. Crystal Data for [Bis(dimethylglyoximato)(xanthinato)-(tri-*n*-butylphosphine)cobalt(III)] Monohydrate Monomethanolate

$a = 16.694$ (6) Å	$CoPO_9N_8C_{26}H_{52}$
$b = 14.159$ (6) Å	Space group $C2/c$
$c = 30.199$ (17) Å	$d_{measd} = 1.33$ (1) g cm^{-3}
$\beta = 102.06$ (4)°	$d_{calcd} = 1.35$ g cm^{-3}
$V = 6980.61$ Å^3	$Z = 8$
Mol wt = 710.66	$\mu = 6.2$ cm^{-1}

methanol (30 ml). Attempts to isolate the intermediate cobalt complex, presumed to be $[(Bu_3P)Co(DH)_2H_2O]CH_3CO_2$, were unsuccessful. The use of $[(Bu_3P)Co(DH)_2H_2O]NO_3$, which could be isolated, was not as successful as using the acetate solution. To the acetate solution was added a solution of purine (10^{-2} mol) in 0.1 *M* NaOH (100 ml with warming). The resulting reaction mixture was heated for 1-2 hr and left in a hood overnight. The orange crystalline material which formed was collected, washed well with water (200 ml), and dried over $CaSO_4$ under vacuum for 24 hr. More product could be obtained by warming the filtrate (1 hr) and letting it evaporate for several days.

Adeninato complex: yield = 84%. Anal. Calcd for $C_{25}CoH_{45}N_9O_4P$: C, 48.0; H, 7.2. Found: C, 48.3; H, 7.0. ^1H NMR data (CH_2Cl_2): oxime-CH_3, δ 2.24; C(2)-H, 7.99; C(8)-H, 7.24.

Hypoxanthinato complex: yield = 78%. Anal. Calcd for $C_{25}CoH_{44}N_8O_5P$: C, 47.9; H, 7.0. Found: C, 47.6; H, 7.0. ^1H NMR data (CH_2Cl_2): oxime-CH_3, δ 2.21; C(2)-H, 7.72; C(8)-H, 7.29.

Xanthinato complex: yield = 95%. Anal. Calcd for $C_{25}CoH_{44}N_8O_6P$: C, 46.7; H, 6.8. Found: C, 46.4; H, 7.0. ^1H NMR data (CH_2Cl_2): oxime-CH_3, δ 2.27; C(8)-H, 7.02.

Alkylation Reactions. The hypoxanthinato or the xanthinato complex (3×10^{-3} mol) was dissolved in CH_2Cl_2 (100 ml, $CHCl_3$ worked equally well) and the alkylating reagent (6×10^{-3} mol) was added. The reaction mixture was stored in the dark in a sealed erlenmeyer flask. A white or pale yellow material usually became evident after 1 day. However, the material was normally collected after 3-4 days and washed with CH_2Cl_2. Further product could be obtained from the filtrate over long periods. The products were recrystallized from hot dimethyl sulfoxide by allowing the solvent to evaporate slowly under a hood. All were white products after recrystallization.

7-Methylhypoxanthine: yield = 64%. Anal. Calcd for $C_6H_6N_4O$: C, 48.0; H, 4.0. Found: C, 47.9; H, 4.0.

7-Methylxanthine: yield = 86%. Anal. Calcd for $C_6H_6N_4O_2$: C, 43.4; H, 3.7. Found: C, 43.1; H, 3.7.

7-Benzylhypoxanthine: yield = 39%. Anal. Calcd for $C_{12}H_{10}N_4O$: C, 63.7; H, 4.3. Found: C, 63.5; H, 4.3.

7-Benzylxanthine: yield = 77%. Anal. Calcd for $C_{12}H_{10}N_4O_2$: C, 59.5; H, 4.1. Found: C, 59.3; H, 4.3. Mp 297-299° (lit. 295°).

Para-substituted benzylxanthines. (a) Cyano: Anal. Calcd for $C_{13}H_9N_5O_2$: C, 58.4; H, 3.4. Found: C, 58.3; H, 3.6. (b) Phenyl: Anal. Calcd for $C_{18}H_{14}N_4O_2$: C, 67.9; H, 4.4. Found: C, 67.7; H, 4.2. (c) Chloro: Anal. Calcd for $C_{12}ClH_9N_4O_2$: C, 52.2; H, 3.3. Found: C, 52.3; H, 3.2.

Isolation of $[(Bu_3P)Co(DH)_2X]$ (X = Br, I). The cobalt products from the alkylation reaction were identified as the Br or I complex (depending on whether RBr or RI was used as the alkylating agent) by spectral comparisons with the known products. Additionally, these CH_2Cl_2 soluble complexes could be isolated from the reaction mixtures by adding ethanol, and they were recrystallized from CH_2Cl_2-CH_3CH_2OH. Anal. Calcd for $BrC_{20}CoH_{41}N_4O_4P$: C, 42.1; H, 7.2. Found: C, 42.3; H, 7.1. Anal. Calcd for $C_{20}CoH_{41}IN_4O_4P$: C, 38.2; H, 6.6. Found: C, 38.2; H, 6.5.

X-Ray Diffraction Data on the Complex [Bis(dimethylglyoximato)(xanthinato)(tri-*n*-butylphosphine)cobalt(III)]. Crystals suitable for an X-ray diffraction study were grown from a 1:1 by volume solution of methanol and water. The crystals grow as monoclinic prisms with [010] as the prism axis. The crystal system is monoclinic with systematic absences (*hkl*, $h + k = 2n + 1$; *h*0*l*, $l = 2n + 1$) which are consistent with the space groups *Cc* and *C*2/*c*. Unit-cell dimensions and their 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 bouyancy methods in carbon tetrachloride and cyclohexane and indicated one formula unit plus two water molecules and one methanol of crystallization per asymmetric volume. Complete crystal data are given in Table I.

A crystal with dimensions 0.43 × 0.33 × 0.15 mm^3, with the long axis tilted with respect to the diffractometer ϕ-axis, was mounted on a Syntex P$\bar{1}$ computer-controlled diffractometer; molybdenum graphite-monochromatized radiation was employed in the data collection. A total of 8997 reflections (*hkl* and $\overline{hkl}$ octants to $2\theta = 55°$) were measured 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 3° min^{-1} to 24° min^{-1}. Three standards were monitored after every 100 reflections, and their intensities showed no unusual variations over the course of the experiment (maximum deviation of any standard from its mean intensity of ~4%). The 8997 measured intensities, which included standards and glide systematic absences as well as some symmetry related data, were then reduced to a set of 5434 independent reflections with *I* greater than $\sigma(I)$ (about 64% of the independent reflections); these 5434 reflections were then used in the structural solution and refinement. The reflections were assigned observational variances based on the following equation.

