Table VIII. Rigid Group Angular Parameters

Compd	ϕ, deg	α, deg	θ, deg
$(C_6H_5)_4Sn^{a,f}$	7.1	56.5	109.1
$(C_6H_5)_4Sn^{b,f}$	7.7	58.6	110.8
$(C_6F_5)_4Sn^{c,g}$	41.9	53.2	105.5
$(C_6H_5)_4Ge^{d,f}$	7.2	54.2	109.0
$(C_6F_5)_4Ge^{e,g}$	42.0	51.9	105.0

[a] See ref 5. [b] See ref 6. [c] This work. [d] See ref 2. [e] See ref 3; the value of α is incorrectly given in ref 8. [f] Space group $P\bar{4}2_1c$. [g] Space group $I4_1/a$.

IVa tetraphenyl compounds. In tetra(*p*-tolyl)tin[33,34] and tetra(*p*-methoxyphenyl)tin[35] the space group is $I\bar{4}$ and in each case the molecular symmetry is $\bar{4}$. On the other hand, in the pentafluorophenyl structures the tin and germanium atoms retain $\bar{4}$ symmetry in the crystal, but the space group is the centrosymmetric $I4_1/a$. In this space group close packing of molecules is not favored because adjacent molecules are related by mirror planes.[10] It is apparent that close packing is not a sufficient criterion for the retention of the highest molecular symmetry ($\bar{4}$) possible in the solid state.

The shortest intermolecular F· · ·F and F· · ·C nonbonded distances in $(C_6F_5)_4Sn$ are F(4)· · ·F(4)($\bar{y}$, $-^1/_2 + x$, $^1/_4 + z$), 2.919 Å, and F(3)· · ·C(3)($\bar{y}$, $-^1/_2 + x$, $^1/_4 + z$), 3.123 Å. For $(C_6F_5)_4Ge$ the corresponding distances are 2.943 and 3.089 Å for the same atom–atom contacts. The shortest intramolecular nonbonded distances are 3.018 Å in $(C_6F_5)_4Sn$ and 2.899 Å in $(C_6F_5)_4Ge$ for the F(2)· · ·F(6)(y, $\bar{x}$,$\bar{z}$) contact. From these distances a value of 1.46 Å is obtained for the van der Waals radius of fluorine which is consistent with that tabulated (1.47 Å) by Bondi.[36] The use of 1.46 Å for the fluorine van der Waals radius and the above C· · ·F contact distances leads to a van der Waals radius of 1.65 Å for carbon. This is about 0.1 Å less than the values given by Bondi[36] for an aromatic carbon.

Acknowledgment. Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. $(C_6F_5)_4Sn$, 1065-49-2; $(C_6F_5)_4Ge$, 1452-12-6.

Supplementary Material Available. A listing of structure factor amplitudes (Tables I and II) 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 $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-811.

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Synthesis and Molecular Structure of Bis(6-mercapto-9-benzylpurine)palladium(II)-Dimethylacetamide

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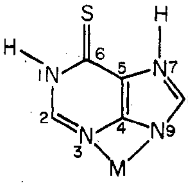
Received August 24, 1973

The compound bis(6-mercapto-9-benzylpurine)palladium(II)-dimethylacetamide, $C_{28}H_{27}N_9OS_2Pd$, was synthesized by allowing palladium(II) chloride to react with 6-mercapto-9-benzylpurine in dimethylacetamide, followed by the diffusion of 1-propanol vapors into the reaction solution. The crystals formed are monoclinic and belong to the space group $C2/c$ with eight molecules per unit cell of dimensions $a = 24.80$ (1) Å, $b = 11.95$ (1) Å, $c = 22.03$ (1) Å, and $\beta = 114.73$ (5)°. The structure was solved by conventional heavy-atom methods using data collected on an automated four-circle diffractometer. The structure was refined on F to $R_1 = 0.076$ and $R_2 = 0.069$. The two phenyl groups were refined as rigid bodies. Both purine ligands are coordinated to palladium through the sulfur and N(7) atoms to form a five-membered chelate ring. The coordination geometry is a slightly distorted square with angles S1-Pd-S2 = 85.8 (1)° and N7A-Pd-N7B = 98.3 (4)°. The dimethylacetamide molecule is not coordinated. The presence of the metal atom does not influence the general tendency for purine rings to stack in a solid lattice, and stacking of this kind is a major intermolecular feature of the structure.

