

when both are present.¹⁰ In the title complex, the 102.6° Cu-O-Cu bridge angle corresponds to an antiferromagnetic interaction, and this interaction would be expected to predominate over the ferromagnetic interaction of the smaller Cu-O-Cu angle of 95.7°. This is especially so since the ferromagnetic pathway corresponds to somewhat weaker Cu-O linkages. This surprising result may be as much due to unreasonable expectations as to the numerical data. There are a number of factors to be considered in accounting for these observations.

(1) The experimentally observed J vs. ϕ trend applies strictly for a set of hydroxy-bridged Cu(II) complexes. It has also been shown that distortion from planar toward tetrahedral decreases the magnitude of $-J$, in four-coordinated Cu complexes, while noncoplanarity of the principal ligand planes produces a similar result,⁵¹ as do a number of other structural features.²⁷⁻³³ Thus, the J vs. ϕ trend should not be overinterpreted.

(2) When both p and s orbital contributions to the bridging bonds are taken into consideration,⁵² the magnitude of the calculated ferromagnetic interaction should peak at a Cu-O-Cu angle of about 96°. Thus the ferromagnetic component

may be unusually large, here, given the 95.7° bridging angle, and in this special case the ferromagnetic interaction may slightly dominate a less effective antiferromagnetic path.

(3) The J vs. ϕ correlation applies to Cu-(OH)-Cu linkages. The acetate bridges are markedly different from OH, and thus a large substituent effect at the bridging O atoms could make the generalizations about the J vs. ϕ trend less applicable here. Such large substituent effects are already known in other complexes both due to the nature of the R group on O-R and the angle it makes with the metal bridging framework.⁵²

Thus despite a large amount of work done on the correlation between structure and magnetism in binuclear complexes, there can be surprises when antiferent bridging groups are placed together. In this case a presumably ferromagnetic and a presumably antiferromagnetic bridging group are seen together. Work is in progress on the synthesis of other analogues which will provide additional data on the new category of copper dimers.⁵³

Acknowledgment. Support received under NSF Grant No. CHE77-01372 is gratefully acknowledged.

Registry No. [Cu(NMe₂EtOHSal)CH₃COO]₂·H₂O·C₂H₅OH, 76430-68-7.

Supplementary Material Available: A table of coefficients of least-squares planes and a listing of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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Synthesis and Solution and Solid-State Studies of Cobaloxime Complexes Containing Alkylated 6-Aminopurine Ligands. Molecular and Crystal Structure of the Complex with N(7)-Bound 3-Benzyladenine and Dimethyl Phosphonate as the Axial Ligands

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Received August 8, 1980

In order to ascertain the effect on complex stability of long bonds from a metal to an endocyclic nitrogen center of a nucleic acid base, we have examined the formation of complexes containing good trans-directing ligands. Conditions leading to isolable complexes of formula LCo(DH)₂X (where L = 3- or 9-alkylated adenine; X = alkyl or P(O)(OCH₃)₂; DH = monoanion of dimethylglyoxime) have been found. In Me₂SO-*d*₆ solutions the complex is in equilibrium with the 6-aminopurine base and the solvato complex. The equilibrium was quantified for L = 3-alkyladenine by measuring the areas of the ¹H NMR signals of the oxime methyl groups. The measured stability constants are about 300-500 times smaller than those found earlier for LCo(acac)₂NO₂ (where acac = monoanion of acetylacetone). A complete structural characterization of (3-benzyladenine)Co(DH)₂(P(O)(OCH₃)₂)·EtOH·H₂O was undertaken. The complex crystallizes from chloroform (containing 0.75% EtOH and 2 drops of H₂O/100 mL) in the monoclinic system, space group *P*2₁/*c*, with cell data *a* = 14.674 (5) Å, *b* = 13.607 (3) Å, *c* = 16.735 (9) Å, β = 111.23 (3)°, *Z* = 4, and *V* = 3114.7 Å³. The structure was solved by standard heavy-atom methods and has been refined to a final *R* value of 0.093. Both O...H...O protons in the equatorial plane appear to be localized on one of the two dimethylglyoxime ligands, yielding a neutral and a dianionic ligand. This less usual arrangement for cobaloximes is probably due to the presence of interligand hydrogen bonding involving the 6-amino group of the axial 3-benzyladenine base and the dianionic equatorial dimethylglyoxime ligand. The complex has a long Co-N(7) distance of 2.101 (7) Å and a relatively short Co-P distance of 2.229 (3) Å. The observed length of the Co-N(7) bond most likely arises from a combination of the σ -donor power of the trans dimethyl phosphonate ligand and of steric interactions between the 6-amino group and the equatorial dimethylglyoxime system. The relative instability of the dimethylglyoxime vs. the acetylacetonate complexes is proposed to result from these same two considerations.

Introduction

For some time now, we have been investigating how the exocyclic functional groups on purine and pyrimidine ligands influence metal binding of these heterocyclic compounds.¹ It is now clear that these exocyclic groups influence both binding

site selection and complex stability via nonbonded repulsive and hydrogen-bonding attractive interactions with other ligands in the coordination environment. The nature of the other attached ligands (e.g., size and hydrogen-bonding affinity) can

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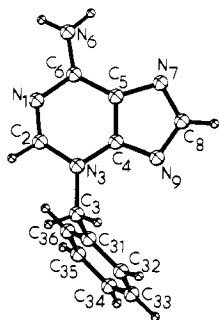
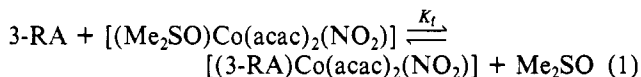


Figure 1. Molecular structure and atomic numbering scheme for the 3-benzyladenine molecule.

alter the bonding preference of a given metal center, particularly for first-row "octahedral" metal centers such as Co(III) and Mn(II).¹

For example, we have recently shown that the complex anion $[\text{Co}^{\text{III}}(\text{acac})_2(\text{NO}_2)_2]^-$, where acac = the monoanion of acetylacetone) reacts preferentially with adenine nucleosides and adenine derivatives to the near exclusion of the other common purine and pyrimidine nucleosides.² In these N(7)-bound adenine complexes, a favorable bifurcated hydrogen-bonding system involving the exocyclic amino group at position 6 of the purine ring and two of the coordinated oxygen atoms from two different acac ligands of the equatorial "Co(acac)₂" framework is formed. The presence of such favorable hydrogen-bonding interactions in 6-aminopurine nucleoside complexes and the projected presence of unfavorable repulsive interligand interactions in potential nucleoside complexes with guanosine, cytidine, and thymidine (uridine) allow a rationalization of the stability trend in the Co(acac)₂ complexes.² Of particular note, adenine derivatives alkylated at N(3) (abbreviated 3-RA) formed very stable $[(\text{base})\text{Co}(\text{acac})_2(\text{NO}_2)]$ complexes, with formation constants (eq 1) on the order of 60 times greater than those for complexes containing N(9)-substituted adenine derivatives.^{2,3}