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

where S, B_1, and B_2 are the scan and background counts, T_S and T_B are the scan and individual background countings times ($T_B = \frac{1}{4}T_S$ for all reflections), and p was taken to be 0.03 and represents the expected error proportional to the diffracted intensity.[11] Intensities and their standard deviations were corrected for Lorentz and polarization effects, but no correction for absorption was applied ($\mu = 6.2$ cm^{-1}); the maximum error introduced by the neglect of absorption effects was estimated to be about 7% in *I*. The squared-structure factors were placed on an approximate absolute scale by the method of Wilson.[12]

The position of the cobalt and the phosphorus atoms as well as nine C, N, or O atoms was determined from a three-dimensional Patterson synthesis. A structure factor–Fourier calculation based on the positions of these 11 atoms (space group $C2/c$; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.42$) allowed the positioning of 31 more heavy atoms. A second calculation, based now on 42 atoms, revealed the remaining three heavy atoms (a water molecule and the methanol of crystallization). Seven cycles of least-squares refinement, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$, reduced the *R* value to 0.14. In the last two cycles, the Co and P atoms were refined with anisotropic temperature factors.

At this stage a difference Fourier map was computed. Acceptable positions for all hydrogen atoms except those off two of the terminal methyl groups of the tri-*n*-butylphosphine ligand were derived from this map. It was also determined from this map that only ten atoms other than the Co and P had extensive anistropic thermal motion. In particular, the methanol of crystallization showed quite large anisotropy. The refinement was then continued with a total of 241 parameters being allowed to vary (a scale factor, 12 atoms with anisotropic thermal parameters and 33 atoms with isotropic thermal parameters; no attempt was made to refine the hydrogen atom parameters). After three cycles in this mode, the refinement was judged to have reached a satisfactory level of convergence (all shifts/error less than 0.7 except *y* (1.39) and B_{22} (1.47) on the oxygen atom of the methanol molecule). The final *R* value is 0.115. The final weighted *R* $((\Sigma w(F_o - F_c)^2/\Sigma wF_o{}^2)^{1/2})$ and goodness-of-fit $((\Sigma w(F_o - F_c)^2/(NO - NV))^{1/2}$ where NO = 5434 observations and NV = 241 parameters) were 0.092 and 1.9, respectively.

Neutral scattering factors for all the nonhydrogen atoms were taken from the compilation of Hanson, Herman, Lea, and Skillman;[13] the scattering curve for H was that of Stewart, Davidson, and Simpson.[14] In the final cycles of refinement, the Co and P form factor tables were adjusted for the real part of the anomalous dispersion correction.[15] Final heavy-atom parameters are collected in Table II; while those for the hydrogen atoms are given in Table III.[16] A complete list of calculated and observed structure factor amplitudes is given in Table IV.[16] The structure factor and Fourier calculations were done using the X-RAY 67 series of programs;[17] the least-squares refinements were performed with an extensively modified version of ORFLS;[18] best planes were computed with the program of Pippy and Ahmed;[19] the illustrations were prepared

Table II. Final Heavy-Atom Parameters[a]

Atom	x	y	z	B
Co	1624 (0.5)	527 (0.7)	3738 (0.3)	*b*
P	346 (1)	694 (1)	3889 (1)	*b*
O(2)	2747 (3)	735 (5)	2082 (2)	*b*
O(6)	5155 (3)	396 (4)	3095 (2)	*b*
O(10)	1021 (3)	1369 (4)	2877 (2)	*b*
O(11)	2363 (3)	1447 (4)	4567 (2)	*b*
O(12)	1001 (3)	−400 (4)	2900 (1)	*b*
O(13)	2157 (3)	−303 (3)	4604 (2)	*b*
O(14)	1662 (3)	557 (6)	461 (2)	*b*
O(15)	2964 (3)	583 (4)	1190 (2)	*b*
O(19)	787 (4)	4951 (9)	4194 (2)	*b*
N(1)	3935 (3)	535 (4)	2605 (2)	3.2 (1)
N(3)	2673 (3)	603 (4)	2818 (2)	3.2 (1)
N(7)	4158 (3)	286 (4)	3831 (2)	3.4 (1)
N(9)	2763 (3)	410 (4)	3633 (2)	2.3 (1)
N(10)	1394 (3)	1520 (4)	3308 (2)	2.8 (1)
N(11)	1994 (3)	1554 (4)	4125 (2)	2.7 (1)
N(12)	1287 (3)	−495 (4)	3346 (2)	3.0 (1)
N(13)	1831 (3)	−446 (4)	4170 (2)	2.8 (1)
C(2)	3091 (4)	637 (5)	2473 (2)	3.3 (1)
C(4)	3082 (4)	478 (5)	3257 (2)	2.4 (1)
C(5)	3924 (4)	391 (5)	3377 (2)	2.8 (1)
C(6)	4401 (4)	440 (5)	3037 (2)	3.0 (1)
C(8)	3450 (4)	284 (5)	3970 (2)	3.1 (1)
C(10)	1568 (4)	2355 (5)	3464 (2)	3.0 (1)
C(11)	1948 (4)	2377 (5)	3946 (2)	3.0 (1)
C(12)	1369 (4)	−1333 (5)	3527 (3)	3.4 (1)
C(13)	1680 (4)	−1300 (5)	4013 (2)	3.3 (1)
C(14)	1352 (5)	3243 (6)	3192 (3)	4.7 (2)
C(15)	2263 (5)	3242 (7)	4203 (3)	5.3 (2)
C(16)	1132 (6)	−2226 (7)	3259 (3)	5.5 (2)
C(17)	1865 (6)	−2163 (7)	4305 (3)	5.6 (2)
C(19)	924 (7)	4964 (10)	4630 (4)	*b*
C(20)	−200 (4)	1715 (5)	3611 (2)	3.0 (1)
C(21)	−1078 (4)	1842 (5)	3687 (2)	3.6 (1)
C(22)	−1427 (5)	2786 (6)	3525 (3)	4.9 (2)
C(23)	−1535 (6)	2946 (7)	3032 (3)	6.4 (2)
C(30)	−346 (5)	−308 (5)	3737 (2)	3.9 (2)
C(31)	−727 (5)	−446 (6)	3237 (3)	4.9 (2)
C(32)	−1461 (7)	−1134 (9)	3142 (4)	8.4 (3)
C(33)	−1253 (8)	−2051 (10)	3235 (4)	9.4 (3)
C(40)	352 (4)	825 (5)	4489 (2)	3.0 (1)
C(41)	482 (5)	1801 (6)	4695 (3)	4.1 (2)
C(42)	331 (6)	1810 (7)	5177 (3)	5.6 (2)
C(43)	441 (7)	2762 (8)	5399 (4)	7.6 (3)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	17 (0.3)	34 (0.5)	7 (0.1)	1 (0.4)	5 (0.1)	−0 (0.2)
P	19 (0.6)	33 (1)	8 (0.2)	1 (0.7)	5 (0.3)	0 (0.4)
O(2)	28 (2)	153 (6)	8 (1)	14 (3)	5 (1)	7 (2)
O(6)	17 (2)	99 (4)	10 (1)	3 (2)	5 (1)	−0 (1)
O(10)	30 (2)	67 (4)	7 (1)	−2 (2)	2 (1)	3 (1)
O(11)	31 (2)	53 (3)	9 (1)	0 (2)	3 (1)	−2 (1)
O(12)	33 (2)	72 (4)	8 (1)	0 (2)	1 (1)	−5 (1)
O(13)	36 (2)	54 (3)	8 (1)	6 (2)	6 (1)	2 (1)
O(14)	38 (3)	202 (8)	15 (1)	10 (4)	8 (1)	−16 (2)
O(15)	58 (3)	84 (4)	11 (1)	3 (3)	7 (1)	−4 (2)
O(19)	32 (3)	404 (15)	17 (1)	34 (5)	5 (1)	27 (3)
C(19)	78 (7)	190 (13)	16 (2)	43 (7)	11 (3)	17 (4)