Introduction

6-Mercaptopurine was first synthesized by Hitchings[2] as a purine antimetabolite, with possible carcinostatic activity. A number of transition metal complexes[3] of this compound have been investigated as possible antitumor agents.[4] The reported complexes are amorphous, hydrated materials and are insoluble in organic solvents. The chief means of characterization of these complexes has been chemical analysis.

Grinberg[3b] proposed two types of metal attachment to the 6-mercaptopurine anion in these complexes. In the first type of attachment, the metal forms a four-membered chelate ring with atoms N3 and N9 (see **1**). Coordination



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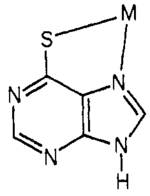
through these ring atoms has been observed in several crystal structures of metal complexes of unsubstituted purines.[5] In the second type of attachment, the metal atom forms a five-membered chelate ring by bonding to the sulfur and N7 atoms (see **2**). This type of structure was proposed for several platinum and palladium[3b] complexes of 6-mercaptopurine.



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No X-ray structural studies of 6-mercaptopurine-metal complexes have been reported, until the present work. The crystal structure of a copper complex of 9-methylhypoxanthine, an oxygen analog of 6-mercaptopurine, has been determined,[6] however, in which the copper atom is attached only to the N7 atom. The absence of chelate ring formation was explained on geometric grounds.[6] The angle θ of a hypothetical chelate (shown in Figure 1) was calculated to be *ca.* 90°, while the maximum overlap of metal orbitals with the sp^2 orbitals of N7 would occur when this angle was ~135°. Because of the poor overlap with N7 this hypothetical structure was assumed to be energetically less favorable than the observed structure where the angle θ is 135°.

Recently a number of experiments have been carried out on complexation of *p*-hydroxymercuribenzoate, mercuric chloride, and related mercurials with 6- and 8-thioguanosine[7,8] (Figure 2). Both of these compounds show a stronger affinity for mercury than non-sulfur-containing nucleosides, thus confirming an earlier comparison of 6-mercaptopurine with hypoxanthine.[9] The observed formation constants were higher for 6-thioguanosine compared to 8-thioguanosine. One explanation for this difference is the formation of a five-membered chelate ring by 6-thioguanosine while the 8-thio compound could only form a less stable, four-membered chelate.[10] To test the hypothesis of a stable, five-membered chelate, a direct structural study of a 6-mercaptopurine-metal complex was undertaken. To simulate a riboside, N9 was blocked by a benzyl substituent. A preliminary account of this work has been given.[7]

Experimental Section

Palladium chloride, potassium tetrachloroplatinate, and dimethylacetamide (Spectrograde) were used without further purification. 6-Mercapto-9-benzylpurine was synthesized by the method of Montgomery and Temple[11] from commercially available 4,6-dichloro-5-aminopyrimidine (Sigma) and identified by its pmr spectrum. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

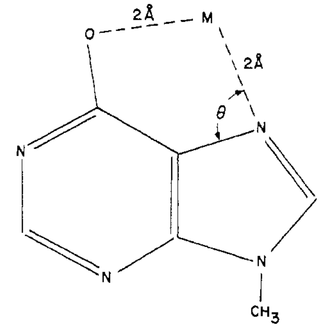

Figure 1. Hypothetical metal chelate of 9-methylhypoxanthine.

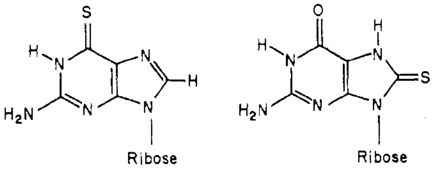

Figure 2. (Left) 6-thioguanosine. (Right) 8-thioguanosine.

Bis(6-mercapto-9-benzylpurine)palladium(II)-Dimethylacetamide. Palladium chloride (0.069 g, 0.40 mmol) and 6-mercapto-9-benzylpurine (0.194 g, 0.80 mmol) were refluxed for 20 min in 5 ml of dimethylacetamide. The red solution was filtered into a clean vial which was placed in a desiccator containing 1-propanol. After 3 days 0.117 g (43%) of orange crystals was filtered off and washed with 1-propanol and ether. *Anal.* Calcd for $C_{28}H_{27}N_9OS_2Pd$: C, 49.7; H, 4.03; N, 18.7; S, 9.49. Found: C, 50.2; H, 4.27; N, 18.7; S, 10.06.