Similarly, we have successfully prepared octahedral complexes of 6-oxopurine ligands when hydrogen-bond-donating ligands were present in the coordination sphere of Co(III).¹ However, except for the acac complexes discussed above, we have not been successful in obtaining other N(7)-bound 6-aminopurine Co(III) complexes. It occurred to us that if the length of the M–N(7) bond were increased, steric repulsion might be decreased and such compounds might be isolable. To investigate this hypothesis, we chose to study the reactions of the cobaloxime system $\text{LCo}(\text{DH})_2\text{X}$, where L = a neutral ligand, X = an anionic ligand, and DH = the monoanion of dimethylglyoxime. It is known that the length of the bond between the ligating atom L and the Co(III) center is a function of the nature of the trans ligand X.⁴ Our initial synthetic efforts focused on utilizing the strongly coordinating N(3)-substituted adenine ligands, as in eq 2, with X = an alkyl

$$[(\text{H}_2\text{O})\text{Co}(\text{DH})_2\text{X}] + 3\text{-RA} \rightarrow [(\text{3-RA})\text{Co}(\text{DH})_2\text{X}] + \text{H}_2\text{O} \quad (2)$$

Table I. Crystal Data for the 3-Benzyladenine–Cobaloxime Complex, as the Monohydrate Monoethanolate Solvate

$a = 14.674(5) \text{ \AA}$	formula $\text{CoPO}_3\text{N}_9\text{C}_{24}\text{H}_{39}$
$b = 13.607(8) \text{ \AA}$	space group $P2_1/c$
$c = 16.735(9) \text{ \AA}$	$D_{\text{meas}} = 1.466(6) \text{ g cm}^{-3}$
$\beta = 111.23(3)^\circ$	$D_{\text{calcd}} = 1.466 \text{ g cm}^{-3}$
$V = 3114.7 \text{ \AA}^3$	$Z = 4$
mol wt 687.5	$\mu[\lambda(\text{Mo K}\alpha) = 0.71069 \text{ \AA}] = 6.9 \text{ cm}^{-1}$

or a phosphonate $[(\text{O})\text{P}(\text{OR})_2]$ ligand. Such efforts were successful for a variety of N(3)-substituted adenine derivatives, and we later discovered that the less strongly coordinating 9-methyladenine ligand would also yield isolable products.

Finally, we have determined the molecular and crystal structure of the complex where L = 3-benzyladenine (Figure 1) and X = dimethyl phosphonate. We believe this to be the first structural study of a coordinated phosphonate complex in cobaloxime chemistry.

Experimental Section

Syntheses. The alkylated adenine derivatives were prepared following literature methods.^{3,5,6} Common abbreviations employed below are as follows: 3-MeA, 3-methyladenine; 3-ECMA, 3-((ethoxycarbonyl)methyl)adenine; 3-BzA, 3-benzyladenine; 9-MeA, 9-methyladenine. All solvents were reagent grade. All newly synthesized complexes gave satisfactory analyses (see the supplementary material).

(a) $[(\text{H}_2\text{O})\text{Co}(\text{DH})_2(\text{P}(\text{O})(\text{OCH}_3)_2)]$ was prepared by the method of Trogler, Epps, and Marzilli.⁷

(b) $[(\text{H}_2\text{O})\text{Co}(\text{DH})_2(\text{X} = i\text{-C}_3\text{H}_7, \text{C}_2\text{H}_5, \text{CH}_3, \text{CH}_2\text{Br})]$ were prepared according to the procedure of Cartano and Ingraham.⁸ The complex $[(\text{py})\text{Co}(\text{DH})_2(\text{X})](1.0 \text{ g})$ was suspended in 50 mL of 80:20 by volume MeOH/H₂O with approximately 1.0 g of the H⁺ form of 50W-X8 ion-exchange resin (Bio-Rad). The mixture was stirred and gently warmed for about 30 min, filtered, and set aside in a hood for crystallization (usually overnight). The product was collected, dried, and washed well with CH₂Cl₂. Yields were about 60–80%.

(c) $[(\text{L})\text{Co}(\text{DH})_2(\text{X})]$ [L = 3-BzA, X = $i\text{-C}_3\text{H}_7, \text{C}_2\text{H}_5, \text{CH}_3, \text{CH}_2\text{Br}, \text{P}(\text{O})(\text{OCH}_3)_2$; L = 3-ECMA, X = $i\text{-C}_3\text{H}_7, \text{CH}_3, \text{CH}_2\text{Br}, \text{P}(\text{O})(\text{OCH}_3)_2$; L = 3-MeA, X = $\text{CH}_3, \text{P}(\text{O})(\text{CH}_3)_2$] were synthesized by dissolving 1.0 g of $[(\text{H}_2\text{O})\text{Co}(\text{DH})_2(\text{X})]$ in 25 mL of absolute MeOH and adding a slight excess of the appropriate ligand L. The suspension was heated gently and stirred for about 30 min. For L = 3-BzA, the complexes precipitated and were collected on a filter, washed with 15 mL of absolute ether, and air-dried. For L = 3-MeA and 3-ECMA, the solutions formed were filtered and concentrated on a rotary evaporator. The resulting products were treated as above for the 3-BzA complexes. The complexes may be recrystallized by dissolving them in warm, dry chloroform, filtering, and precipitating with absolute ether. The powders obtained in this manner contain no solvent of crystallization.

Orange crystals of $[(3\text{-BzA})\text{Co}(\text{DH})_2(\text{P}(\text{O})(\text{OCH}_3)_2) \cdot \text{H}_2\text{O} \cdot \text{EtOH}]$ suitable for X-ray analysis were obtained from reagent grade chloroform (Mallinckrodt; containing 0.75% EtOH) with 2 drops of added water/100 mL.

(d) $[(9\text{-MeA})\text{Co}(\text{DH})_2(\text{X} = i\text{-C}_3\text{H}_7, \text{CH}_3, \text{P}(\text{O})(\text{OCH}_3)_2)]$ were prepared by suspending 0.4 g of $[(\text{H}_2\text{O})\text{Co}(\text{DH})_2\text{X}]$ and an equimolar amount of 9-MeA in 20 mL of chloroform and stirring for 45 min (X = $i\text{-C}_3\text{H}_7, \text{CH}_3$) or overnight (X = $\text{P}(\text{O})(\text{OCH}_3)_2$). The products were precipitated by the careful addition of absolute ether and collected.