[a] Estimated standard deviations are enclosed in parentheses. The fractional coordinates and anisotropic thermal parameters have been multiplied by 10^4. [b] The anisotropic thermal ellipsoid is defined by the following equation: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

with the aid of the program ORTEP.[20] All other calculations were performed with locally written programs.

Results and Discussion

Conditions have been found for the high yield syntheses of the complexes $[(Bu_3P)Co(DH)_2(pur)]$, where pur = the deprotonated forms of adenine, xanthine, or hypoxanthine. Consideration of molecular models suggested that the coordination of these purine anions would be limited to two sites: N(9) or N(3). If coordination were to occur at N(7) or N(1), severe nonbonded repulsions between the exocyclic groups at C(6) and C(2) and the dimethylglyoxime ligand system would have to be overcome. The differences in nucleophilicity for the four nitrogen[1] atoms in these heterocycles are not expected to be large enough to override the steric factors to reaction at N(1) and N(7). Therefore, the most nucleophilic and unhindered position, N(9), was believed to be coordinated to the cobalt.

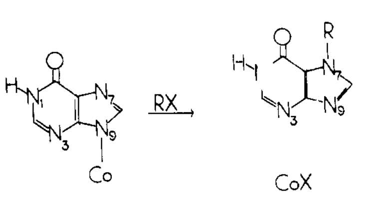


Figure 1. General scheme for the alkylation reactions.

An extensive series of preparative reactions was undertaken with the aim of defining those purines or pyrimidines which would coordinate to the $[(Bu_3P)Co(DH)_2]^+$ moiety. It was found that exocyclic groups on C(2) and C(4) of the pyrimidines prevented coordination presumedly due to unfavorable steric interaction with the dimethylglyoxime ligand system. Also, the normally excellent ligand theophylline (deprotonated)[21] did not react. The theophylline anion has exocyclic groups at both C(6), a carbonyl function, and N(3), a methyl substituent. Normally, the exocyclic oxygen of the carbonyl group does not prevent coordination of theophylline via N(7) when a hydrogen bond donor ligand is present.[21] The dimethylglyoxime ligand system, however, is relatively negative and repulsive interactions, as opposed to the favorable hydrogen bond interactions, are anticipated between the exocyclic oxygen and the chelate system; apparently, these steric factors are sufficiently strong to preclude the coordination of the theophylline ligand. This result is in complete agreement with the lack of coordination of the pyrimidine ligands, as noted above, and suggests that steric factors are affecting not only the choice of coordination site in the purine complexes but are sufficiently strong as to preclude coordination at all in some systems.

Alkylation Reactions. The general scheme for the alkylation reactions is presented in Figure 1, using hypoxanthine as an example. It was clear from the ^{1}H NMR spectra that only one alkylation product was formed from the xanthinato or hypoxanthinato complexes. Identification of the reaction products by comparison to the literature was not usually feasible since often the physical or spectroscopic properties reported for two of the isomers were similar and samples of all of the isomers were not on hand. In the hypoxanthine case, the weight of evidence pointed toward N(7) as the site of alkylation. Moreover, Montgomery and Thomas[22] have shown that benzyl derivatives of hypoxanthine can be easily identified by ^{1}H NMR spectroscopy. The resonances of the product obtained from the reaction of benzylbromide with the hypoxanthinato complex matched closely those reported for 7-benzylhypoxanthine[22] (Table V) and were significantly different from the other possible isomers. Where ^{1}H NMR data are available for monoalkylated xanthine or hypoxanthine compounds,[23] the data have usually been obtained under atypical conditions (such as in D_2O at 70°). For the methylated hypoxanthine isomers under these conditions, the only isomer having coincident C(2)-H and C(8)-H proton resonances was the 7-methyl derivative. The methylated hypoxanthine derivative obtained from the reaction of CH_3I with the hypoxanthinato complex also had coincident C(2)-H and C(8)-H resonances (δ 7.88 in D_2O at ambient temperatures and a methyl resonance at δ 3.82), and this suggests that the methylat-

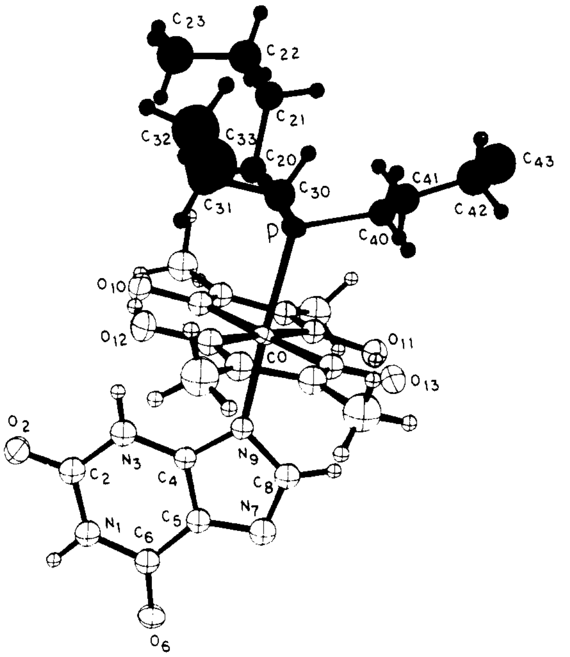


Figure 2. A perspective view of the [bis(dimethylglyoximato)(xanthinato)(tri-*n*-butylphosphine)cobalt(III)] complex. The thermal ellipsoids are drawn at the 40% probability level.

