

Transition Metal Compounds of N(3)-Alkylated 6-Aminopurines. Synthesis and Unusually High Stability of Bis(acetylacetonato)(nitro)(N(3)-alkylated 6-aminopurine)-cobalt(III) Complexes. Crystal and Molecular Structure of the Triacanthine Complex

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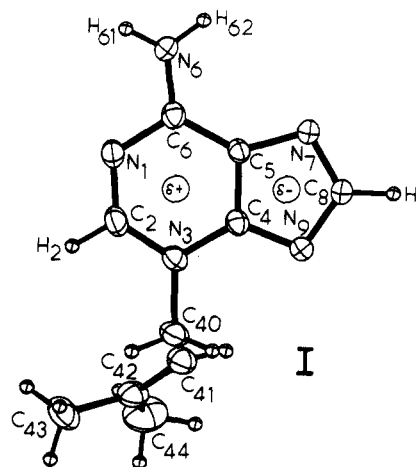
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Abstract: The synthesis, stability constants, and ^1H NMR spectra of three complexes of the type $[\text{Co}^{\text{III}}(\text{acac})_2(\text{NO}_2)\text{B}]$, where B = an N(3)-alkylated 6-aminopurine and acac = acetylacetonate, are reported. The structure of one of the complexes $[\text{Co}^{\text{III}}(\text{acac})_2(\text{NO}_2)(\text{triacanthine})]$ [triacanthine is 6-amino-3-(γ,γ -dimethylallyl)purine] has been determined by x-ray diffraction methods. The complex crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 8.562(4)$, $b = 16.189(10)$, $c = 21.030(8)$ Å; $\beta = 98.41(3)^\circ$; $V = 2883.8$ Å 3 ; $Z = 4$; $d_{\text{measd}} = 1.36(1)$, $d_{\text{calcd}} = 1.38$ g cm $^{-3}$. Intensities for 3301 independent reflections were collected by counter methods on an automated diffractometer operating in the θ - 2θ mode and employing Mo K α monochromated radiation. The structure was solved by standard heavy-atom Patterson methods. Full-matrix least-squares refinement has led to final R , weighted R , and goodness of fit values of 0.064, 0.049, and 1.6, respectively. The cobalt(III) center is six coordinate with two bidentate acac ligands in equatorial positions and the N-bonded nitro group and the N(7)-bonded triacanthine [Co(III)-N(7) distance = 2.003(4) Å] occupying axial positions. This structure represents the first on an N(3)-substituted adenine derivative in a metal compound. The complex in its adopted conformation has a bifurcated hydrogen-bond system between one of the exocyclic amino hydrogens on the purine ring and two of the coordinated acac oxygens. The purine ring is very planar, suggesting a high degree of aromaticity. An association constant for the $[\text{Co}(\text{acac})_2(\text{NO}_2)(\text{triacanthine})]$ complex of 7.8×10^3 M $^{-1}$ was measured in $\text{Me}_2\text{SO}-d_6$. This association constant, based on ^1H NMR data, for the triacanthine complex is ~ 100 times larger than for other adenine derivatives or the common adenine ribonucleosides. ^1H NMR studies show two other interesting features: (1) on coordination at N(7), the pyrimidine proton H(2) of triacanthine shows the largest effect, whereas other N(7)-bonded adenine derivatives show the largest effect at the imidazole ring proton H(8); (2) the interligand hydrogen bonding causes inequivalence in the amino protons on the ring. The related N(3)-methyl and N(3)-benzyl compounds were also prepared and studied. The assignment of the H(2) and H(8) signals in the uncoordinated purines and the exchange of the H(2) proton in preference to the H(8) proton in N(3)-alkylated adenines was confirmed.

Introduction

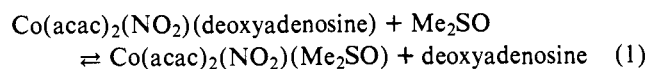
Metal ions mediate the biochemistry of pyrimidine and purine nucleosides, nucleotides, and nucleic acids.¹⁻³ Successful synthetic and structural studies of pertinent metal complexes have largely been limited to this decade.²⁻⁵ In contrast to the historically well-studied metal amino acid and peptide complexes, interligand hydrogen bonding is a ubiquitous aspect of these structures. The existence of such hydrogen bonds in solutions has been used (a) to guide the successful syntheses of complexes of unique types,⁴ (b) to interpret stability trends in solution,^{3,4} (c) to explain the unusually stable chelate ring conformers found in Cr(III)-nucleotide enzyme inhibitors and substrates,⁶ and (d) even to rationalize the effectiveness of certain metallo-antineoplastic agents.⁵ This latter suggestion draws additional support from the recent observation of interligand hydrogen bonding on the complex formed between tRNA and *trans*-Pt^{II}(NH $_3$) $_2$ Cl $_2$.⁷ However, to date, direct evidence has been lacking for such hydrogen bonding in solution.

We have now found such evidence in a study of complexes of 3-alkylated adenines. There have been no previous in-depth studies of metal complexes of these purines, although one of the purines, triacanthine (6-amino-3-(γ,γ -dimethylallyl)purine)(I), is a naturally occurring alkaloid^{8a} and N-3 alkylation of adenine may be an important reaction product when the carcinogen *N*-methyl-*N*-nitrosourea interacts with DNA.^{8b} Our interest in complexes of 3-alkylated adenines derives from the insight which may be gained into the chemistry of the more widely important 9-alkylated adenine derivatives. The physical and chemical properties of 3-alkylated purines are highly contrastible to their more common 9- and 7-substituted analogues.⁸ These differences have led to the suggestion that there



is a shift of π -electron density from the six- to the five-membered ring.⁸

We have recently shown that in aqueous solution the complex $[\text{Co}(\text{acac})_2(\text{NO}_2)_2]^-$ reacts only with adenine nucleosides and not with nucleosides of guanine, thymine (uracil), or cytosine.⁹ The $[\text{Co}(\text{acac})_2(\text{NO}_2)(\text{deoxyadenosine})]$ complex was shown to equilibrate in Me_2SO according to the equation



By introducing competitive heterocyclic bases, the stability constants for complex formation of many purine and pyrimidine bases were determined. However, triacanthine, 3-(γ,γ -dimethylallyl)adenine, formed such a stable compound that

we were not able to determine the formation constant of the [Co(acac)₂(NO₂)(triacanthine)] complex.

We report here an investigation of the preparation, solution properties, and crystal structure of the triacanthine complex. This investigation was undertaken for several reasons: (1) we wished to determine whether the high association constant for the triacanthine complex was due to electronic effects or to some unusual steric factor; (2) we wished to establish the generality of the high stability of complexes of 3-alkylated adenines in this system; (3) we knew of no structural data on 3-substituted 6-aminopurine metal complexes.