¹H NMR Studies. ¹H NMR spectra of the complexes were taken in CDCl₃ solution referenced to Me₄Si on either a JEOL MH-100 or a Varian T-60 spectrometer. The exocyclic 6-amino resonances were too broad to be observed in this solvent.

The equilibrium constants in Me₂SO-d₆ were determined for many of the newly synthesized 3-alkylated adenine complexes. ¹H NMR spectra were recorded on the JEOL MH-100 spectrometer at 32 °C

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Table II. Final Nonhydrogen Atom Coordinates ($\times 10^4$)^a

atom	x	y	z	atom	x	y	z
Co	2268 (1)	1310 (1)	2255 (7)	C(10)	3136 (5)	1294 (6)	3992 (5)
P	805 (2)	1255 (2)	2376 (1)	C(11)	3007 (6)	2335 (6)	3746 (5)
O(1)	223 (4)	378 (4)	1972 (4)	C(12)	1585 (6)	287 (6)	732 (5)
O(2)	880 (4)	1382 (4)	3324 (4)	C(13)	1408 (6)	1336 (7)	485 (6)
O(3)	288 (5)	2241 (5)	1967 (5)	C(14)	3582 (7)	932 (7)	4884 (5)
O(4)	2785 (4)	-275 (3)	3427 (3)	C(15)	3358 (7)	3162 (6)	4352 (6)
O(5)	2347 (4)	3351 (3)	2579 (3)	C(16)	1355 (7)	-539 (7)	99 (6)
O(6)	2128 (4)	-770 (4)	1864 (3)	C(17)	952 (7)	1662 (7)	-413 (5)
O(7)	1560 (4)	2866 (4)	1020 (4)	C(18)	855 (10)	575 (11)	3836 (8)
N(1)	5819 (5)	-256 (4)	2728 (4)	C(19)	-556 (9)	2602 (9)	2025 (8)
N(3)	6034 (4)	1226 (4)	2080 (4)	C(31)	6333 (5)	1849 (5)	807 (5)
N(6)	4485 (4)	-601 (4)	3069 (4)	C(32)	6201 (7)	2713 (6)	351 (6)
N(7)	3651 (4)	1456 (4)	2161 (3)	C(33)	5907 (10)	2719 (7)	-533 (7)
N(9)	4698 (4)	2373 (4)	1717 (4)	C(34)	5767 (8)	1860 (9)	-980 (6)
N(10)	2790 (4)	714 (4)	3332 (4)	C(35)	5876 (8)	1006 (7)	-550 (6)
N(11)	2547 (4)	2451 (4)	2933 (4)	C(36)	6163 (7)	998 (6)	325 (6)
N(12)	1971 (4)	159 (4)	1549 (4)	W(1)	-1592 (5)	68 (5)	2034 (5)
N(13)	1688 (5)	1895 (5)	1154 (4)	O(20) ^b	8669 (29)	1383 (33)	3720 (25)
C(2)	6307 (5)	327 (6)	2438 (5)	O(21) ^b	9416 (31)	1365 (33)	5039 (24)
C(3)	6660 (6)	1832 (5)	1762 (5)	C(20) ^b	8104 (58)	1965 (63)	4072 (62)
C(4)	5120 (5)	1517 (5)	2024 (4)	C(21) ^b	8547 (61)	1563 (55)	4749 (50)
C(5)	4526 (5)	936 (5)	2319 (4)	C(22) ^b	8187 (70)	1035 (71)	4380 (64)
C(6)	4907 (5)	21 (5)	2714 (4)	C(23) ^b	8476 (30)	371 (32)	4098 (28)
C(8)	3825 (5)	2291 (5)	1812 (5)				

^a Estimated standard deviations in the least significant figure are enclosed in parentheses in this and succeeding tables. ^b Atoms associated with the disordered ethanol of solvation; in each case the atomic population was taken to be 0.5.

and at 2 Hz/cm spectral width. The equilibrium constants were derived from a comparison of the methyl oxime resonances of the solvated and the base-coordinated complexes using the cut and weigh method.

Collection, Reduction, and Refinement of the X-ray Diffraction Data. Preliminary oscillation and Weissenberg photographs showed the crystal system of the [(3-BzA)Co(DH)₂(P(O)(OCH₃)₂)] complex to be monoclinic, with systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) consistent with the space group $P2_1/c$. Unit-cell dimensions and their associated standard deviations are derived from a least-squares fit to the setting angles for 15 reflections measured on a Syntex P1 automated diffractometer. The crystal density, measured by the neutral buoyancy method, confirmed the presence of one complex and of one water and one ethanol molecule in the asymmetric volume. Complete crystal data are collected in Table I.

The intensities of 5241 reflections in the octants hkl and $h\bar{k}\bar{l}$ to $2\theta = 50^\circ$ were measured on the diffractometer, with use of graphite-monochromatized Mo $K\alpha$ radiation. The crystal used in the data collection was mounted approximately parallel to the crystallographic c axis and had the following mean separations between principal faces: (100)-(100), 0.15 mm; (010)-(010), 0.30 mm; (001)-(001), 0.30 mm. Intensity data were collected in the θ - 2θ scan mode with individual scan speeds (2 - $24^\circ \text{ min}^{-1}$) determined from a rapid scan at the calculated Bragg peak. The intensities of three standards were monitored after every 100 reflections and showed no systematic variation over the course of the experiment. Observational variances were assigned on the basis of counting statistics plus a term $(pI)^2$, where p was taken to be 0.03 and represents an estimate of the error proportional to the diffracted intensity. The intensities and their standard deviations were corrected for Lorentz and polarization effects. An absorption correction was also applied on the basis of the dimensions and crystal face assignments given above. The measured intensities were symmetry averaged and reduced to a set of 4443 independent reflections, of which 3197 with $I > 0.5\sigma(I)$ were considered observed and formed the basis of the structural solution and refinement. An approximate absolute scale was obtained by the method of Wilson.⁹