Table V. Summary of ^{1}H NMR Data for Alkylated Derivatives[a] (δ values)

N(7) substituent	CH_3	$-CH_2-$	C_6H_5	H_8	H_2
		Hypoxanthine			
CH_3	3.83			7.85	8.02
Bz		5.63	7.40	8.05	8.46
Bz[b]		5.61	7.35	8.02	8.41
		Xanthine			
Bz		5.45	7.36	8.16	
p-ClBz		5.45	7.40	8.16	
p-PhBz		5.50	7.38–7.75	8.19	
p-CNBz		5.55	7.47, 7.85	8.16	
CH_3	3.76			7.71	

[a] DMSO, TMS reference. [b] Reference 22.

ed compound, like the benzylated compound, can be identified as the N(7) isomer.

^{1}H NMR data for the alkylated xanthine products (Table V) were less definitive, although, again the balance of the evidence suggested N(7) as the site of alkylation. The lack of definitive evidence led us to undertake a crystallographic analysis of the reaction product obtained from the xanthinato complex. The X-ray results confirmed that the reaction product was indeed 7-methylxanthine.[24]

We believe then that the combined spectroscopic and X-ray results support previous structural assignments which have been based on specific synthetic procedures. Furthermore, these results indicate that the major product, very small amounts of other isomers being undetectable, of alkylation of the xanthinato and hypoxanthinato complexes is the N(7) isomer.

X-Ray Crystallographic Results. As noted above, the structure of the xanthinato complex was determined with several objectives in mind: (1) a general assessment of the molecular geometry of this class of complexes, (2) as a means of identification of the site of binding of the complex cation to the purine anions, (3) as an indirect means of assessing the magnitude of the trans influence in carbon-bonded Co(III) systems. All of these objectives have been met and the details of the structure determination are described in this section.

(1) General Aspects of the Molecular Structure. A perspective view of the [bis(dimethyglyloximato)(xanthinato)(tri-*n*-butylphosphine)cobalt(III)] complex is shown in Figure 2. As is typical of the bis(*vic*-dioximes),[25] the monoanions of dimethylglyoxime are arranged about the metal center in an approximately coplanar array. The tri-*n*-butylphosphine and the xanthine monoanion, bonded through the imidazole nitrogen N(9), complete the distorted octahedral coordination sphere about the cobalt atom. The molecular conformation of this complex is nearly identical with a carbon-bonded pyridine complex reported by Adams and Lenhert,[5] namely, [bis(dimethylglyoximato)(4-pyridinato)cobalt(III)]. In an attempt to visualize the uniformity of the molecular conformations of the xanthine and carbon-bonded pyridine complexes, we present in Figure 3 a view down the P-Co bond for each case. As can be seen, the relative molecular arrangements of the tri-*n*-butylphosphine ligands are nearly mirror images differing only at the terminal methyl groups of the butyl chains. This is not unexpected since the α-carbon atoms, and to a lesser extent the β-carbon atoms, have distinctive interactions with the two DH ligands; the similarity of the conformations simply confirms that the tri-*n*-butylphosphine ligands have reached essentially the same degree of interaction with the $(DH)_2$ ligand system in each complex. The relative conformation at the terminus of the butyl chains is, however, primarily a function of the intermolecular environment about each chain.

As can be seen in Figures 2 and 3A, the plane of the N(9)-bonded xanthine ligand is rotated about the Co-N(9) bond so as to become somewhat parallel to one of the N-O bonds of the equatorial dimethylglyoxime ligands. This observed orientation of the plane of the xanthine ligand is probably in response to the formation of the interligand hydrogen bond between the hydrogen atom off N(3) of the base and O(10) of one of the DH ligands and to a lesser extent to the formation of the favorable C(8)-H(8)···O(13) interaction shown in Figure 3A.

(2) An Assessment of the Trans Influence in Carbon-Bonded Co(III) Systems. The near equivalence of the conformation and intramolecular contacts of the tri-*n*-butylphosphine ligands in the N(9)-coordinated xanthine complex reported here and the carbon-bonded pyridine complex of Adams and Lenhert[5] is of particular importance. Randaccio and Zangrando[26] have recently summarized crystallographic data, and Guschl, Stewart, and Brown[27] and Guschl and Brown[28] have reported solution data which extend the suggestion that there is a substantial trans influence associated with alkyl carbon bonded ligands in cobaloxime systems. Further evidence for the trans-influence effect can be gained by a direct comparison of the Co(III)-P distances in the xanthine and the carbon-bonded pyridine complexes. Such a trans influence seems to be present: Co(III)-P distance = 2.342 (1) Å in the pyridine complex, and Co(III)-P distance = 2.285 (2) Å in the xanthine complex. The difference in Co(III)-P bond distances of 0.06 Å is consistent with that found in other cobaloxime complexes with alkyl ligands.[26] Furthermore, the comparison of these distances is unaffected by steric factors which may be present in other situations, since as we have noted the tri-*n*-butylphosphine ligands are in nearly equivalent molecular conformations and have nearly equivalent molecular contacts.

(3) The Equatorial Dimethylglyoxime Ligand System. The two dimethylglyoxime ligands are in an approximately coplanar arrangement about the cobalt center (Figures 2 and 3A). The average Co-N distance of 1.886 (5) Å (individual values are collected in Table VII) is in agreement with the