Bis(6-mercapto-9-benzylpurine)platinum(II)-Dimethylacetamide. This complex was synthesized in the same manner from K_2PtCl_4 in 25% yield. *Anal.* Calcd for $C_{28}H_{27}N_9OS_2Pt$: C, 43.9; H, 3.56; N, 16.49; S, 8.39. Found: C, 43.8; H, 3.67; N, 16.28; S, 9.00.

Collection and Reduction of the X-Ray Data. Preliminary Weissenberg photographs using Cu Kα (λ 1.5418 Å) radiation showed the crystal to have Laue symmetry $2/m$ with systematic absences hkl, $h + k \neq 2n$, and $h0l$, $l \neq 2n$, indicating the space group as either C/c or $C2/c$ (No. 9 or No. 15).[12] Space group $C2/c$ was assumed and appears to be justified by the successful refinement. Oscillation and zero- and first-level Weissenberg photographs of the platinum complex showed it to be isomorphous with the palladium derivative.

For data collection a roughly rectangular prism with dimensions 0.066 mm × 0.13 mm × 0.40 mm, obtained by breaking a larger crystal, was mounted on a glass fiber along its longest dimension which corresponded to b^*. The crystal was placed on a Picker four-circle automated diffractometer. The mosaic spread was measured by ω scans of several strong reflections with an open counter. The maximum width at half-height was 0.15°.

The cell constants obtained from film data permitted reflections to be centered in the counter window using Zr-filtered Mo Kα (λ 0.71069 Å) radiation. The setting angles χ, ϕ, and 2θ were refined by NUMODE[13] to give $a = 24.80$ (1) Å, $b = 11.95$ (1) Å, $c = 22.03$ (1) Å, and $\beta = 114.73$ (5)°. The calculated density of 1.515 g/cm^3 for $Z = 8$ is in good agreement with the observed value of 1.51 ± 0.02 g/cm^3, obtained by flotation in aqueous KI.

More than 2950 reflections for which $2\theta < 40°$ were taken at *ca.* 23° over a period of about 1 week. The (225), (91$\bar{3}$), (22$\bar{3}$), and (020) reflections were used as standards. The standards varied about ±3% from their mean values. A slight (~1%) decline in intensity was noted over the course of the run. Because of the irregularity in radiation exposure time between standards caused by mechanical problems, fitting of the standards to a linear correction function was not attempted.

The data were collected by scanning 2θ symmetrically about the Bragg angle. The scan angle was 1.25° plus a correction for the Kα_1-Kα_2 separation. The scan rate was 1°/min. The takeoff angle was

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Table I. Final Atomic Positional and Thermal Parameters of Bis(6-mercapto-9-benzylpurine)palladium(II)–Dimethylacetamide