The main elements of the structure (positional parameters for the complex and the water molecule of solvation) were readily obtained from a combination of Patterson and structure factor-difference Fourier techniques. At this stage it became obvious that the ethanol molecule of solvation was disordered over at least two sites. A two-site model was developed on the basis of a difference-Fourier map, with equal populations for both sites. This model, while satisfactorily reducing the positive density in the difference-Fourier synthesis, is

probably too simplistic but a more sophisticated model was not readily apparent. Several cycles of isotropic refinement, minimizing the quantity $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, successfully reduced the R value ($\sum ||F_o| - |F_c|| / \sum |F_o|$) to 0.15. Two further cycles, employing anisotropic thermal parameters for the nonhydrogen atoms of the complex and the oxygen atom of the water molecule and isotropic thermal parameters for the nonhydrogen atoms of the disordered ethanol molecule, gave an R value of 0.10. A difference-Fourier synthesis allowed the positioning of the hydrogen atoms of the complex and the water molecule. In particular, the difference map showed peaks at 0.5 and 0.6 e/ $\text{\AA}^3$ for the two bridging oxime protons. Three subsequent cycles of refinement, holding the hydrogen atom parameters fixed, led to convergence (all shift/error values less than 0.5, except for those associated with the ethanol molecule which were all less than 1) and gave a final R value of 0.093. The final weighted R value $[(\sum w(|F_o| - |F_c|)^2) / \sum w|F_o|^2]^{1/2}$ and goodness of fit $[(\sum w(|F_o| - |F_c|)^2) / (\text{NO} - \text{NV})]^{1/2}$, where NO = 3197 observations and NV = 394 variables] were 0.072 and 1.4, respectively. A final difference-Fourier synthesis was featureless, except for peaks at ± 0.7 e/ $\text{\AA}^3$ near the region of the disordered ethanol molecule.

Neutral scattering factor curves for the nonhydrogen¹⁰ and hydrogen¹¹ atoms were taken from standard sources. Anomalous dispersion corrections were applied to the scattering curves for all the nonhydrogen atoms.¹² Final atomic positional parameters for the nonhydrogen atoms are collected in Table II. Tables of thermal parameters, parameters for the hydrogen atoms, and final observed and calculated structure factor amplitudes are available.¹³ The crystallographic computations were performed with a standard set of computer programs.¹⁴

Results and Discussion

Conditions have been found which yield isolable cobaloxime complexes containing N(9)- or N(3)-substituted 6-aminopurine ligands. We have studied various aspects of these systems, including ¹H NMR spectra, formation constants in Me₂SO,

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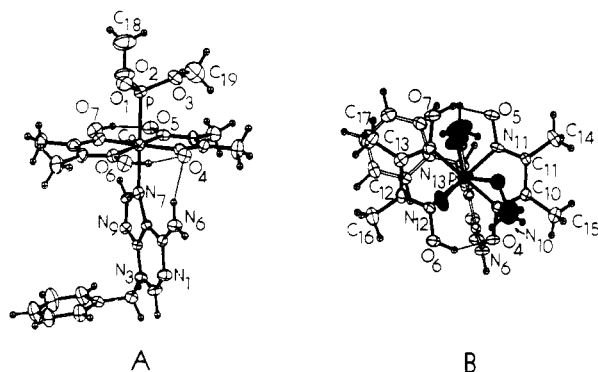


Figure 2. Two views of the 3-benzyladenine-cobaloxime complex: (A) perspective view emphasizing the interligand hydrogen bonds (denoted by thin lines); (B) projection view of the complex down the P-Co bond.

and the molecular structure of one of the N(3)-substituted 6-aminopurine complexes. We first present the structural results and discussion and follow this with a discussion of the solution studies, focusing primarily on the formation constant data.

Structural Results. For a variety of reasons, we have undertaken the structure determination of the complex where X = dimethyl phosphonate and the substituted 6-aminopurine is 3-benzyladenine (Figure 1). First, we wanted to give a general description of the molecular geometry of this class of compounds. Second, we hoped to be able to assess the magnitude of the trans influence ability of the dimethyl phosphonate ligand. Third, we expected that the observed molecular structure would provide an indirect means of evaluating the degree of steric strain involving the N(3)-alkylated 6-aminopurine ligand and the equatorial cobaloxime framework.

(1) General Aspects of the Molecular Structure of the 3-Benzyladenine Complex. A perspective view of the 3-benzyladenine cobaloxime complex is presented in Figure 2A, with intramolecular bond lengths and angles given in Table III. The complex is six-coordinate with the N(7)-bound 3-benzyladenine (Figure 1) and the dimethyl phosphonate ligands in trans positions across the equatorial cobaloxime frame. We also present in Figure 2B a projection view of the complex down the P-Co(III) bond. It is easily seen in this projection view that the orientation of the dimethyl phosphonate ligand is such that the formal P=O bond nearly parallels one of the Co-N equatorial bonds. In spite of the potentially unfavorable interligand steric factors in such an arrangement, the observed Co-P bond length of 2.229 (3) Å is one of the shortest known¹⁵ for a cobaloxime complex; we suggest that the short Co-P bond length may be a consequence of the strong σ -donating power of the negatively charged dimethyl phosphonate ligand.¹⁶

A second consequence of the σ -donating power of the dimethyl phosphonate ligand should be a significant trans influence on the Co-N(7) bond of the 3-benzyladenine ligand.⁴ In fact, the Co-N(7) bond length observed here at 2.101 (7) Å is over 0.1 Å longer than the Co-N(9) distance (1.999 (5) Å) in the complex bis(dimethylglyoximate)(xanthinato)(tri-*n*-butylphosphine)cobalt(III),^{4a} where the tri-*n*-butylphosphine ligand is expected to exert a much weaker trans influence. It is tempting to suggest then that the quite long Co-N(7) bond length in the 3-benzyladenine complex is a direct result of the

Table III. Final Nonhydrogen Atom Interatomic Distances (Å) and Angles (Deg)

(a) Coordination Sphere about the Cobalt Atom			
Co-P	2.229 (3)	Co-N(11)	1.879 (7)
Co-N(7)	2.101 (7)	Co-N(12)	1.915 (7)
Co-N(10)	1.869 (7)	Co-N(13)	1.902 (7)

P-Co-N(7)	176.4 (2)	N(7)-Co-N(13)	89.6 (4)
P-Co-N(10)	88.3 (2)	N(10)-Co-N(11)	81.5 (4)
P-Co-N(11)	88.8 (2)	N(10)-Co-N(12)	99.3 (4)
P-Co-N(12)	91.0 (2)	N(10)-Co-N(13)	177.7 (4)
P-Co-N(13)	89.7 (2)	N(11)-Co-N(12)	179.1 (4)
N(7)-Co-N(10)	92.5 (4)	N(11)-Co-N(13)	99.4 (4)
N(7)-Co-N(11)	87.8 (4)	N(12)-Co-N(13)	79.8 (4)
N(7)-Co-N(12)	92.4 (4)		

(b) The Dimethyl Phosphonate Ligand

P-O(1)	1.481 (7)	O(2)-C(18)	1.40 (2)
P-O(2)	1.560 (7)	O(3)-C(19)	1.37 (1)
P-O(3)	1.571 (7)		