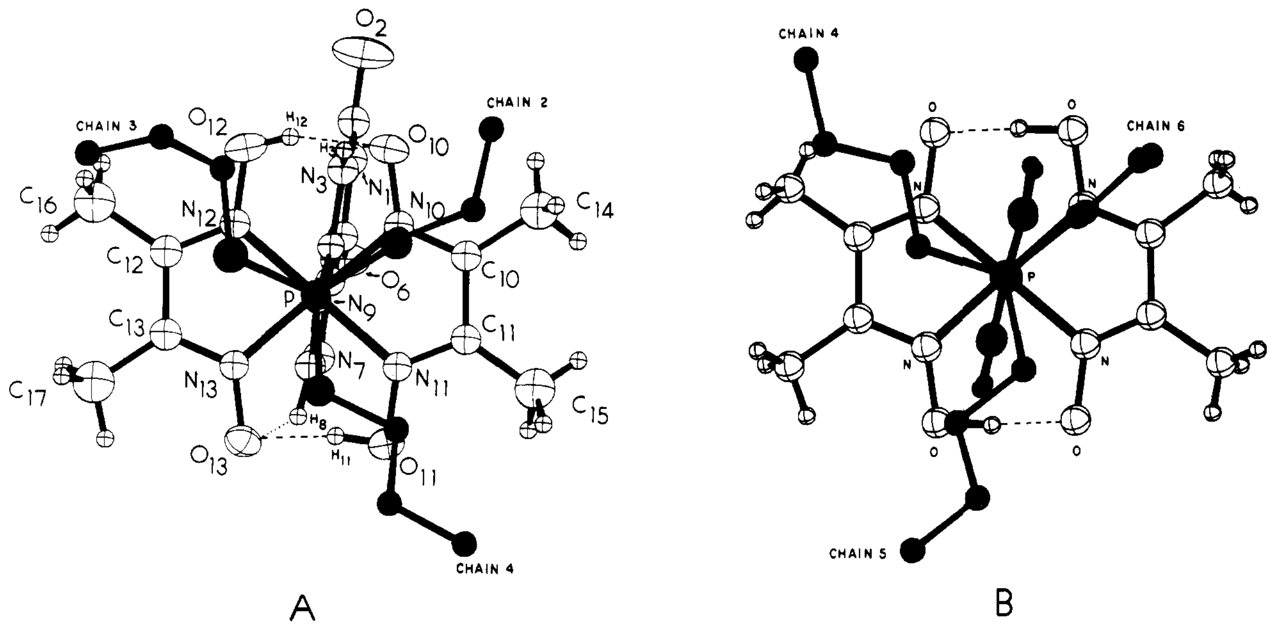


Figure 3. (A) A view of the [bis(dimethylglyoximato)(xanthinato)(tri-*n*-butylphosphine)cobalt(III)] complex down the P-Co bond; (B) an illustration of the [bis(dimethylglyoximato)(pyridinato)(tri-*n*-butylphosphine)cobalt(III)] complex viewed down the P-Co bond.

value of 1.891 (1) Å reported in the carbon-bonded pyridine complex,[5] and with the averaged value found in two other recently studied cobaloximes,[29,30] 1.890 (5) Å. Interpretation of an intermediate difference Fourier map was consistent with the localization of the hydrogen atoms in the interligand dimethylglyoxime hydrogen bond system yielding then an asymmetric hydrogen bond system. It has been noted in some *vic*-dioxime complexes[31,32] that the localization of the $(DH)_2$ N-OH hydrogen atoms leads to characteristic changes in the N-O and N-OH bond lengths and some bond angles in the $(DH)_2$ ligands. In pursuit of such detailed information we have made an extensive search for symmetric and asymmetric hydrogen bond linkages in *vic*-dioximes. The results of this search are summarized in Table VIII. We were somewhat surprised to find that the hydrogen atoms in the bis(*vic*-dioximes) were in the majority of cases asymmetrically located between the dioxime oxygen atoms. In fact, in only one case, [bis(ethylmethylglyoximato)nickel(II)],[33] were the hydrogen atoms indicated to be symmetrically located between the oxygen atoms. We were, however, able to find four accurate structures in which the hydrogen atoms were asymmetrically located.[29-32] Another surprising feature of this search was that the hydrogen atoms were localized in two[29,30] of the four cases on one ligand leading to a formulation of one DH_2 and one D. In the other two cases,[31,32] the bis(*vic*-dioxime) group had approximately a twofold axis normal to the ligand plane as is the case for the xanthine complex and the carbon-bonded pyridine complexes, Figure 3. We have, nonetheless, averaged all the molecular parameters for the asymmetric complexes; these results and the values of Adams and Lenhert,[5] and the xanthine complex reported here are presented in Table VIII. Scrutiny of Table VIII leads to the following conclusions. (a) There are some differences to be expected when the hydrogen atoms are asymmetrically located between the oxygen atoms—a somewhat longer N-OH bond than N-O bond, and small angular variances in M-N-C and C-N-OH angles. (b) These differences are by no means consistent across the set of complexes with asymmetrically bonded hydrogen atoms (note, for example, the large standard deviations from the average in Table VIII). In some of the complexes, the N-OH and N-O bond lengths differed by 0.04 Å,[31,32] while in others the difference was as small as 0.01 Å.[29,30] It should also be noted that in the carbon-bonded pyridine complex of Adams and Lenhert[5] the trend is reversed and the N-O bond is slightly longer than the N-OH bond. (c) The reason for the small differences in the molecular parameters in the symmetrical and asymmetrical hydrogen bond complexes is probably a result of the consistency of the O···O distances in the bis(*vic*-dioxime) complexes of the first-row transition metal series (2.48[29,30] to 2.58 Å[31,32]). It has been deduced[25] that at about a value of 2.50 Å is where the hydrogen bond is likely to be found to be symmetrical. In all of the cases we have surveyed, the O···O distances are within 0.08 Å of the 2.50 Å limit, and thus there is a good possibility that there is only a small alteration in the $(DH)_2$ molecular parameters in response to the localization of the hydrogen atoms.

In describing the planarity of the bis(*vic*-dioxime), it makes some difference in the xanthine complex reported here whether one considers each of the DH rings alone or the complete dimeric hydrogen bonded system, Table VI.[16] The individual DH planes fold about a line passing through the cobalt atom and the midpoints of the $(DH)_2$ oxygen atoms with a dihedral angle of 3.6 (5)° which is consistent with the pyridine complex[5] (4.4 (2)°) and similar systems.[25] The cobalt is displaced by 0.02 Å from the plane of the two DH ligands toward the phosphine ligand.