During the course of the investigation it proved necessary to assign the H(2) and H(8) resonances of triacanthine. The assignment of these resonances in 3-alkylated adenines is based on 3-benzyladenine.¹⁰ Since the anisotropy of the benzyl group could have influenced the position of the resonances, we undertook to confirm the analogy between the shifts in 3-benzyladenine and other 3-alkylated adenines. Part of this investigation involved confirming that the proton at position 2 undergoes exchange in D₂O in preference to the proton at position 8.¹¹

Experimental Section

Benzyl bromide, methyl iodide, and 4-*tert*-butylpyridine were obtained from Aldrich. Triacanthine, adenine, and deuterated solvents were from either Sigma or Aldrich. All solvents were reagent grade and these along with other common chemicals were obtained from scientific supply houses. Commercial analyses were performed by the Het-Chem-Co.

(a) Na[Co(acac)₂(NO₂)₂] was prepared by the method of Boucher and Bailar.¹²

(b) [Co(acac)₂(NO₂)(triacanthine)]·H₂O was prepared by adding 0.19 g (0.5 mmol) of Na[Co(acac)₂(NO₂)₂] in a minimum amount of water to 0.10 g (0.5 mmol) of triacanthine in 30 mL of hot water. The solution was stirred for 1 min and a brown precipitate was collected and air dried. Anal. Calcd for C₂₀CoH₂₉N₆O₇: C, 45.8; H, 5.6; N, 16.0. Found: C, 45.5; H, 5.6; N, 16.2.

Crystalline samples of x-ray quality were obtained by recrystallization from dimethylformamide. Since the crystals slowly decompose in air, they were coated with a thin film of low molecular weight grease and sealed in thin-walled Lindemann glass capillaries.

(c) [Co(acac)₂(NO₂)(3-benzyladenine)]·0.5H₂O. This compound was made in an analogous manner to the triacanthine complex. The precipitate was washed with ethanol and was not recrystallized, yield ~90%. Anal. Calcd for C₂₂CoH₂₆N₆O_{6.5}: C, 49.1; H, 4.8; N, 15.6. Found: C, 48.8; H, 4.8; N, 15.5.

(d) [Co(acac)₂(3-methyladenine)]. A solution of 3-methyladenine (0.75 g) in methanol (30 mL) was added to a solution of Na[Co(acac)₂(NO₂)₂] (1.9 g) in water (90 mL). An immediate precipitate formed and the mixture was kept stirring for 20 min. The product was collected and washed liberally with water and then ethanol (95%). After air drying, it was recrystallized by dissolving the product in chloroform (50 mL) followed by the addition of ethanol (95%, 50 mL), yield 1.4 g. Anal. Calcd for C₁₆CoH₂₁N₆O₆: C, 42.5; H, 4.7; N, 18.6. Found: C, 42.3; H, 4.6; N, 18.9.

(e) [Co(acac)₂(NO₂)(4-*t*-Bupy)]·H₂O was prepared by adding 0.1860 g (5 × 10⁻⁴ mol) of Na[Co(acac)₂(NO₂)₂] in H₂O to 0.0676 g (5 × 10⁻⁴ mol) of 4-*tert*-butylpyridine in H₂O. The solution was stirred for 20 min and a light brown precipitate was collected and washed with H₂O. A sample was recrystallized from ethanol and analyzed. Anal. Calcd for C₁₉CoH₂₇N₂O₂: C, 52.1; H, 6.2; N, 6.4. Found: C, 52.4; H, 6.2; N, 6.2.

(f) **Alkylated and Deuterated Adenine Derivatives.** The alkylated adenine derivatives used in this study, except for triacanthine itself, were prepared by literature procedures or slight modifications of these procedures^{7,10} and gave satisfactory C, H, and N analyses and ¹H NMR spectra consistent with literature values. However, we found that dimethyl sulfoxide was an excellent solvent for recrystallization of 3-alkylated derivatives and this solvent was used in the purification of these purines. A small amount of 3-methyladenine was purchased from Fox Chemical Co. and the properties of this authentic compound agreed well with those of the material we prepared. Deuterated alkylated derivatives were prepared either from adenine-*d*₈ or by refluxing the purine in D₂O for 72 h.

¹H NMR Studies. All ¹H NMR spectra were recorded, using Me₂SO-*d*₆ as the solvent and referenced to Me₄Si, on either a 60-MHz Varian A-60 spectrometer at 33 °C or a 100-MHz Varian HA-100 spectrometer at 33 °C. The relative ratios of the solvato and base complexes and the free and coordinated butyl resonance of 4-*tert*-butylpyridine were obtained both by the cut and weigh method and by spectrometer integration. The cut and weigh data were obtained from spectra recorded at 2 Hz/cm while the spectrometer integrations were recorded at 20 Hz/cm.

Collection and Reduction of the X-Ray Intensity Data. The external morphology of the burnt-orange crystals of the title complex was that of an elongated plate; the long axis of the crystals was identified as the *a* axis of a monoclinic cell. Further photographic data revealed the space group to be P2₁/c (systematic absences: 0*k*0, *k* = 2*n* + 1; *h*0*l*, *l* = 2*n* + 1). Unit-cell dimensions and their associated standard deviations were derived on the basis of a least-squares fit to the setting angles for 14 reflections measured on a Syntex P-1 automated diffractometer. The crystal density was measured by neutral buoyancy methods in a mixture of cyclohexanol and carbon tetrachloride. Standard crystallographic data are as follows: *a* = 8.562 (4) Å, *b* = 16.189 (10) Å, *c* = 21.030 (8) Å, β = 98.41 (3)°, *V* = 2883.8 Å³, *Z* = 4, empirical formula [(C₅O₂H₇)₂(NO₂)(C₁₀N₅H₁₃)Co]·H₂O·DMF, mol wt 586.2, *d*_{measd} = 1.36 (1) g cm⁻³, *d*_{calcd} = 1.38 g cm⁻³, μ(Mo Kα) = 6.7 cm⁻¹.

Intensity data were collected on a platelet with the following crystal faces and dimensions: (001)–(00 $\bar{1}$), 0.10 mm; (010)–(0 $\bar{1}$ 0), 0.13 mm; (100)–(1 $\bar{0}$ 0), 0.40 mm. The long axis of the crystal was aligned approximately along the φ axis of the spectrometer. The intensities of 8470 reflections (including standards and systematic absences) in the +*h* hemisphere to 2θ = 45° were collected in the θ–2θ mode employing graphite-monochromatized Mo Kα radiation. Individual scan speeds were determined by a rapid scan at the calculated Bragg peak, and the rate of scanning (2θ) varied from 1.5° min⁻¹ (less than 100 counts in the rapid scan) to 12° min⁻¹ (more than 1000 counts in the rapid scan). The intensities of three standards were monitored after every 100 reflections and showed no systematic variation over the course of the experiment (the maximum deviation of any standard from its mean intensity was about 4%).