Atom[a]	x[b]	y	z	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0.20951 (4)	0.13792 (8)	0.05268 (5)	1.93 (2)	7.54 (8)	2.07 (3)	0.95 (5)	0.93 (2)	0.33 (5)
S1	0.1190 (1)	0.1492 (3)	0.0584 (2)	2.20 (9)	10.1 (3)	2.7 (1)	0.8 (1)	1.51 (8)	−0.1 (2)
S2	0.2467 (1)	0.2339 (3)	0.1529 (2)	2.5 (1)	10.7 (4)	2.6 (1)	0.7 (1)	1.35 (9)	−0.9 (2)
C6A	0.0779 (6)	0.092 (1)	−0.0188 (6)	1.7 (3)	8 (1)	3.9 (5)	0.8 (5)	1.1 (3)	0.1 (6)
C6B	0.3196 (6)	0.234 (1)	0.1643 (7)	2.3 (4)	8 (1)	3.0 (4)	−0.3 (6)	0.9 (4)	0.5 (6)
N1A	0.0183 (5)	0.0855 (9)	−0.0474 (6)	2.7 (4)	10 (1)	3.7 (4)	0.0 (5)	1.6 (3)	−1.3 (6)
N1B	0.3643 (6)	0.2780 (8)	0.2174 (5)	2.2 (3)	10 (1)	2.7 (4)	0.1 (5)	0.9 (3)	−0.5 (5)
C2A	−0.0073 (5)	0.039 (1)	−0.1087 (8)	1.9 (4)	11 (1)	4.5 (6)	0.5 (6)	1.4 (4)	−0.2 (8)
C2B	0.4201 (7)	0.272 (1)	0.2188 (7)	3.3 (5)	11 (1)	2.7 (5)	−1.2 (7)	0.0 (4)	0.1 (7)
N3A	0.0172 (5)	−0.0025 (9)	−0.1491 (5)	1.5 (3)	11 (1)	3.1 (4)	0.1 (5)	0.5 (3)	−0.9 (5)
N3B	0.4363 (5)	0.2279 (9)	0.1722 (6)	3.3 (4)	8 (1)	3.0 (4)	−0.3 (5)	1.5 (4)	−0.6 (6)
C4A	0.0763 (6)	0.008 (1)	−0.1188 (7)	2.3 (4)	7 (1)	3.2 (5)	0.8 (6)	1.4 (4)	0.1 (6)
C4B	0.3891 (7)	0.184 (1)	0.1212 (7)	3.0 (5)	6 (1)	2.0 (5)	0.1 (6)	0.8 (4)	0.5 (6)
C5A	0.1068 (6)	0.054 (1)	−0.0559 (6)	1.9 (4)	7 (1)	2.3 (4)	1.6 (5)	1.1 (4)	0.4 (6)
C5B	0.3316 (6)	0.187 (1)	0.1146 (7)	1.8 (4)	7 (1)	2.9 (5)	0.2 (5)	1.3 (4)	0.0 (6)
N7A	0.1667 (4)	0.0568 (8)	−0.0388 (5)	1.7 (3)	7.2 (9)	2.6 (4)	0.7 (4)	1.1 (3)	0.4 (5)
N7B	0.2938 (4)	0.1369 (8)	0.0575 (5)	2.3 (3)	6.2 (8)	2.0 (3)	−0.7 (4)	1.1 (3)	−1.2 (5)
C8A	0.1737 (6)	0.014 (1)	−0.0912 (7)	2.2 (4)	11 (1)	2.4 (4)	0.3 (6)	0.8 (4)	0.0 (6)
C8B	0.3288 (6)	0.1082 (9)	0.0276 (6)	2.3 (4)	7 (1)	2.6 (4)	−0.2 (5)	0.8 (4)	−0.1 (5)
N9A	0.1199 (6)	−0.0167 (8)	−0.1399 (5)	2.8 (3)	7 (1)	2.6 (4)	1.1 (5)	1.0 (3)	0.1 (5)
N9B	0.3866 (5)	0.1334 (9)	0.0641 (5)	2.1 (3)	9.9 (1)	2.4 (3)	0.8 (5)	1.1 (3)	0.7 (6)
CMA	0.1102 (6)	−0.069 (1)	−0.2049 (7)	2.5 (4)	13 (1)	2.7 (5)	0.5 (7)	1.1 (3)	−1.3 (7)
CMB	0.4368 (6)	0.106 (1)	0.0453 (7)	2.3 (4)	12 (2)	3.2 (5)	0.6 (6)	1.3 (4)	0.5 (7)
CO	0.3173 (8)	0.141 (2)	0.391 (1)	2.3 (5)	19 (3)	8 (1)	−2 (1)	−0.5 (5)	8 (2)
CC	0.3365 (8)	0.091 (1)	0.3338 (8)	7.1 (7)	24 (3)	4.8 (6)	1 (1)	4.4 (6)	−2 (1)
OO	0.2937 (4)	0.0719 (9)	0.4167 (5)	3.4 (3)	15 (1)	5.6 (4)	−0.5 (5)	1.3 (3)	3.6 (6)
NN	0.3314 (6)	0.234 (2)	0.4067 (9)	2.8 (4)	19 (2)	6.5 (7)	−2.2 (8)	−0.5 (4)	4 (1)
CN1	0.3132 (7)	0.276 (1)	0.4648 (7)	6.3 (7)	23 (2)	3.1 (5)	3 (1)	2.8 (6)	−0.5 (9)
CN2	0.3603 (7)	0.316 (1)	0.3805 (8)	5.8 (6)	13 (2)	7.1 (8)	−4.1 (8)	2.6 (5)	3.6 (9)