(4) **The Tri-*n*-butylphosphine Ligand.** The phosphine ligand has approximately the same molecular dimensions as that observed by Adams and Lenhert.[5] The P-C distances average to 1.821 (6) Å while the same value in the pyridine complex is very similar at 1.836 (2) Å. The close proximity of the interior carbon atoms to the DH ligands in the equatorial plane causes the same increase in the Co-P-C angles and the same decrease in the C-P-C angles as noted by Adams and Lenhert.[5]

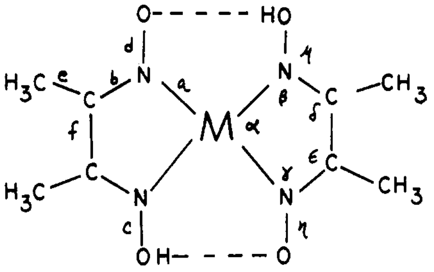
In the pyridine structure[5] all of the butyl groups adopt the trans conformation (leading to an approximately coplanar arrangement of the carbon atoms),[34] while we find two of the butyl groups in gauche conformations and the third (C(40-43)) in the trans conformation. We believe this minor difference in the conformations of the butyl chains is due to intermolecular packing forces. This would seem to be reinforced by the fact that the three planes of the butyl groups and the equatorial plane have the following dihedral

Table VII. Heavy-Atom Interatomic Distances and Angles[a]

(a) Coordination Sphere about the Cobalt			
Bond Lengths (Å)			
Co–P	2.285	Co–N(11)	1.887
Co–N(9)	1.999	Co–N(12)	1.880
Co–N(10)	1.898	Co–N(13)	1.879
Bond Angles (deg)			
P–Co–N(9)	177.4	N(9)–Co–N(12)	90.3
P–Co–N(10)	89.8	N(9)–Co–N(13)	90.4
P–Co–N(11)	89.7	N(10)–Co–N(11)	81.1
P–Co–N(12)	92.1	N(10)–Co–N(12)	98.5
P–Co–N(13)	88.9	N(10)–Co–N(13)	178.6
N(9)–Co–N(10)	90.9	N(11)–Co–N(12)	178.2
N(9)–Co–N(11)	87.9	N(11)–Co–N(13)	98.4
		N(12)–Co–N(13)	82.0
(b) The Tri-*n*-butylphosphine Ligand			
Bond Lengths			
P–C(20)	1.818	C(30)–C(31)	1.524
P–C(30)	1.827	C(31)–C(32)	1.545
P–C(40)	1.819	C(32)–C(33)	1.358
C(20)–C(21)	1.541	C(40)–C(41)	1.512
C(21)–C(22)	1.499	C(41)–C(42)	1.528
C(22)–C(23)	1.479	C(42)–C(43)	1.500
Bond Angles			
Co–P–C(20)	112.9	C(20)–C(21)–C(22)	111.9
Co–P–C(30)	115.9	C(21)–C(22)–C(23)	115.0
Co–P–C(40)	113.5	P–C(30)–C(31)	117.4
C(20)–P–C(30)	105.8	C(30)–C(31)–C(32)	114.6
C(20)–P–C(40)	106.1	C(31)–C(32)–C(33)	114.0
C(30)–P–C(40)	101.6	P–C(40)–C(41)	118.2
P–C(20)–C(21)	115.1	C(40)–C(41)–C(42)	111.2
		C(41)–C(42)–C(43)	113.8
(c) The Dimethylglyoxime Ligands			
Bond Lengths			
N(10)–O(10)	1.337	N(12)–O(12)	1.338
N(11)–O(11)	1.357	N(13)–O(13)	1.325
C(10)–N(10)	1.283	C(12)–N(12)	1.302
C(11)–N(11)	1.280	C(13)–N(13)	1.304
C(10)–C(11)	1.462	C(12)–C(13)	1.452
C(10)–C(14)	1.504	C(12)–C(16)	1.509
C(11)–C(15)	1.486	C(13)–C(17)	1.501
Bond Angles			
Co–N(10)–O(10)	122.3	Co–N(12)–O(12)	123.6
Co–N(10)–C(10)	115.7	Co–N(12)–C(12)	116.5
C(10)–N(10)–O(10)	121.9	C(12)–N(12)–O(12)	119.9
Co–N(11)–O(11)	123.1	Co–N(13)–O(13)	123.5
Co–N(11)–C(11)	117.2	Co–N(13)–C(13)	115.7
C(11)–N(11)–O(11)	119.5	C(13)–N(13)–O(13)	120.6
N(10)–C(10)–C(11)	113.8	N(12)–C(12)–C(13)	112.3
N(10)–C(10)–C(14)	124.0	N(12)–C(12)–C(16)	123.1
C(11)–C(10)–C(14)	122.1	C(13)–C(12)–C(16)	124.6
N(11)–C(11)–C(10)	112.1	N(13)–C(13)–C(12)	113.5
N(11)–C(11)–C(15)	123.1	N(13)–C(13)–C(17)	122.8
C(10)–C(11)–C(15)	124.8	C(12)–C(13)–C(17)	123.6
(d) The Xanthine Ligand and the Methanol of Crystallization			
Bond Lengths			
N(1)–C(2)	1.389	N(9)–C(4)	1.355
N(1)–C(6)	1.379	N(9)–C(8)	1.377
N(3)–C(2)	1.371	C(2)–O(2)	1.208
N(3)–C(4)	1.370	C(4)–C(5)	1.382
N(7)–C(5)	1.353	C(5)–C(6)	1.426
N(7)–C(8)	1.334	C(6)–O(6)	1.236
		C(19)–O(19)	1.29
Bond Angles			
C(2)–N(1)–C(6)	128.3	N(3)–C(4)–N(9)	128.1
C(2)–N(3)–C(4)	120.7	N(3)–C(4)–C(5)	122.6
C(5)–N(7)–C(8)	103.4	N(9)–C(4)–C(5)	109.3
Co–N(9)–C(4)	132.9	N(7)–C(5)–C(4)	109.8
Co–N(9)–C(8)	124.5	N(7)–C(5)–C(6)	130.4
C(4)–N(9)–C(8)	102.5	C(4)–C(5)–C(6)	119.8
N(1)–C(2)–O(2)	122.6	N(1)–C(6)–O(6)	119.7
N(3)–C(2)–O(2)	122.2	N(1)–C(6)–C(5)	113.4
N(1)–C(2)–N(3)	115.2	C(5)–C(6)–O(6)	126.9
		N(7)–C(8)–N(9)	115.0

[a] Estimated standard deviations: Co–P, 0.002 Å; Co–N, 0.005 Å; P–C, 0.006 Å; N–O, 0.007 Å; N–C, 0.008 Å; C–C, 0.010 Å; bond angles 0.3–0.5°; C(19)–O(19), 0.02 Å.