The 8470 measured intensities were assigned observational variances based on the equation σ²(*I*) = *S* + (*B*₁ + *B*₂)(*T*_S/2*T*_B)² + (*pI*)², where *S*, *B*₁, and *B*₂ are the scan and extremum background counts, *T*_S and *T*_B are the scan and individual background counting times (*T*_B = *T*_S/4), and *p* was taken to be 0.03 and represents the expected error proportional to the diffracted intensity.¹³ Reflections with *I* < 0.2σ(*I*) were assigned intensities of 0.0.

The intensities and their standard deviations were corrected for Lorentz and polarization effects and for the effect of absorption (maximum and minimum transmission factors were 0.94 and 0.91, respectively). The data were subsequently averaged to yield an independent set of 3795 reflections [494 of these reflections with *I*_{av} < σ(*I*_{av})/*n*, where *n* is the number of observations contributing to the average, were considered statistically unobserved and removed from the data set]. The *R* value on the averaging process was 0.036.¹⁴ An approximate absolute scale was determined by the method of Wilson.¹⁵

Solution and Refinement of the Structure. The positional parameters of the Co and the four coordinated oxygen atoms of the acac groups were deduced from a three-dimensional Patterson synthesis. A subsequent structure factor–difference Fourier calculation revealed the rest of the nonhydrogen atoms in the asymmetric unit, as well as two solvent molecules which were both considered to be water molecules at this stage (*R* = Σ|*F*_o| – |*F*_c||Σ|*F*_o| = 0.37, when all atoms were included). A second difference Fourier showed that one of the solvent molecules was actually a DMF with relatively broad and diffuse peaks.

Four cycles of isotropic refinement, minimizing the quality Σ*w*(|*F*_o| – |*F*_c|)² where *w* = 4*F*_o²/σ²(*F*_o²), reduced the *R* value to 0.13 for the 2653 reflections with sin θ/λ ≤ 0.46. Two cycles of refinement with anisotropic thermal parameters assigned to all nonhydrogen atoms lowered the *R* value to 0.076. At this stage, a difference Fourier with the DMF removed clearly showed that two of the atoms of the DMF of solvation were resolvably disordered. Approximate occupancy factors of 0.6 and 0.4 were deduced from the peak heights of the disordered atoms. The difference Fourier also allowed the positioning of the 27 hydrogen atoms on the complex and the two hydrogen atoms on the water of crystallization. No attempt was made to assign the

Table I. Final Nonhydrogen Atomic Parameters^a

atom	x	y	z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Co(1)	1704 (0.7)	1785 (0.4)	1295 (0.3)	99 (1)	25 (0.3)	19 (0.2)	1 (0.5)	13 (0.3)	-0 (0.2)
O(16)	2876 (3)	940 (2)	1761 (1)	124 (6)	31 (2)	23 (1)	4 (3)	9 (2)	1 (1)
O(17)	3318 (3)	2592 (2)	1425 (1)	112 (6)	33 (2)	25 (1)	-5 (3)	14 (2)	-2 (1)
O(18)	522 (3)	2616 (2)	828 (1)	117 (6)	31 (2)	23 (1)	0 (3)	16 (2)	2 (1)
O(19)	113 (3)	977 (2)	1172 (1)	108 (6)	28 (2)	25 (1)	-1 (3)	11 (2)	-1 (1)
O(20)	1486 (4)	1308 (3)	37 (2)	201 (8)	89 (3)	25 (1)	9 (4)	8 (3)	-14 (2)
O(21)	3835 (4)	1349 (2)	507 (2)	142 (7)	81 (3)	31 (1)	24 (4)	26 (3)	-8 (2)
N(1)	186 (5)	4334 (2)	2565 (2)	162 (8)	26 (2)	32 (2)	-1 (3)	29 (3)	-4 (1)
N(3)	-623 (4)	3337 (2)	3279 (2)	119 (7)	34 (2)	22 (1)	9 (3)	17 (3)	-3 (1)
N(6)	1380 (5)	4002 (2)	1701 (2)	220 (9)	24 (2)	31 (2)	-10 (4)	45 (3)	-0 (1)
N(7)	874 (4)	2147 (2)	2094 (2)	133 (7)	23 (2)	20 (1)	-2 (3)	15 (3)	-1 (1)
N(9)	-259 (4)	1907 (2)	2996 (2)	158 (8)	27 (2)	23 (1)	4 (3)	27 (3)	1 (1)
N(21)	2429 (4)	1435 (2)	519 (2)	126 (7)	38 (2)	24 (1)	9 (3)	13 (2)	-3 (1)
C(2)	-433 (6)	4113 (3)	3077 (2)	151 (9)	30 (2)	32 (2)	11 (4)	21 (3)	-6 (2)
C(4)	-156 (5)	2719 (3)	2899 (2)	85 (8)	28 (3)	21 (2)	4 (4)	7 (3)	-3 (2)
C(5)	527 (5)	2897 (3)	2350 (2)	100 (8)	24 (2)	18 (2)	-3 (3)	9 (3)	-4 (2)
C(6)	720 (5)	738 (3)	2186 (2)	105 (9)	30 (3)	23 (2)	2 (4)	10 (3)	-3 (2)
C(8)	371 (5)	1602 (3)	2495 (2)	148 (10)	23 (3)	22 (2)	4 (4)	18 (3)	0 (2)
C(18)	4689 (5)	2470 (3)	1751 (2)	106 (9)	44 (3)	25 (2)	-5 (5)	9 (3)	-14 (2)
C(19)	5177 (5)	1738 (3)	2061 (2)	132 (10)	43 (3)	29 (2)	15 (5)	-9 (3)	-0 (2)
C(20)	4287 (6)	1029 (3)	2048 (2)	170 (11)	36 (3)	19 (2)	15 (5)	11 (3)	-4 (2)
C(21)	5735 (6)	3214 (4)	1777 (3)	175 (11)	65 (4)	38 (2)	-50 (6)	16 (4)	-15 (2)
C(22)	4975 (7)	279 (4)	2402 (3)	208 (10)	58 (3)	29 (2)	26 (5)	-3 (4)	7 (2)
C(23)	-961 (5)	2573 (3)	637 (3)	126 (9)	34 (3)	22 (2)	7 (4)	15 (3)	2 (2)
C(24)	-1872 (5)	1888 (3)	698 (2)	98 (9)	42 (3)	32 (2)	3 (4)	-1 (3)	1 (2)
C(25)	-1308 (5)	1128 (3)	944 (2)	110 (9)	36 (3)	21 (2)	-6 (4)	12 (3)	-2 (2)
C(26)	-1676 (6)	3332 (3)	321 (3)	182 (11)	49 (3)	43 (2)	35 (5)	18 (4)	16 (2)
C(27)	-2408 (6)	408 (3)	949 (3)	139 (10)	45 (3)	38 (2)	-19 (5)	10 (4)	0 (2)
C(40)	-1349 (5)	3148 (3)	3852 (2)	151 (10)	46 (3)	22 (2)	10 (5)	23 (3)	-3 (2)
C(41)	-3083 (6)	2978 (3)	3681 (2)	143 (10)	43 (3)	26 (2)	-6 (4)	18 (3)	-4 (2)
C(42)	-4236 (6)	3441 (3)	3839 (2)	126 (10)	48 (3)	28 (2)	8 (4)	22 (3)	4 (2)
C(43)	-4017 (7)	4197 (4)	4234 (3)	224 (12)	59 (4)	35 (2)	45 (6)	30 (4)	-5 (2)
C(44)	-5913 (7)	3228 (4)	3600 (3)	168 (12)	97 (5)	54 (3)	5 (7)	31 (5)	10 (3)
Solvents									
O(30) ^a	-1601 (4)	665 (2)	3740 (2)	219 (7)	37 (2)	44 (1)	-1 (3)	48 (3)	-2 (1)
O(60) ^b	540 (1)	71 (1)	404 (1)	25 (1)	24 (1)	10 (1)	-4 (1)	9 (1)	-5 (1)
N(60) ^b	326 (1)	97 (1)	448 (1)	19 (1)	12 (1)	7 (1)	-1 (1)	5 (1)	-3 (1)
C(60) ^{b,c}	455 (2)	121 (1)	429 (1)	27 (1)	12 (1)	8 (1)	2 (2)	4 (1)	3 (1)
C'(60) ^{b,d}	464 (3)	55 (2)	452 (1)	33 (7)	12 (2)	7 (1)	-1 (3)	10 (2)	0 (1)
C(61) ^{b,c}	243 (3)	152 (1)	482 (1)	70 (6)	14 (1)	9 (1)	14 (3)	15 (2)	-2 (1)
C'(61) ^{b,d}	240 (3)	78 (2)	506 (1)	56 (6)	10 (2)	9 (1)	2 (3)	18 (2)	-1 (1)
C(62) ^b	236 (1)	47 (1)	401 (1)	46 (3)	15 (1)	16 (1)	-4 (1)	-1 (1)	1 (1)