Hydrogen Atoms

Atom	x	y	z	Atom	x	y	z
H2A	−0.053 (5)	0.02 (1)	−0.134 (6)	HMA1	0.071 (6)	−0.06 (1)	−0.226 (7)
H2B	0.448 (6)	0.29 (1)	0.254 (6)	HMA2	0.133 (6)	−0.03 (1)	−0.223 (7)
H8A	0.216 (5)	0.01 (1)	−0.088 (6)	HMB1	0.404 (5)	0.11 (1)	−0.012 (6)
H8B	0.317 (6)	0.07 (1)	−0.008 (7)	HMB2	0.459 (6)	0.16 (1)	0.061 (7)

[a] See Figure 3 for atom labeling. Hydrogen labels denote carbon atoms to which they are attached. [b] Values in parentheses represent the standard deviations in last significant figure. [c] The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$. Hydrogens were assigned a fixed isotropic temperature factor of 6.0. Values are × 10^3.

2.0°. Ten second background counts were taken at both ends of the scan range. The symmetrically varying receiving aperture was set at 4 mm × 4 mm at a distance of 22 cm from the crystal. The peaks were monitored on a chart recorder, and no sign of peak overlaps was noted.

The raw data were corrected for background, Lorentz, and polarization factors by ACAC. The background correction is computed as

$$I_{\text{cor}} = E - (T_{\text{E}}/2T_{\text{B}})(B_1 + B_2)$$

where E is observed count for time T_{E}, and B_1 and B_2 are background counts at either end of scan taken for time T_{B}. Because of the low linear absorption coefficient (8.05 cm^{-1}) no absorption correction was made. A test calculation showed the transmission factors ranged from 0.89 to 0.95. The output of ACAC contains F^2 and $\sigma(F^2)$, computed according to the formulas

$$F^2 = (Lp)^{-1}(I_{\text{cor}})$$

$$\sigma(F^2) = (Lp)^{-1}[E + 0.25(T_{\text{E}}/T_{\text{B}})^2(B_1 + B_2) + \epsilon^2 I^2_{\text{cor}}]^{1/2}$$

where Lp is Lorentz-polarization factor and ϵ is the so-called "ignorance" factor[14] designed to prevent overweighting of strong reflections, set equal to 0.04.

Prior to scaling the corrected data, the values of F^2 for the equivalent $0kl$ and $0k\bar{l}$ reflections were averaged and the results assigned to the $0kl$ reflections. The values $\sigma_1 = {}^1/_2\,|F^2{}_{0kl} - F^2{}_{0k\bar{l}}|$ and $\sigma_2 = {}^1/_2[\sigma(F^2{}_{0kl}) + \sigma(F^2{}_{0k\bar{l}})]$ were computed and $\sigma(F^2)$ for the $0kl$ reflections were taken as the greater of the two values. As a general test of the data quality, the R factor for the averaging of the equivalent reflections

$$R = \Sigma|F^2{}_{0kl} - F^2{}_{0k\bar{l}}|/{}^1/_2\Sigma(F^2{}_{0kl} + F^2{}_{0k\bar{l}})$$

was computed and found to be equal to 0.064.

The corrected values of F^2 were placed on an approximate absolute scale using a modification of Wilson's method[15] by the program XDATA.

Solution and Refinement of the Structure. The structure was solved by conventional heavy-atom methods. The assignment of the atoms of the dimethylacetamide molecule was checked by test refinements of alternative assignments and by comparison of the thermal parameters when carbon scattering factors were used for all six atoms. For the final refinement the two phenyl groups were refined as rigid bodies. The function $\Sigma w(|F_{\text{o}}| - |F_{\text{c}}|)^2$ was minimized and the residuals were defined as

$$R_1 = \Sigma||F_{\text{o}}| - |F_{\text{c}}||/\Sigma|F_{\text{o}}|$$

$$R_2 = [\Sigma w(|F_{\text{o}}| - |F_{\text{c}}|)^2/\Sigma wF_{\text{o}}{}^2]^{1/2}$$

where w is the weight assigned to each reflection in the refinement, equal to $\sigma^{-2}(F)$ with $\sigma(F) = \sigma(F^2)/2F$. Scattering factors (for neutral atoms) were those of Hanson,[16] *et al.* Correction was made for the anomalous scattering of palladium using the values of Cromer and Liberman.[17] Hydrogen atoms, located on a difference Fourier map, were assigned an isotropic temperature factor of 6.0 and only the positional parameters were refined. Only the four purine hydrogens and the four methylene hydrogens were included in the final refinement. A test refinement showed the inclusion of the fixed phenyl hydrogens to have no significant effect. Using 2216 reflections where $F^2 > \sigma(F^2)$ the structure was refined to final values of R_1 and R_2 of 0.076 and 0.063, respectively.[18]

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(18) See paragraph at end of paper regarding supplementary material.