Table VIII. A Comparison of Chemically Equivalent Parameters for Several Vicinal Dioximes[f]



	AL[a]	MESK[b]	SYM[c]	ASYM[d]
		Distance, Å		
a	1.891 (1)	1.886 (5)		
b	1.305 (2)	1.292 (8)	1.298 (6)	1.298 (15)
c	1.343 (2)	1.347 (7)	1.347 (5)	1.372 (28)
d	1.355 (2)	1.331 (7)		1.350 (13)
e	1.511 (3)	1.500 (10)	1.502 (7)	1.502 (18)
f	1.455 (3)	1.457 (10)	1.462 (7)	1.476 (13)
g[e]	2.473 (2)	2.506 (7)	2.454 (6)	2.537 (59)
		Angle, deg		
α	81.5 (1)	81.6 (3)	82.5 (2)	80.8 (5)
β	116.2 (1)	116.8 (4)	116.3 (3)	117.2 (7)
γ	116.5 (1)	115.7 (4)		116.5 (6)
δ	112.7 (2)	112.2 (5)	112.5 (4)	112.6 (7)
ε	112.9 (2)	113.6 (5)		112.7 (6)
μ	120.5 (2)	119.7 (5)	119.8 (4)	119.2 (14)
η	121.1 (2)	121.2 (5)		121.0 (7)

[a] Averaged values of Adams and Lenhert.[5] [b] Averaged values from this study. [c] Averaged values of ref 33 where the hydrogen atoms in the DH ligands are symmetrically located between the $(DH)_2$ oxygen atoms. [d] Averaged values of ref 29, 30, 31, and 32 where the hydrogen atoms in the DH ligands are asymmetrically located between the $(DH)_2$ oxygen atoms. Values in parentheses are the standard deviation from the average. [e] Averaged values for the O···O distances between the equatorial $(DH)_2$ system. [f] It should be emphasized that in all of the complexes compared in this table that the hydrogen atom assignments are based solely on X-ray diffraction data. In no case have these assignments been confirmed, for example, by neutron diffraction data. This is especially pertinent to those cases where the (DH_2) formulation is given.[29,30]

Table IX. Distances (Å) and Angles (deg) in Selected Intermolecular Contacts of the Type, D–H···A

D	H	D–H	A	H···A	D···A	D–H···A
N(1)	H(1)	0.92	O(6)[a]	1.94	2.856	178
N(3)	H(3)	0.88	O(10)[b]	2.20	3.003	151
N(3)	H(3)	0.88	O(12)[b]	2.52	3.187	133[f]
C(8)	H(8)	0.99	O(13)[b]	2.60	3.278	126[f]
C(8)	H(8)	0.99	O(11)[b]	2.77	3.259	111[f]
O(11)	H(11)	0.90	O(13)[b]	1.62	2.507	169
O(12)	H(12)	0.81	O(10)[b]	1.74	2.506	158
O(14)	H(14)	1.31	O(15)[b]	1.62[g]	2.752	139
O(14)	H(15)	1.34	O(13)[c]	1.58[g]	2.899	166
O(15)	H(16)	1.11	O(2)[b]	1.83[g]	2.800	143
O(15)	H(17)	1.14	O(19)[d]	1.81[g]	2.739	135
O(19)	H(18)	1.14	N(7)[e]	1.63[g]	2.753	167

[a] Symmetry transforms: $1 - x, y, \frac{1}{2} - z$. [b] x, y, z. [c] $x, -y, -\frac{1}{2} + z$. [d] $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$. [e] $-\frac{1}{2} + x, \frac{1}{2} + y, z$. [f] These entries are not in the expected range for a hydrogen bond type of interaction. All other entries may be considered to be hydrogen bonds. [g] In these interactions, the long D–H distances make the H···A distances shorter than expected.

angles: 74, 19, and 32°, and that the analogous values in the pyridine complex are 88, 23, and 27°.

The C-C bond lengths in the butyl groups are in reasonable agreement with those in the pyridine complex[5] and in other structures[34] especially when one considers the effects of thermal motion on the derived bond lengths. The

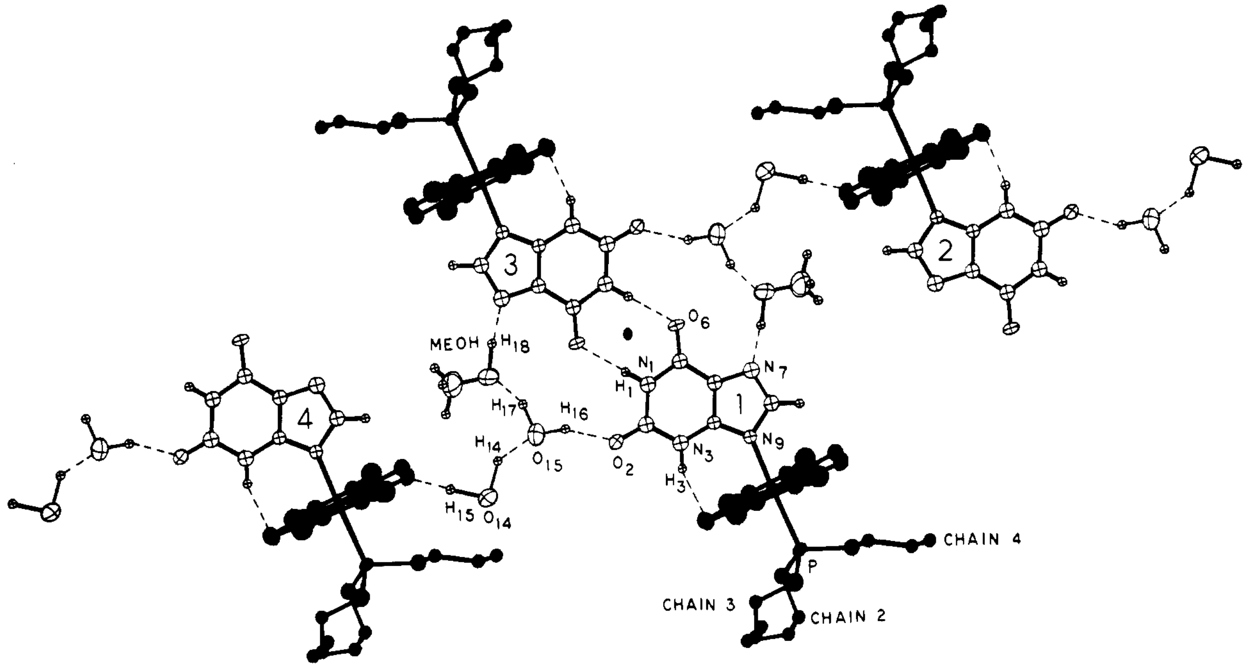


Figure 4. An illustration of the crystal packing in [bis(dimethylglyoximato)(xanthinato)(tri-*n*-butylphospine)cobalt(III)] dihydrate monomethanolate. The view direction is along the $+b$ axis. Dashed lines indicate hydrogen bonds. The four labeled molecules have the following symmetry transforms relative to Table II: (1) x, y, z; (2) $1 - x, -y, 1 - z$; (3) $1 - x, y, \frac{1}{2} - z$.