^a Parameters $\times 10^4$; estimated standard deviations are enclosed in parentheses. The form of the anisotropic thermal ellipsoid is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. ^b Positional and thermal parameters $\times 10^3$. ^c Occupation parameter of 0.6. ^d Occupation parameter of 0.4.

hydrogen atoms of the DMF, nor were any of the hydrogen parameters varied in any of the subsequent cycles of refinement.

Four further cycles of refinement, in which the atoms associated with the disordered DMF were also assigned anisotropic thermal parameters, led to convergence (all shift/error less than 1) and to a final *R* value of 0.064. The final weighted *R* value [$R_w = (\sum w(|F_o| - |F_c|)^2) / \sum w|F_o|^2$]^{1/2} and goodness of fit [$(\sum w(|F_o| - |F_c|)^2) / (\text{NO} - \text{NV})$]^{1/2}, where NO = 3301 independent observations and NV = 325 parameters] were 0.049 and 1.6, respectively. A final difference Fourier map had a peak of 0.45 e/Å³ near one of the methyl groups of the DMF of solvation; no other peak on the map exceeded ± 0.3 e/Å³.

Neutral scattering factors for all nonhydrogen atoms were taken from a recent compilation;¹⁶ the scattering factor curve for hydrogen was that of Stewart, Davidson, and Simpson.¹⁷ The real part of the scattering factor for Co was corrected for anomalous dispersion effects.¹⁸ Final nonhydrogen atom parameters are collected in Table I, while the parameters for the hydrogen atoms are given in Table II. A list of final observed and calculated structure factor amplitudes is available.¹⁹ The crystallographic calculations were performed with the following programs: structure factor and least squares, ORFLS;²⁰ Fourier maps, FORDAP;²¹ best planes, MEAN PLANE;²² illustrations, ORTEP.²³ Calculations not cited were performed with locally written programs.

Results and Discussion

Description of the Molecular and Crystal Structure of the Bis(acetylacetonato)(nitro)(triacanthine)cobalt(III) Complex.

The molecular conformation of the triacanthine complex is presented in the stereoview of Figure 1. The cobalt(III) center is six coordinate, with the two bidentate acac ligands occupying the four coordination sites in the equatorial plane and the N-bonded nitro group, Co-N(21) distance = 1.915 (4) Å, and the N(7)-bonded triacanthine ligand, Co-N(7) distance = 2.003 (4) Å, in axial positions. The triacanthine plane is oriented about the Co-N(7) vector such that it approximately bisects the two equatorial acac ligands, Figure 1. In this orientation, the exocyclic amino group, -N(6)H₂, on the purine framework forms a bifurcated hydrogen bond system to two of the coordinated oxygen atoms of the acac ligands (Figure 1). Consistent with the formation of the interligand hydrogen bonds,^{24,25} the exocyclic angles at N(7) are highly dissymmetric, with the Co-N(7)-C(5) angle being about 14° larger than the Co-N(7)-C(8) angle, Table IV. The magnitude of this dissymmetry is on the order of that which we have found in several other systems where interligand hydrogen bonds are