Co-P-O(1)	113.6 (2)	O(1)-P-O(3)	112.4 (4)
Co-P-O(2)	111.9 (2)	O(2)-P-O(3)	101.2 (4)
Co-P-O(3)	105.1 (2)	P-O(2)-C(18)	121.8 (7)
O(1)-P-O(2)	111.7 (4)	P-O(3)-C(19)	125.6 (8)

(c) The Dimethylglyoxime Groups

N(10)-O(4)	1.355 (8)	N(12)-O(6)	1.357 (8)
N(11)-O(5)	1.346 (8)	N(13)-O(7)	1.342 (9)
N(10)-C(10)	1.30 (1)	N(12)-C(12)	1.29 (1)
C(10)-C(11)	1.47 (1)	C(12)-C(13)	1.48 (1)
C(10)-C(15)	1.48 (1)	C(12)-C(16)	1.50 (1)
C(11)-C(14)	1.48 (1)	C(13)-C(17)	1.48 (1)
C(11)-N(11)	1.29 (1)	C(13)-N(13)	1.29 (1)
Co-N(10)-O(4)	121.7 (5)	Co-N(12)-O(6)	123.6 (5)
Co-N(10)-C(10)	116.9 (6)	Co-N(12)-C(12)	117.3 (6)
O(4)-N(10)-C(10)	121.3 (6)	O(6)-N(12)-C(12)	119.1 (7)
N(10)-C(10)-C(11)	112.1 (7)	N(12)-C(12)-C(13)	113.0 (8)
N(10)-C(10)-C(15)	123.2 (8)	N(12)-C(12)-C(16)	123.4 (8)
C(11)-C(10)-C(15)	124.6 (8)	C(13)-C(12)-C(16)	123.6 (8)
N(11)-C(11)-C(10)	112.2 (7)	N(13)-C(13)-C(12)	110.9 (8)
N(11)-C(11)-C(14)	123.3 (8)	N(13)-C(13)-C(17)	126.2 (8)
C(10)-C(11)-C(14)	124.4 (8)	C(12)-C(13)-C(17)	122.8 (8)
Co-N(11)-O(5)	121.4 (5)	Co-N(13)-O(7)	124.1 (5)
Co-N(11)-C(11)	116.9 (6)	Co-N(13)-C(13)	118.9 (6)
O(5)-N(11)-C(11)	121.5 (6)	O(7)-N(13)-C(13)	117.0 (7)

(d) The 3-Benzyladenine Ligand

N(1)-C(2)	1.28 (1)	C(4)-C(5)	1.39 (1)
N(1)-C(6)	1.38 (1)	C(5)-C(6)	1.43 (1)
N(3)-C(2)	1.36 (1)	C(3)-C(31)	1.49 (1)
N(3)-C(3)	1.47 (1)	C(31)-C(32)	1.38 (1)
N(3)-C(4)	1.37 (1)	C(32)-C(33)	1.38 (2)
N(6)-C(6)	1.31 (1)	C(33)-C(34)	1.36 (2)
N(7)-C(5)	1.40 (1)	C(34)-C(35)	1.35 (2)
N(7)-C(8)	1.34 (1)	C(35)-C(36)	1.37 (1)
N(9)-C(4)	1.33 (1)	C(36)-C(31)	1.38 (1)
N(9)-C(8)	1.35 (1)		
C(2)-N(1)-C(6)	119.9 (7)	N(1)-C(6)-N(6)	115.4 (7)
C(2)-N(3)-C(3)	122.8 (6)	N(1)-C(6)-C(5)	117.4 (6)
C(2)-N(3)-C(4)	114.6 (6)	N(6)-C(6)-C(5)	127.2 (7)
C(3)-N(3)-C(4)	122.5 (6)	N(7)-C(8)-N(9)	117.3 (6)
C(5)-N(7)-C(8)	101.8 (6)	N(3)-C(3)-C(31)	113.2 (6)
C(4)-N(9)-C(8)	102.1 (6)	C(3)-C(31)-C(32)	122.2 (8)
N(1)-C(2)-N(3)	127.6 (8)	C(3)-C(31)-C(36)	122.2 (7)
N(3)-C(4)-N(9)	125.9 (6)	C(32)-C(31)-C(36)	115.6 (8)
N(3)-C(4)-C(5)	122.3 (6)	C(31)-C(32)-C(33)	121.7 (9)
N(9)-C(4)-C(5)	111.7 (6)	C(32)-C(33)-C(34)	121.6 (11)
N(7)-C(5)-C(4)	107.1 (6)	C(33)-C(34)-C(35)	118.8 (11)
N(7)-C(5)-C(6)	134.8 (7)	C(34)-C(35)-C(36)	120.6 (10)
C(4)-C(5)-C(6)	118.0 (6)	C(35)-C(36)-C(31)	122.6 (9)
Co-N(7)-C(5)	141.3 (5)	Co-N(7)-C(8)	116.9 (5)

trans influence of the dimethyl phosphonate ligand. In part this is surely correct, but we are reluctant to put forth such a straightforward interpretation in the face of the potentially demanding protrusion of the 6-amino group of the 3-benzyladenine ligand into the equatorial plane (Figure 2). Our collected equilibrium constant data (see below) suggest that

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Table IV. Details of the D-H...A Hydrogen-Bonding Interactions

D	H	D-H, Å	A	D...A, Å	H...A, Å	D-H...A, deg
O(6)	H(O6)	0.97	O(4) ^a	2.53 (1)	1.69	143
O(7)	H(O7)	0.97	O(5) ^a	2.53 (1)	1.68	143
N(6)	H(N6A)	0.88	N(9) ^b	2.98 (1)	2.17	153
N(6)	H(N6B)	0.91	O(4) ^a	2.80 (1)	1.91	164
W(1)	H(W1A)	1.04	O(1)	2.74 (1)	1.69	175
W(1)	H(W1B)	0.93	O(5) ^c	2.76 (1)	1.83	178

^a Intracomplex hydrogen bonds. ^b Symmetry transform: $1 - x, -1/2 + y, 1/2 - z$. ^c Symmetry transform: $-x, -1/2 + y, 1/2 - z$.

these 3-RA complexes are less stable than other systems—notably Co(acac)₃ complexes—where steric demands are reduced and could be taken to imply that the lengthening of the Co-N bond may in part be in response to intramolecular, interligand steric factors.