Table II. Final Phenyl Group Parameters

Group Parameters

Group	X_c[a,b]	Y_c	Z_c	ϕ[c]	θ	ρ
A	0.1589 (2)	−0.2970 (4)	−0.1884 (2)	−1.093 (9)	2.120 (5)	3.036 (9)
B	−0.0059 (2)	0.3952 (5)	0.1025 (3)	2.373 (9)	2.188 (5)	−0.394 (8)

Group Atom Parameters[d]

Atom	x	y	z	B, Å^2
CA1	0.1356 (7)	−0.1893 (7)	−0.1959 (6)	4.3 (3)
CA2	0.1225 (4)	−0.2673 (8)	−0.1572 (4)	4.9 (3)
CA3	0.1458 (5)	−0.3750 (5)	−0.1497 (5)	5.9 (3)
CA4	0.1823 (7)	−0.4047 (7)	−0.1809 (6)	6.5 (3)
CA5	0.1954 (4)	−0.3266 (8)	−0.2197 (4)	6.4 (3)
CA6	0.1721 (5)	−0.2189 (6)	−0.2272 (4)	4.6 (3)
CB1	−0.0335 (7)	0.4962 (7)	0.0755 (4)	4.5 (3)
CB2	0.0018 (5)	0.4877 (6)	0.1437 (4)	6.6 (3)
CB3	0.0294 (4)	0.3867 (9)	0.1707 (3)	7.2 (3)
CB4	0.0217 (7)	0.2943 (7)	0.1295 (4)	6.9 (3)
CB5	−0.0136 (5)	0.3028 (5)	0.0612 (4)	5.7 (3)
CB6	−0.0412 (3)	0.4038 (8)	0.0342 (3)	5.1 (3)

[a] X, Y, and Z are fractional coordinates of ring centers. [b] Values in parentheses represent standard deviation in last significant figure. The atom labels are identified in Figure 3. [c] ϕ, θ, and ρ (in radians) were defined by J. A. Ibers and R. Eisenberg, *Inorg. Chem.*, **4**, 773 (1965). [d] Derived from group parameters.

Table III. Root-Mean-Square Amplitudes of Vibration (Å)[a,b]

Atom	Min	Intermed	Max
Pd	0.195 (2)	0.202 (2)	0.256 (2)
S1	0.185 (5)	0.249 (5)	0.279 (5)
S2	0.195 (5)	0.255 (4)	0.294 (5)
C6A	0.19 (2)	0.25 (2)	0.29 (2)
C6B	0.23 (2)	0.24 (2)	0.27 (2)
N1A	0.22 (2)	0.26 (2)	0.30 (1)
N1B	0.23 (2)	0.24 (2)	0.28 (1)
C2A	0.21 (2)	0.28 (2)	0.31 (2)
C2B	0.21 (2)	0.27 (2)	0.36 (2)
N3A	0.20 (2)	0.25 (2)	0.30 (1)
N3B	0.22 (2)	0.25 (2)	0.29 (2)
C4A	0.20 (2)	0.25 (2)	0.26 (2)
C4B	0.19 (2)	0.22 (2)	0.29 (2)
C5A	0.16 (2)	0.21 (2)	0.27 (2)
C5B	0.19 (2)	0.23 (2)	0.24 (2)
N7A	0.19 (2)	0.22 (2)	0.25 (2)
N7B	0.16 (2)	0.22 (2)	0.26 (1)
C8A	0.22 (2)	0.24 (2)	0.28 (2)
C8B	0.22 (2)	0.23 (2)	0.26 (2)
N9A	0.21 (2)	0.23 (2)	0.29 (2)
N9B	0.21 (2)	0.22 (2)	0.27 (2)
CMA	0.21 (2)	0.25 (2)	0.32 (2)
CMB	0.23 (2)	0.25 (2)	0.29 (2)
CO	0.22 (2)	0.25 (3)	0.57 (3)
CC	0.20 (2)	0.43 (2)	0.44 (2)
OO	0.25 (2)	0.29 (1)	0.41 (1)
NN	0.24 (2)	0.30 (2)	0.50 (2)
CN1	0.20 (2)	0.35 (2)	0.46 (2)
CN2	0.15 (2)	0.38 (2)	0.47 (2)

[a] Along the principal axes of the thermal ellipsoids. The orientation of these axes may be seen in Figure 3. [b] Values in parentheses represent the standard deviation in the last significant figure.