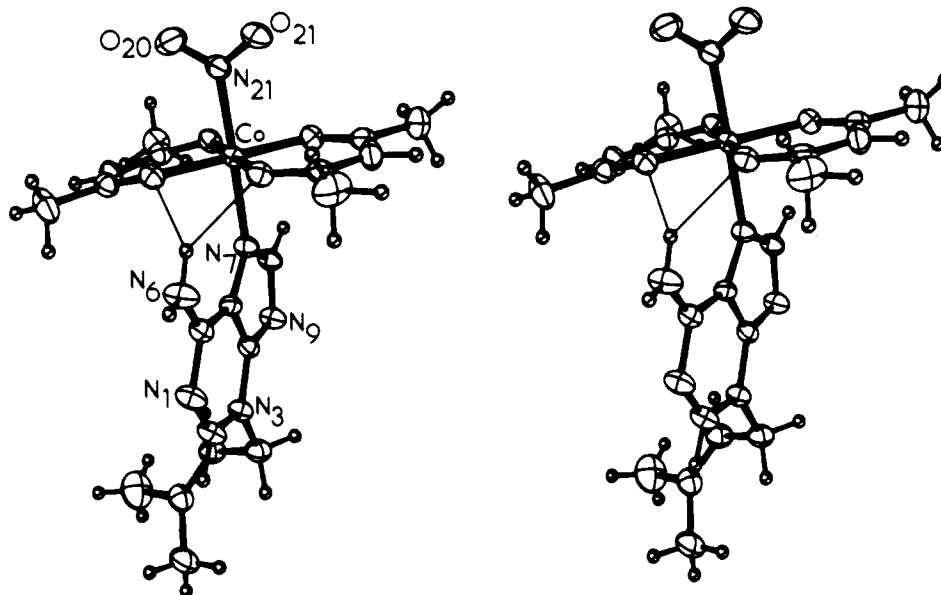


Figure 1. A stereoview of the bis(acetylacetonato)(nitro)(triacanthine)cobalt(III) complex. The thermal ellipsoids are drawn at the 30% probability level. In this, and all subsequent figures, the isotropic thermal parameters of the hydrogen atoms have been arbitrarily set at 1.0 \AA^2 . The bifurcated interligand hydrogen bond system is indicated by thin lines.

Table II. Hydrogen Atom Parameters

atom	x^a	y	z	B^b
H(2)	-81	456	333	5.0
H(8)	45	100	242	5.0
H(61)	166	452	166	6.0
H(62)	174	365	143	6.0
H(19)	623	172	231	6.0
H(24)	-301	193	53	6.0
H(211)	548	359	211	7.0
H(212)	602	334	137	7.0
H(213)	670	312	207	7.0
H(221)	487	30	285	7.0
H(222)	607	21	237	7.0
H(223)	424	-18	231	7.0
H(261)	-110	356	1	7.0
H(262)	-279	328	21	7.0
H(263)	-172	378	65	7.0
H(271)	-232	5	60	6.0
H(272)	-235	14	136	6.0
H(273)	-349	60	90	6.0
H(401)	-121	360	415	5.0
H(402)	-83	267	407	5.0
H(411)	-339	249	341	5.0
H(431)	-293	427	444	7.0
H(432)	-430	469	398	7.0
H(433)	-467	423	457	7.0
H(441)	-645	359	329	9.0
H(442)	-609	262	355	9.0
H(443)	-656	316	394	9.0
H(301)	-280	79	381	7.0
H(302)	-146	116	350	7.0

^a Positional parameters $\times 10^3$. ^b Unscaled isotropic thermal parameters.

formed between exocyclic groups on purine ligands and other ligands in the coordination sphere about a metal center. The Co–N(7) vector lies $3.6 (4)^\circ$ out of the purine plane, as is consistent with the formation of the interligand hydrogen bonds to equatorial sites.²⁶ Furthermore, in the adopted conformation of the triacanthine ligand, the hydrogen atom off the imidazole carbon atom C(8) forms favorable contacts with the remaining oxygen atoms of the acac groups (Figure 2). The parameters in the bifurcated hydrogen bond system and the C(8)–H(8)···O(acac) contacts are given in Table III.

The conformational properties discussed above for the

triacanthine complex are very similar to that which we have found in the related complexes $[\text{Co}(\text{acac})_2(\text{NO}_2)(\text{deoxyadenosine})]_9$ and $[\text{Co}(\text{acac})_2(\text{NO}_2)(2\text{-aminopyrimidine})]_{27}$. The one major conformational difference is the relationship of the NO_2 ligand to the remainder of the system. In the deoxyadenosine and 2-aminopyrimidine complexes, the NO_2 plane and the purine or pyrimidine ligand are essentially coplanar, whereas in the triacanthine complex the dihedral angle between the NO_2 plane and the purine framework is $87.4 (5)^\circ$ (Figure 2B). The two orientations of the NO_2 plane in relationship to the acac ligands seem about equally favorable sterically, with mean $\text{O}(\text{NO}_2)\cdots\text{O}(\text{acac})$ intramolecular contacts of $2.85 (7) \text{ \AA}$ in the deoxyadenosine complex⁹ and $2.89 (4) \text{ \AA}$ in the triacanthine complex. Whether electronic or crystal packing forces have led to the different orientations of the NO_2 plane to the acac group and the base planes is presently unclear.

There are a variety of other conformational features of the triacanthine complex that are worthy of mention. As can be seen in Table V and Figure 2, the cobalt atom lies essentially in the plane of the acac ligands, but the two acac planes are not coplanar, with a dihedral angle of $11.2 (5)^\circ$. However, only one of the acac ligands [O(16)–O(18)] is substantially noncoplanar with respect to the equatorial plane, with a dihedral angle of $10.1 (5)^\circ$. This noncoplanarity is easily seen in Figure 2A, and is apparently attributable to several close contacts of this acac ligand with the allyl group of a glide-related complex.

The nine-atom framework of the triacanthine ligand is planar within experimental error with no measurable fold about the C(4)–C(5) bond as has been commonly observed in the deoxyadenosine complex⁹ and many other coordinated and uncoordinated purine systems.²⁸ This planarity is consistent with the high degree of aromaticity suggested by the chemical and ^1H NMR studies cited above for 3-substituted adenine derivatives.

The dimensions in the primary coordination sphere are consistent with expectations. The bond angles about the cobalt(III) center are all close to 90° , the only minor exceptions being associated with the bidentate acac groups' bite angles. The parameters in the acac and NO_2 ligands are consistent with other observations.²⁷ The molecular dimensions of the triacanthine ligand are of some detailed interest. We have made several attempts to deduce the effect of coordination in several 9-substituted purine complexes.²⁵ While the effect of

Table III. Distances and Angles in the Interactions of the Type D-H...A

D	H	A	H...A	D...A	$\angle D-H...A$
Hydrogen Bonds					
N(6) ^d	H(62)	O(17) ^a	2.18	2.930 (6)	141
N(6) ^d	H(62)	O(18) ^a	2.26	2.924 (6)	131
N(6)	H(61)	O(30) ^b	2.03	2.863 (7)	157
O(30)	H(301)	O(60) ^c	1.69	2.737 (7)	163
O(30)	H(302)	N(9) ^a	1.99	2.887 (7)	154
C-H...O Contacts					
C(8)	H(8)	O(19) ^a	2.60	2.938 (6)	100
C(8)	H(8)	O(16) ^a	2.66	3.017 (6)	101
C(2)	H(2)	O(19) ^b	2.56	3.398 (6)	144

^a x, y, z . ^b $-x, 1/2 + y, 1/2 - z$. ^c $-1 + y, y, z$. ^d The interligand hydrogen bonds.