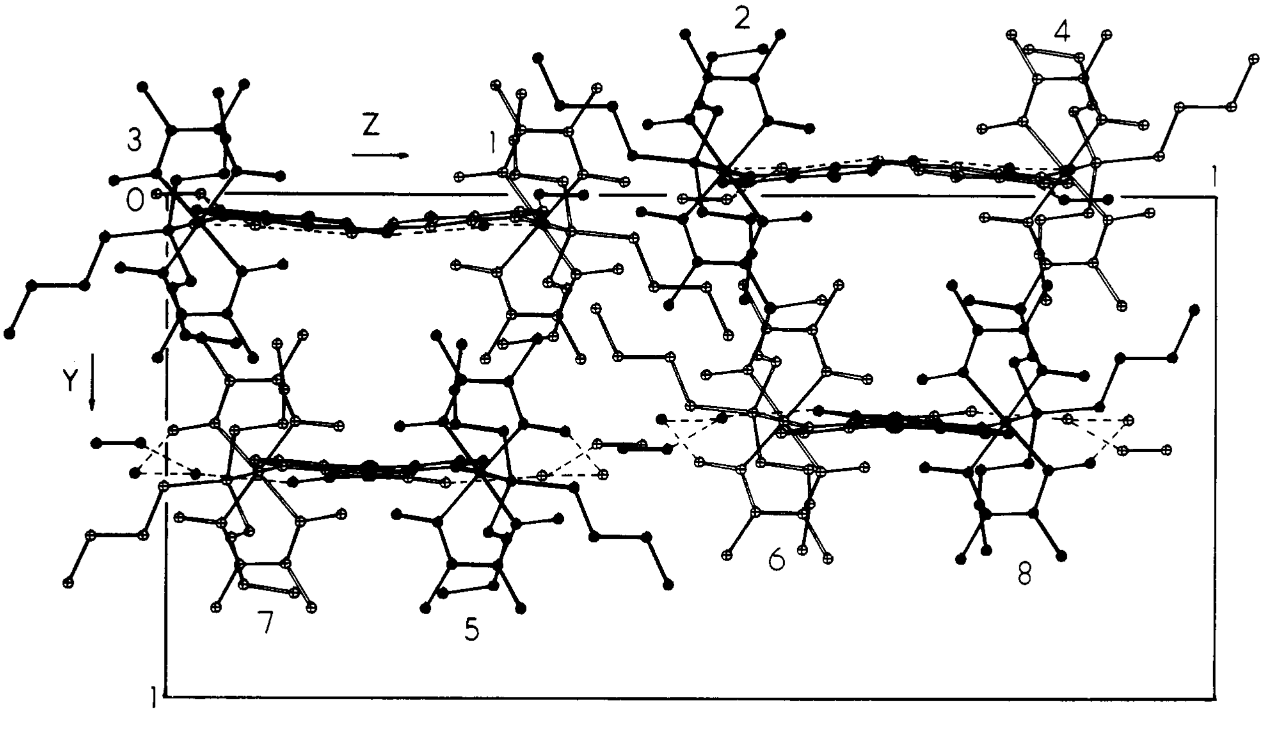


Figure 5. An illustration of the crystal packing viewed normal to the *bc* plane. Dashed lines indicate hydrogen bonds. The eight labeled molecules have the following symmetry transforms relative to Table II: (1) x, y, z; (2) $1 - x, -y, 1 - z$; (3) $1 - x, y, \frac{1}{2} - z$; (4) $x, -y, \frac{1}{2} + z$; (5) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (6) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (7) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (8) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

C(32)-C(33) bond distance is anomalously short and probably indicates disorder in one or both of the atoms.

(5) The Xanthine Ligand. The xanthine ligand is coordinated to the Co through N(9) and the Co-N(9) bond length, 1.999 (5) Å, is somewhat longer, ~0.04 Å, than we have observed in other Co(III)-purine complexes bonded through N(9) or N(7),[21,35,36] but substantially shorter than observed in B_{12} coenzymes.[6] The rest of the bond lengths and angles in the coordinated xanthine anion are about what is expected by analogy to other purine ligands.[21,35,36] To our knowledge no other structures of Co(III)-xanthine complex have been reported.

The nine-atom framework of the coordinated xanthine is nominally planar (Table VI).[16] As is typical of purines,[37,38] the xanthine moiety folds about the C(4)-C(5) bond with a dihedral of 0.8 (4)°. The imidazole ring is somewhat more planar than the pyrimidine ring and the exocyclic oxygen atom O(6) lies about 0.05 Å out of the plane. This is probably due to hydrogen bonding requirements.

(6) The Methanol of Crystallization. The C-O bond length in the methanol of crystallization at 1.29 (2) Å is considerably shorter than the expected value of 1.427 (7) Å.[39] This result is not particularly surprising since the methanol molecule in this structure has very large thermal motion as indicated by the anisotropic thermal parameters in Table II and the thermal ellipsoids as shown in Figure 4. The high degree of thermal motion exhibited by the methanol molecule suggests some sort of disordering. A careful scrutiny of a difference Fourier failed to yield any easily interpretable model; we have thus refined the molecular parameters in the usual way acknowledging that the thermal motion as derived from the refinement may not coincide with physical reality.

(7) **Description of the Crystal Structure.** A view of the crystal packing down the *b* axis is shown in Figure 4. There is an extensive array of hydrogen bonds displayed in a plane approximately parallel to the *ac* plane of the unit cell. The parameters in these hydrogen bonds, as well as the intramolecular hydrogen bonds noted above, are given in Table IX. The interpurine hydrogen bond system, N(1)-H(1)···O(6), links two complexes about the crystallographic twofold axis parallel to *b*. The coupling of complexes about the crystallographic twofold axis is further reinforced by the water, O(15), to methanol to N(7)(xanthine) hydrogen bond bridges on the exterior of the interpurine hydrogen bond system. The extension of the hydrogen bonding to include the second water molecule O(14) and a third complex through the $(DH)_2$ oxygen O(13) is also shown in Figure 4.

A second view of the unit-cell packing, down the *a** axis, is shown in Figure 5. This view clearly shows the interlocking of the complexes in sheets approximately parallel to the *ac* plane. The interaction between these sheets is primarily of the normal van der Waals type involving the butyl groups of the tri-*n*-butylphosphine ligand and the methyl groups of the DH ligands. Intermolecular contacts are collected in Table X.[16]

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Supplementary Material Available. Tables III, IV, VI, and X 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 JACS-75-3351

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