(2) The Equatorial Ligand System. We have interpreted both intermediate and final difference-Fourier syntheses as being consistent with the following model: (1) the two acidic protons are asymmetrically located between the dioxime oxygen atoms and (2) both localized protons are attached to one of the two dimethylglyoxime ligands, yielding one neutral and one dianion (Figure 2 and Table IV). Such a proton shift from the conventionally observed bis(dimethylglyoximate)-cobalt(III) formulation was first convincingly shown by Palenik and co-workers in cobaloxime complexes with sulfanilamide or 4-chloroaniline as one of the axial ligands.¹⁷ These authors¹⁷ argued that localized ligand-ligand π - π interactions between the dimethylglyoxime groups and the phenyl ring of the axially bound sulfanilamide or 4-chloroaniline ligand stabilizes the proton shift. Randaccio¹⁸ has recently found another example of such a proton shift in the dinitro cobaloxime complex anion. In this complex anion, π - π interligand interactions as proposed by Panenik et al.¹⁷ are surely not important, but no alternative hypothesis was offered to explain the observed proton shift.

In the present instance, we believe the the localization of the two protons on one dimethylglyoxime ligand is primarily stimulated and stabilized by the presence of an interligand hydrogen bond involving the amino group of the 3-benzyladenine ligand and one of the dimethylglyoxime groups (Figure 2). As found in many N(7)-coordinated 6-aminopurine complexes,¹ the exocyclic amino group acts as an interligand hydrogen-bond donor, and, in this case, one of the oxime oxygen atoms of the dianion ligand acts as the acceptor (Table IV). The difference in local environment owing to the presence of this interligand hydrogen bond appears to be sufficient to induce the proton shift. The steric demands associated with the formation of this interligand hydrogen bond are considerable and can best be appreciated by comparing some of the intramolecular features found here and those displayed by the bis(dimethylglyoximate)(xanthinato)(tri-*n*-butylphosphine)-cobalt(III) complex, which also displays an interligand hydrogen bond involving the purine ligand but no observable proton shift.^{4a} In this latter system, the purine anion is bound through N(9), and the N(3) position of the base bears a proton which forms an interligand hydrogen bond to one of the oxime oxygen atoms.^{4a} Comparison of the exocyclic angles at N(9) are Co-N(9)-C(8) = 124.5 (3)° and Co-N(9)-C(4) = 132.9

(3)° and can be contrasted to the significantly more dissymmetric exocyclic angles at N(7) in the 3-benzyladenine complex, Co-N(7)-C(8) = 116.9 (5)° and Co-N(7)-C(5) = 141.3 (5)°. Clearly the cobaloxime complex demands a much larger distortion in the exocyclic angles at N(7) in order to form the interligand hydrogen bond. In fact, the disparity (25°) displayed here for the exocyclic angles at N(7) is the largest known for an N-bound purine complex involved in an interligand hydrogen-bonding scheme.¹

In spite of the severe distortion demanded in the 3-benzyladenine complex, the interligand hydrogen bond appears, judged by the D...A contact distance, stronger [N(6)...O = 2.80 (1) Å] than in the xanthinato complex [N(3)...O = 3.003 (8) Å]. This observation is possibly related to the utilization of the dianionic dimethylglyoxime ligand as the acceptor site in the 3-benzyladenine complex.

One geometrically distinct consequence of the proton shift upon which all authors^{4,17,18} agree is that the Co-N bond lengths are about 0.02–0.03 Å shorter for the dianion compared to those to the neutral glyoxime ligand. Similarly, we find the average Co-N bonds to the dianion (1.874 (7) Å) to be 0.034 Å shorter than the average Co-N bonds to the neutral (1.908 (9) Å). In fact, only the Co-N distances seem to be unequivocally affected by the proton shift, as we find in agreement with earlier work no really systematic trend on comparing the parameters within the neutral and dianionic ligands (Table IV).^{4,17,18}

Finally, a point of some interest is the degree of coplanarity of the two dimethylglyoxime ligands.^{4,17,18} An appropriate reference frame in the 3-benzyladenine complex is the essentially planar group defined by the Co(III) center and the four coordinated nitrogen atoms. The neutral ligand makes a dihedral angle of 2.3 (5)° with this reference plane, while the dianionic ligand has a significantly larger dihedral angle at 5.4 (5)°; the resulting dihedral angle between these two planes is 7.7 (5)°. Regarding the larger folding of the dianionic plane, we note that it is such as to enhance the interligand hydrogen bond to the 3-benzyladenine ligand. In each case, the Co atom lies out of the plane toward the 3-benzyladenine ligand (0.10 Å for the neutral and 0.17 Å for the dianionic ligand).

(3) The 3-Benzyladenine and Dimethyl Phosphonate Ligands. The parameters in the N(7)-coordinated 3-benzyladenine ligand are collected in Table III. It is now well-known¹ that metal coordination to purine ligands through the nitrogen base binding sites produces only subtle effects on the primary geometrical parameters of the base, and the present case appears to be no exception. Comparison of the molecular parameters reported in Table III, for example, with those found in free triacanthine [3-(γ,γ -dimethylallyl)adenine]¹⁹ and the coordinated triacanthine ligand³ in the complex bis(acetylacetonato)(nitro)(triacanthine)cobalt(III) bear out this contention, although, as expected, the parameters in the coordinated 3-benzyladenine ligand are in somewhat better agreement with those in the coordinated triacanthine ligand than those for the free triacanthine molecule.

The nine-atom framework of the 3-benzyladenine ligand is reasonably planar, with an expected²⁰—but slight—fold about the C(4)–C(5) bond at 1.5 (5)°. The phenyl ring of the benzyl moiety makes a dihedral angle of 81.6 (6)° with the purine ring, comparable to the analogous angles of 76.2 (2) and 68.4 (3)° between the dimethylallyl group and the purine system in free¹⁹ and coordinated³ triacanthine, respectively.

The parameters in the dimethyl phosphonate ligand merit some attention as this is to our knowledge^{15b} the first structural

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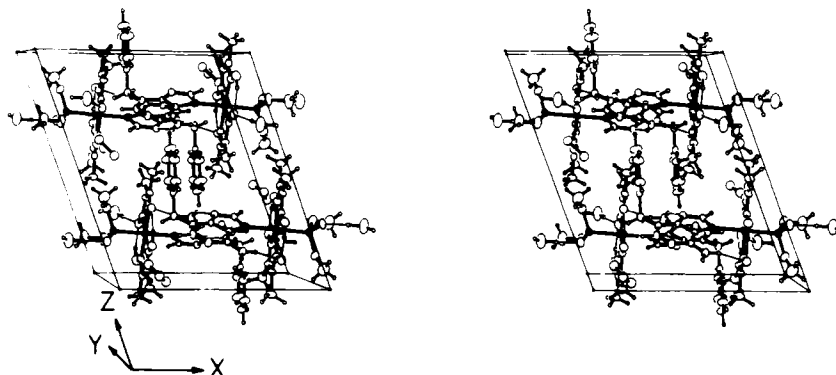


Figure 3. Stereoview of the crystal packing. Only one orientation of the disordered ethanol of solvation is illustrated.