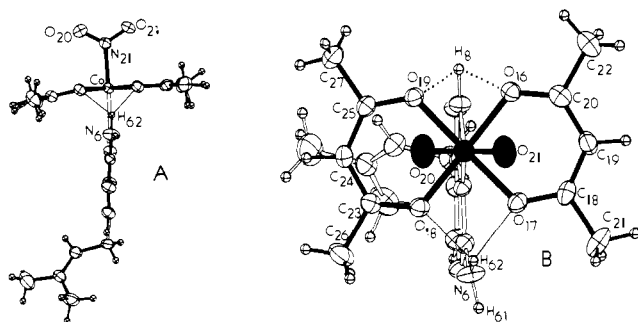


Figure 2. Two projection views of the bis(acetylacetonato)(nitro)(triacanthine) cobalt(III) complex. (A) A view parallel to the purine ring system and approximately perpendicular to the plane of the nitro ligand. (B) A view parallel to the N(21)(nitro)-Co(III) bond.

coordination on the molecular parameters is usually small, they give some indication of the rearrangement of the electron density in the ring system owing to coordination. We know of only two accurate determination of N(3)-substituted purines, that of 3-ethyladenine³⁰ and triacanthine itself.³¹ Comparing the differences in the coordinated triacanthine to those in free triacanthine and 3-ethyladenine leads to the following conclusions. There is a significant shortening of the N(9)-C(8) bond in the imidazole ring owing to coordination, but the major bond length and bond angle adjustments lie in the pyrimidine ring. The exocyclic bond length C(6)-N(6) is rather dramatically shortened from 1.330 (3) Å in 3-ethyladenine³⁰ and 1.327 (3) Å in free triacanthine³¹ to 1.308 (6) Å in coordinated triacanthine. This bond shortening is accompanied by elongation in the adjacent C(4)-C(5) and C(5)-C(6) bonds and leads to the conclusion that there is a significant flow of electron density into the C(6)-N(6) bond which may also be stimulated by the formation of the interligand hydrogen bond system at N(6). There are also some significant bond angle adjustments in the pyrimidine ring which are consistent with the bond length changes noted above.

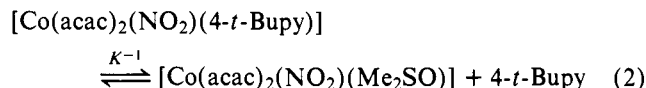
The major features of the crystal packing in the triacanthine complex are illustrated in Figure 3. Besides being involved in the interligand hydrogen bond system, the exocyclic amino group also forms a strong hydrogen bond to the water of crystallization. The water of crystallization also denotes two strong hydrogen bonds—one to the imidazole nitrogen N(9) of triacanthine and one to the carbonyl oxygen of the DMF of crystallization. The parameters in these intermolecular hydrogen bonds are tabulated in Table III.

The disordered DMF has no significant contacts besides the hydrogen bonding to the water molecule. The lack of significant interaction for the $-N(CH_3)_2$ portion of the molecule is consistent with the observed disorder.

Formation Constants for the 3-Alkylated 6-Aminopurine

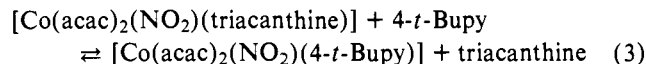
Complexes in Me₂SO. As we have noted above, the formation constant for [Co(acac)₂(NO₂)(triacanthine)] is too large to measure directly in Me₂SO at accessible concentrations. We have, therefore, taken an indirect route, via the 4-*tert*-butylpyridine complex, to obtain an approximate value.

The 4-*tert*-butylpyridine complex yields a measurable equilibrium mixture of the base and solvato complexes in Me₂SO according to



We obtained a value for K from the areas of the methyl resonances of the acac groups of the base and solvato complexes and the ratio of the areas of the butyl resonances for free and coordinated 4-*t*-Bupy. Experiments at two concentrations (0.02 and 0.04 M) gave a value for K of 2800 M⁻¹.

Furthermore, in Me₂SO an equilibrium can be established between 4-*t*-Bupy and the triacanthine complex according to



From the relative areas of the acac methyl resonances of each of the complexes, we were able to establish that the formation constant for the triacanthine complex is about 2.8 times that of the 4-*t*-Bupy complex. This result coupled with the measured formation constant of the 4-*t*-Bupy complex gives a value of $K = 7.8 \times 10^3$ M⁻¹ for the triacanthine complex. Likewise, values of 7.9×10^3 and 6.5×10^3 M⁻¹ were obtained for the 3-methyladenine and 3-benzyladenine complexes, respectively.

The estimated formation constants for these complexes are extremely large compared to any other purine or pyrimidine ligand we have measured with this system.⁹ For example, it is ~25 times larger than the K for purine, where N(9) is probably the principal coordination site, 60 times that of 9-methyladenine—which has the largest value of any 9-substituted purine and where N(7) is the principal coordination site—and about 100 times that of the deoxyadenosine complex, which as we have noted above, has essentially the same conformational parameters.

Clearly, 3-alkylated 6-aminopurines are exceptionally good ligands toward the [Co(acac)₂(NO₂)] moiety. As indicated above, the high stability of these complexes probably has its antecedent in the favorable electronic structure of the purine ring system.

¹H NMR Results. We have been able to obtain ¹H NMR spectra for both free triacanthine and [Co(acac)₂(NO₂)(triacanthine)] in Me₂SO-*d*₆. Chemical shift data for all resonances are contained in Table VI, where similar data for 3-

Table IV. Nonhydrogen Atom Bond Lengths (Å) and Angles (deg)

A. Primary Coordination Sphere			
Bond Lengths			
Co-O(16)	1.884 (3)	Co-O(19)	1.879 (3)
Co-O(17)	1.892 (3)	Co-N(7)	2.003 (4)
Co-O(18)	1.873 (3)	Co-N(21)	1.915 (4)
Bond Angles			
N(7)-Co-O(16)	90.2 (1)	N(21)-Co-O(17)	90.4 (2)
N(7)-Co-O(17)	91.0 (1)	N(21)-Co-O(18)	89.0 (2)
N(7)-Co-O(18)	89.9 (1)	N(21)-Co-O(19)	89.7 (2)
N(7)-Co-O(19)	88.9 (1)	O(16)-Co-O(17)	96.0 (1)
N(7)-Co-N(21)	178.2 (2)	O(16)-Co-O(18)	179.4 (1)
N(21)-Co-O(16)	90.8 (2)	O(16)-Co-O(19)	83.5 (1)
O(18)-Co-O(19)	95.9 (1)	O(17)-Co-O(19)	179.4 (1)
		O(17)-Co-O(18)	84.7 (1)
B. Acetylacetonato Ligands			
Bond Lengths			
O(16)-C(20)	1.277 (6)	O(18)-C(23)	1.276 (6)
C(20)-C(19)	1.376 (7)	C(23)-C(24)	1.373 (7)
C(20)-C(22)	1.499 (7)	C(23)-C(26)	1.486 (7)
C(19)-C(18)	1.387 (7)	C(24)-C(25)	1.393 (7)
C(18)-O(17)	1.285 (6)	C(25)-O(19)	1.265 (5)
C(18)-C(21)	1.497 (7)	C(25)-C(27)	1.500 (7)
Bond Angles			
Co-O(16)-C(20)	124.0 (3)	Co-O(18)-C(23)	124.2 (3)
O(16)-C(20)-C(19)	125.9 (5)	O(18)-C(23)-C(24)	124.6 (4)
O(16)-C(20)-C(22)	114.8 (4)	O(18)-C(23)-C(26)	114.9 (4)
C(19)-C(20)-C(22)	119.3 (5)	C(24)-C(23)-C(26)	120.5 (4)
C(20)-C(19)-C(18)	125.1 (5)	C(23)-C(24)-C(25)	125.3 (5)
C(19)-C(18)-O(17)	124.8 (4)	C(24)-C(25)-O(19)	125.0 (4)
C(19)-C(18)-C(21)	122.2 (5)	C(24)-C(25)-C(27)	120.3 (4)
O(17)-C(18)-C(21)	113.0 (4)	O(19)-C(25)-C(27)	114.7 (4)
Co-O(17)-C(18)	124.2 (3)	Co-O(19)-C(25)	123.8 (3)
O(17)-C(18)-C(21)	113.0 (4)	O(18)-C(23)-C(26)	114.9 (4)
C(19)-C(18)-C(21)	122.2 (5)	C(24)-C(23)-C(26)	120.5 (4)
C(19)-C(20)-C(22)	119.3 (5)	C(24)-C(25)-C(27)	120.3 (4)
O(16)-C(20)-C(22)	114.8 (4)	O(19)-C(25)-C(27)	114.7 (4)
C. Nitro Ligand			
Bond Lengths			
N(21)-O(20)	1.218 (5)	N(21)-O(21)	1.216 (5)
Bond Angles			
Co-N(21)-O(20)	120.1 (3)	O(20)-N(21)-O(21)	120.1 (4)
Co-N(21)-O(21)	119.8 (3)		
D. Triacanthine Ligand			
Bond Lengths			
N(7)-C(5)	1.379 (6)	N(3)-C(40)	1.467 (6)
N(7)-C(8)	1.336 (6)	N(6)-C(6)	1.308 (6)
N(9)-C(4)	1.335 (6)	C(4)-C(5)	1.398 (6)
N(9)-C(8)	1.346 (6)	C(5)-C(6)	1.420 (6)
N(1)-C(2)	1.317 (6)	C(40)-C(41)	1.501 (7)
N(1)-C(6)	1.372 (6)	C(41)-C(42)	1.320 (7)
N(3)-C(4)	1.376 (6)	C(42)-C(43)	1.467 (8)
N(3)-C(2)	1.344 (6)	C(42)-C(44)	1.491 (8)
Bond Angles			
Co-N(7)-C(5)	135.2 (3)	N(7)-C(5)-C(4)	106.4 (4)
Co-N(7)-C(8)	121.6 (3)	N(7)-C(5)-C(6)	135.2 (4)
C(5)-N(7)-C(8)	103.0 (4)	C(4)-C(5)-C(6)	118.4 (4)
C(4)-N(9)-C(8)	101.5 (4)	N(6)-C(6)-N(1)	116.2 (4)
C(2)-N(1)-C(6)	119.5 (4)	N(7)-C(8)-N(9)	117.2 (4)
C(2)-N(3)-C(4)	115.9 (4)	N(1)-C(6)-C(5)	118.2 (4)
C(2)-N(3)-C(40)	122.7 (4)	N(6)-C(6)-C(5)	125.6 (4)
C(4)-N(3)-C(40)	121.3 (4)	N(3)-C(40)-C(41)	111.4 (4)
N(1)-C(2)-N(3)	126.5 (4)	C(40)-C(41)-C(42)	125.8 (5)
N(9)-C(4)-N(3)	126.6 (4)	C(41)-C(42)-C(43)	125.1 (5)
N(9)-C(4)-C(5)	112.0 (4)	C(41)-C(42)-C(44)	120.2 (5)
N(3)-C(4)-C(5)	121.5 (4)	C(43)-C(42)-C(44)	114.7 (5)

methyl- and 3-benzyladenine and reference data for free adenine are also included.

Two very interesting features emerge from these spectra.

First, the NH₂ resonance in the free triacanthine and the other 3-alkylated adenines is a broad singlet as is typically found for amino resonances which normally undergo free rotation on the

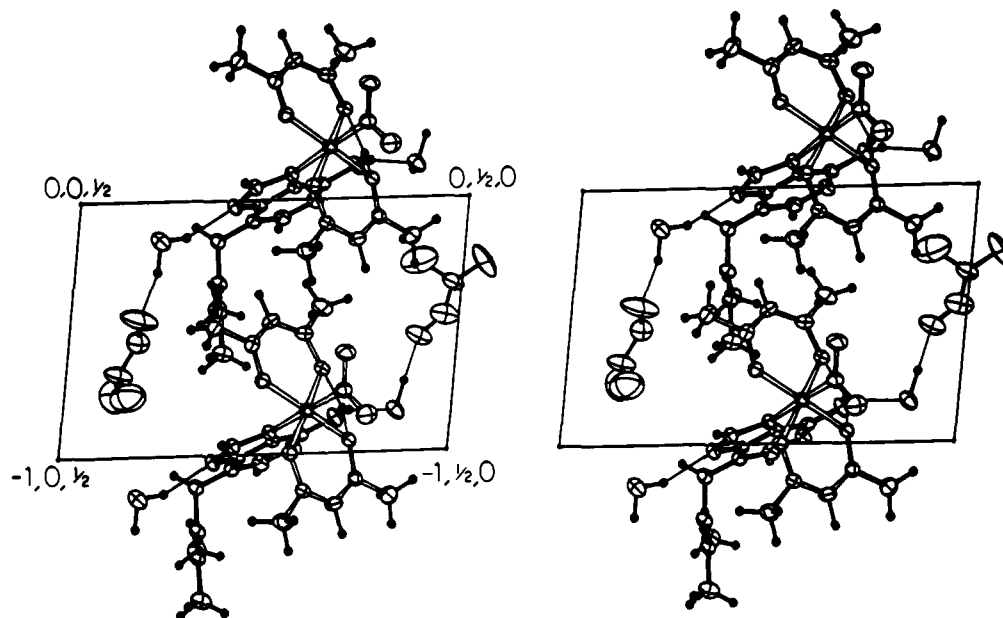


Figure 3. A stereoview of the unit cell packing interactions. Hydrogen bonds are indicated by thin lines. Only one of the disordered orientations (60% population) of the dimethylformamide of solvation is shown (see the text).