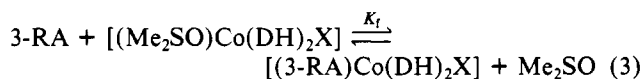
example of a coordinated phosphonate ligand in a cobaloxime complex. The stereochemistry about the P atom is that of a distorted trigonal pyramid, with the formal $\text{P}=\text{O}$ bond length (Table III) some 0.08 Å shorter than the $\text{P}-\text{OCH}_3$ bonds. The $\text{O}-\text{C}$ bond lengths at the exterior of the ligand are systematically shorter than one might expect, owing to the relatively large thermal motion exhibited by the weakly packed methyl groups.

(4) Crystal Packing. The major features of the crystal packing in the 3-benzyladenine complex are illustrated in Figure 3. Besides being involved in the intracomplex hydrogen-bond system described above, the exocyclic amino group of the 3-benzyladenine ligand forms a strong interpurine hydrogen bond, utilizing the imidazole nitrogen atom N(9) of a screw-related complex as an acceptor site (Figure 3 and Table IV). The water molecule of crystallization donates two hydrogen bonds, one involving the $\text{P}=\text{O}$ oxygen atom of the phosphonate ligand and one utilizing an oxygen atom of the dianionic dimethylglyoxime ligand, perhaps further stabilizing the proton shift described above.

The ethanol molecule of solvation offers no significant intermolecular interactions, consistent with its observed disorder.

Solution and Preparative Chemistry. The complexes prepared in this study have been extensively characterized by ^1H NMR techniques (see the supplementary tables).¹³ Although the ^1H NMR spectra of DCCl_3 solutions gave the expected number of resonances for the proposed compounds, spectra taken using $\text{Me}_2\text{SO}-d_6$ as a solvent contain additional signals. It is clear that these signals result from the displacement of the purine ligand by Me_2SO . For example, the same ^1H NMR oxime methyl signals were observed for the proposed $[(\text{Me}_2\text{SO})\text{Co}(\text{DH})_2\text{X}]$ complexes regardless of which of the several purine ligands studied was displaced by solvent or whether $[(\text{H}_2\text{O})\text{Co}(\text{DH})_2\text{X}]$ or various pyridine ligand cobaloximes were dissolved in Me_2SO . The ^1H NMR resonances of the Me_2SO complexes were observed at 2.16, 2.20, 2.18, 2.17, and 2.21 ppm for $\text{X} = \text{CH}_3$, $\text{P}(\text{O})(\text{OCH}_3)_2$, $i\text{-C}_3\text{H}_7$, C_2H_5 , and CH_2Br , respectively.

In addition, if one assumes that the equilibrium described by eq 3 is established in these solutions, equilibrium calcu-



tions using the intensity of the oxime methyl ^1H NMR signals give results consistent with the formation of the solvated species (Table V).

The ^1H NMR spectra of these complexes are, however, of little value in assessing the bonding modes in solution for the purine ligands in these complexes. As seen from the data in Table VI, the H(8) resonance (see Figure 1) is shifted relatively little in the cobaloxime and acac systems. However, the relatively large, and as yet unexplained, shift reported pre-

Table V. Formation Constants (in M^{-1}) for the Equilibrium

$$3\text{-BzA} + [(\text{Me}_2\text{SO})\text{Co}(\text{DH})_2\text{X}] \xrightleftharpoons{K_f} [(\text{3-BzA})\text{Co}(\text{DH})_2\text{X}] + \text{Me}_2\text{SO}$$

X^b	K_f^a	X^b	K_f^a
$\text{P}(\text{O})(\text{CH}_3)_2$	10.1 ^{c,d}	$i\text{-C}_3\text{H}_7$	^e
CH_2Br	37.8 ^c	C_2H_5	15.6
CH_3	29.5 ^{c,d}		

^a Average of two trials at 100 MHz, $T = 32 (\pm 0.5)^\circ\text{C}$, and complex concentration = 0.04 M or 0.08 M in $\text{Me}_2\text{SO}-d_6$. Equilibrium established rapidly (generally <10 min). Estimated error about $\pm 10\%$. Signals from the adenine ligand were of insufficient intensity for reliable K_f determination. ^b Ligands listed in increasing order of electron-donating ability.²¹

^c Similar value obtained for $[(\text{3-ECMA})\text{Co}(\text{DH})_2\text{X}]$. ^d Similar value obtained for $[(\text{3-MeA})\text{Co}(\text{DH})_2\text{X}]$. ^e Rapid ligand exchange (even at 20°C) in the $i\text{-C}_3\text{H}_7$ complexes with 3-BzA and 3-ECMA prevented measurement of their respective equilibrium constants.

Table VI. ^1H NMR Chemical Shift Comparisons for 3-Benzyladenine Complexes in $\text{Me}_2\text{SO}-d_6$ ^a

complex	H(2)	H(8)
3-BzA (free base) ^b	8.53	7.75
$[(\text{3-BzA})\text{Co}(\text{DH})_2\text{P}(\text{O})(\text{OCH}_3)_2]$	8.60	~7.88
$[(\text{3-BzA})\text{Co}(\text{DH})_2(\text{CH}_3)]$	8.60	7.90
$[(\text{3-BzA})\text{Co}(\text{acac})_2(\text{NO}_2)]^b$	8.82	7.82

^a Chemical shifts in ppm from Me_4Si . ^b Taken from ref 3.

viously³ for the H(2) resonance in the acac complexes is not reproduced here in the cobaloxime systems. Also, the NH resonance(s) could not be observed in the cobaloxime complexes, whereas in the acac complexes two NH resonances could be observed and these were assigned to the NH hydrogen bonded to the acac ligands and to the NH pointing toward the bulk solvent.³ The metal-purine bonding may be weaker in the cobaloximes than in the acac system (vide supra) and this may account for the absence of observable NH signals since these resonances may be broadened by ligand exchange or proton exchange with the $\text{O}-\text{H}\cdots\text{O}$ proton of the equatorial ligand system. Relatively rapid rotation about either the $\text{Co}-\text{N}(7)$ or the $\text{N}(6)-\text{C}(6)$ bonds may also result in broadening.

The stability constants in Table V ($10\text{--}40\text{ M}^{-1}$) are considerably lower than for the $3\text{-RACo}(\text{acac})_2\text{NO}_2$ complexes ($6000\text{--}7900\text{ M}^{-1}$).³ An appreciation of the factors influencing the stability constants in Table V can be gained by some comparisons with the K_f values for the relatively unhindered, non-hydrogen-bonding 4-cyanopyridine (CNpy) complexes. The K_f (79 M^{-1}) for $\text{CNpyCo}(\text{acac})_2\text{NO}_2$ is similar to that for $\text{CNpyCo}(\text{DH})_2\text{NO}_2$ (71 M^{-1}). The K_f for $\text{CNpyCo}(\text{DH})_2\text{P}(\text{O})(\text{OCH}_3)_2$ is decreased somewhat to 18 M^{-1} . The compound $3\text{-BzACo}(\text{DH})\text{P}(\text{O})(\text{OCH}_3)_2$ has a value of about

10 M^{-1} even though the pK_a for 3-BzA is $\sim 6^{22}$ and the pK_a for CNpy is $\sim 2^{22}$. This decrease from the value expected on the basis of pK_a considerations suggests destabilization by the 6-amino group. It is clear from these and unpublished data²³ that stability constants for 4-cyanopyridine cobaloximes are higher when X has a lower trans influence. However, for the adenine derivatives, there must be a point where this trend begins to reverse, since as the Co-N(7) bond length decreases (as the trans influence of X decreases) repulsive interactions between the amino group and the dimethylglyoxime equatorial plane must increase. The dissymmetry in bond angles about N(7), alluded to above, would become even more marked, and very poor overlap between the N(7) lone pair and the appropriate metal-bonding orbitals would result.¹ We were not, in fact, successful in preparing any N(7)-bound 6-aminopurine-cobaloxime complexes with weak trans-directing ligands, although a number of preparative approaches were employed.

Furthermore, the exocyclic amino group at C(6) of the adenine derivatives is not able to form as strong a hydrogen bond to the equatorial cobaloxime frame as it can in the acac complex. The oxygen atoms of the cobaloxime complex are already involved with hydrogen bonding between themselves. A weak hydrogen bond is observed (Table IV), but its con-

tribution to the overall molecular stability is expected to be less than that of the bifurcated system in the acac complex.³ The consequences of interligand interactions in adenine complexes are thus, once again, underscored by a comparison of the general properties of the cobaloxime and acac complexes of 3-substituted adenine derivatives.

Acknowledgment. This investigation was supported by the National Institutes of Health through Public Health Services Grants GM 20544 and GM 29222.

Registry No. [(3-BzA)Co(DH)₂(P(O)(OCH₃)₂)]·H₂O·EtOH, 76550-08-8; (3-BzA)Co(DH)₂(CH₂Br), 76550-09-9; (3-BzA)Co(DH)₂(CH₃), 76550-10-2; (3-BzA)Co(DH)₂(*i*-C₃H₇), 76550-11-3; (3-BzA)Co(DH)₂(C₂H₅), 76550-12-4; (3-ECMA)Co(DH)₂(P(O)(OCH₃)₂), 76550-13-5; (3-ECMA)Co(DH)₂(CH₂Br), 76550-14-6; (3-ECMA)Co(DH)₂(CH₃), 76550-15-7; (3-ECMA)Co(DH)₂(*i*-C₃H₇), 76550-16-8; (3-MeA)Co(DH)₂(P(O)(OCH₃)₂), 76550-17-9; (3-MeA)Co(DH)₂(CH₃), 76550-18-0; (9-MeA)Co(DH)₂(P(O)(OCH₃)₂), 76550-19-1; (9-MeA)Co(DH)₂(CH₃), 76550-20-4; (9-MeA)Co(DH)₂(*i*-C₃H₇), 76550-21-5; (H₂O)Co(DH)₂(P(O)(OCH₃)₂), 56403-87-3; (H₂O)Co(DH)₂(*i*-C₃H₇), 28132-41-4; (H₂O)Co(DH)₂(C₂H₅), 26025-30-9; (H₂O)Co(DH)₂(CH₃), 25360-55-8; (H₂O)Co(DH)₂(CH₂Br), 76550-22-6; (Me₂SO)Co(DH)₂(CH₃), 25482-32-0; (Me₂SO)Co(DH)₂(P(O)(OCH₃)₂), 76550-23-7; (Me₂SO)Co(DH)₂(*i*-C₃H₇), 64687-69-0; (Me₂SO)Co(DH)₂(CH₂Br), 76550-24-8; (Me₂SO)Co(DH)₂(C₂H₅), 76550-25-9.

Supplementary Material Available: Tables of elemental analyses, ¹H NMR data, nonhydrogen atom thermal parameters, hydrogen atom parameters, and observed and calculated structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of (C₂H₄)(Cl)Pt(μ-Cl)(μ-C₃H₃N₂)Pt(Cl)(C₂H₄), a Binuclear Platinum(II) Complex with a Single Pyrazolide Bridge

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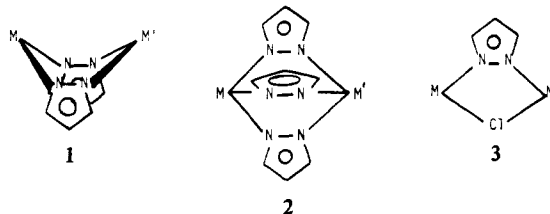
Received August 13, 1980

The binuclear diplatinum(II) complex (C₂H₄)(Cl)Pt(μ-Cl)(μ-C₃H₃N₂)Pt(Cl)(C₂H₄) crystallizes in space group $P2_1/n$ (centrosymmetric, $Z = 4$) with $a = 8.099$ (1) Å, $b = 17.189$ (2) Å, $c = 9.895$ (1) Å, and $\beta = 116.86$ (1)°. The structure was solved by standard Patterson-Fourier methods to $R = 0.040$ for 1182 observed reflections. The Pt₂ClN₂ ring is planar within 0.09 (1) Å, and the plane of the pyrazolide ring makes a 5.7 (4)° angle with this plane. The entire complex, exclusive of the olefin molecules, is planar within 0.35 (2) Å.

Introduction

Binuclear complexes are of interest for their potential as homogeneous catalysts,¹ as models for the transition state in inner-sphere electron transfer,² as models for metalloprotein redox centers,³ and for the unusual electronic and magnetic properties which arise for cases involving strong metal-metal interaction.⁴ The properties (chemical and structural) of these materials are strongly dependent upon the mode of linkage (bridging ligand vs. metal-metal bonds) between the metal centers. The pyrazolide anion (C₃H₃N₂⁻, abbreviated pz) produced by removal of the N-1 proton of pyrazole (C₃H₄N₂) is a versatile bridging ligand found in a number of binuclear

complexes and higher metallooligomers.⁵⁻⁷ For the majority of cases, the intermetallic bridges involve two or more pyrazolide or pyrazolyl groups (1, 2). None of the previously



observed cases of pyrazolide-bridged binuclear species involving

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