Table V. Least-Squares Planes and the Deviation of Individual Atoms from These Planes^f

A. The Equatorial Plane Including the Co (0.4614X - 0.3026Y - 0.8340Z = -2.6317A)			
Co	-0.000	O(17)	-0.002
O(16)	0.002	O(18)	0.002
		O(19)	-0.002
B. The Acetylacetonato Ligands			
(1) (0.4783X - 0.3041Y - 0.8239Z = -2.5642A)			
O(16)	0.002	C(19)	-0.007
O(17)	-0.005	C(20)	0.002
C(18)	0.009	C(21)	0.023*
		C(22)	-0.006*
(2) (0.3009X - 0.2969Y - 0.9063Z = -2.7559A)			
O(18)	-0.005	C(24)	-0.014
O(19)	-0.003	C(25)	0.010
C(23)	0.012	C(26)	0.088*
		C(27)	0.062*
C. Triacanthine Ligand (-0.8340X - 0.0140Y - 0.5516Z = -2.5333A)			
N(1)	0.017	C(5)	-0.003
N(3)	-0.019	C(6)	-0.013
N(7)	-0.004	C(8)	0.009
N(9)	0.006	N(6)	-0.058*
C(2)	0.008	C(40)	-0.007*
C(4)	0.000	Co	0.122*

^f In each of the equations of the planes, X, Y, and Z are coordinates (A) referred to the orthogonal axes: X along a, Y in the ab plane, and Z along c*. Atoms designated by an asterisk were given zero weight in calculating the planes; the atoms used to define the plane were equally weighted.

NMR time scale. However, two NH resonances are observed for coordinated ligands (Figure 4). One of these resonances occurs at approximately the same shift as the amino resonance of the uncoordinated ligand. The other resonance occurs considerably downfield (~0.8 ppm). This observation is entirely consistent with the hydrogen bonding observed in the solid state for the triacanthine complex. The amino H involved in the H-bond formation is expected to shift downfield as is

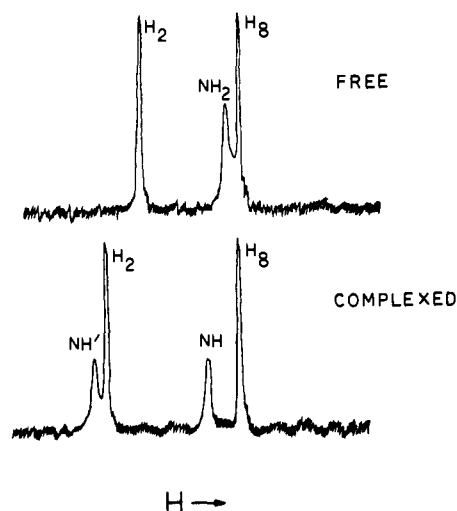


Figure 4. ¹H NMR traces for a portion of the spectra of free triacanthine and [Co(acac)₂(NO₂)(triacanthine)]. The spectra were recorded on a 100-MHz spectrometer at 33 °C in Me₂SO-d₆.

generally observed for H-bond formation.³² The other amino hydrogen can still interact with the solvent and is shifted only a small amount. The rate of rotation of the amino group is thereby hindered on coordination and this effect is unlikely to have been caused by electronic perturbations. This observation is very important because it represents the first conclusive evidence that the interligand hydrogen bonding, which appears to be so widely observed for purine and pyrimidine complexes in the solid^{2,4,25} and which has been suggested previously to explain results in solution,^{3,4,9} persists in solution.

A second interesting observation is that upon coordination the H(2) resonance shifts to a greater extent than the H(8) resonance, even though coordination is at N(7) and the opposite behavior would normally be predicted.³ Furthermore, for the structurally analogous deoxyadenosine complex, it is the H(8) resonance which is shifted most.⁹ Since initially there was no reason to expect such a difference, we reexamined the assignment¹⁰ of the chemical shift for the H(2) and H(8)

Table VI. ¹H NMR Chemical Shift Data in Me₂SO-*d*₆ (δ ppm)

	H(2)	H(8)	NH ₂	acac	R group
				Triacanthine	
F ^a	8.30 ^b	7.75	7.82		1.61, 1.74 CH ₃ 's; 4.90 CH ₂ ; 5.47 CH
C ^a	8.55	7.79	7.97, 8.63	1.96, 5.36	1.70, 1.81 CH ₃ 's; 4.90 CH ₂ ; 5.51 CH
				3-Benzyladenine ^d	
F	8.53 ^{b,c}	7.75 ^c	7.90		~7.3 C ₆ H ₅ ; 5.51 CH ₂
C	8.82	7.82	8.04, 8.72	1.98, 5.40	~7.5 C ₆ H ₅ ; 5.57 CH ₂
				3-Methyladenine	
F	8.25 ^{b,c}	7.73 ^c	~7.76		3.86 CH ₃
C	8.47	7.77	7.94, 8.51	1.97, 5.36	3.89 CH ₃
				Adenine ^d	
F	8.18	8.15 ^c	7.03 ^e		

^a F = free, C = coordinated. ^b Confirmed by exchange with D₂O. ^c Confirmed with adenine-*d*₈ as the starting material. ^d Results in agreement with ref 10. ^e B. M. Lynch, B. C. MacDonald, and J. K. Webb, *Tetrahedron*, **24**, 3595 (1968).

resonances of 3-benzyladenine by preparing it from adenine-*d*₈. Likewise we prepared 3-methyladenine-*d*₈. Heating solutions of these two 3-alkylated adenines (undeuterated) in D₂O caused the disappearance of the H(2) resonance in agreement with suggestions in the literature.¹¹ Heating a solution of triacanthine caused the downfield resonance to disappear and we believe that there is no doubt that the downfield resonance in triacanthine is H(2). It is generally believed that assignment of coordination sites by differences in shifts is a risky procedure. We have now shown that this method would have led to an *incorrect* assignment as to the binding site. Further work is necessary, however, to establish whether or not this unusual shift pattern might be restricted either to 3-alkyladenine, to 3-alkylated purines, or to cobalt(III) complexes.

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Supplementary Material Available: Listings of final calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

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