A final difference Fourier revealed a maximum residual peak of 0.33 e/Å^3, in a position reasonable for a phenyl hydrogen. On this scale a carbon atom shows a maximum electron density of *ca.* 1.7 e/Å^3.

The final atomic positions and thermal parameters are listed in Tables I and II. The root-mean-square amplitudes of vibration are listed in Table III. The major bond distances and angles are listed in Table IV.

Discussion

Description of the Structure. Bis(6-mercapto-9-benzylpurine)palladium(II)-dimethylacetamide is a slightly distorted square-planar complex. As shown in Figure 3 each purine ligand chelates through the sulfur and N7 atoms. The cis configuration is the one expected because it allows maximum π back-bonding to sulfur; the orbitals of the two sulfur atoms can overlap different metal orbitals (d_{xz} and d_{yz}). An examination of the stereochemistry of $M(NS)_2$ chelates[19] shows the energy difference between the cis and trans isomers to be

Table IV. Interatomic Distances and Angles[a]

Coordination Geometry

Atoms	Distance, Å	Atoms	Angle, deg
Pd–S1	2.305 (3)	S1–Pd–S2	85.8 (1)
Pd–S2	2.311 (3)	N7A–Pd–S1	88.1 (3)
Pd–N7A	2.08 (1)	N7B–Pd–S2	87.8 (3)
Pd–N7B	2.047 (9)	N7A–Pd–S2	98.3 (4)

Ligand Geometry

	Distances, Å			Angles, deg	
Atoms	Ligand A	Ligand B	Atoms	Ligand A	Ligand B
C6–S	1.72 (1)	1.72 (1)	C6–N1–C2	117 (1)	117 (1)
C6–N1	1.35 (1)	1.34 (1)	N1–C2–N3	131 (1)	128 (1)
N1–C2	1.35 (2)	1.37 (2)	C2–N3–C4	110 (1)	111 (1)
C2–H2	1.0 (1)	0.8 (1)	N3–C4–C5	124 (1)	125 (1)
C2–N3	1.36 (2)	1.36 (2)	C4–C5–C6	122 (1)	120 (1)
N3–C4	1.34 (1)	1.34 (1)	C5–C6–N1	117 (1)	119 (1)
C4–C5	1.39 (1)	1.37 (1)	C5–C6–S	119 (1)	117 (1)
C5–C6	1.37 (1)	1.37 (1)	C6–C5–N7	127 (1)	129 (1)
C5–N7	1.37 (1)	1.36 (1)	C4–C5–N7	112 (1)	111 (1)
N7–C8	1.34 (1)	1.34 (1)	N1–C6–S	124 (1)	124 (1)
C8–H8	1.0 (1)	0.8 (1)	C5–N7–C8	106 (1)	103 (1)
C8–N9	1.37 (1)	1.35 (1)	N7–C8–N9	110 (1)	113 (1)
N9–C4	1.38 (1)	1.37 (1)	C8–N9–C4	109 (1)	106 (1)
N9–CM	1.48 (1)	1.51 (1)	N9–C4–C5	104 (1)	106 (1)
CM–HM1	0.9 (1)	1.2 (1)	N9–C4–N3	131 (1)	129 (1)
CM–HM2	1.0 (1)	0.8 (1)	N9–CM–C1	111.9 (9)	112.1 (8)
CM–C1	1.51 (2)	1.55 (1)	HM1–CM–HM2	114 (14)	121 (13)

[a] Values in parentheses represent the standard deviation in the last significant figure.

Table V. Best Planes Calculation for Pd, S1, S2, N7A, and N7B

$$0.6594X + 10.39Y - 10.10Z = 1.041^a$$

Atom	Distance from best plane,[b] Å	Atom	Distance from best plane,[b] Å
Pd	−0.0009 (10)	N7A	+0.052 (9)
S1	−0.001 (3)	N7B	−0.006 (9)
S2	+0.008 (3)		

[a] The equation of the plane is in monoclinic coordinates. [b] Values in parentheses represent the standard deviation in the last significant figure.

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(19) R. H. Holm and M. J. O'Connor, *Progr. Inorg. Chem.*, 14, 241 (1971).

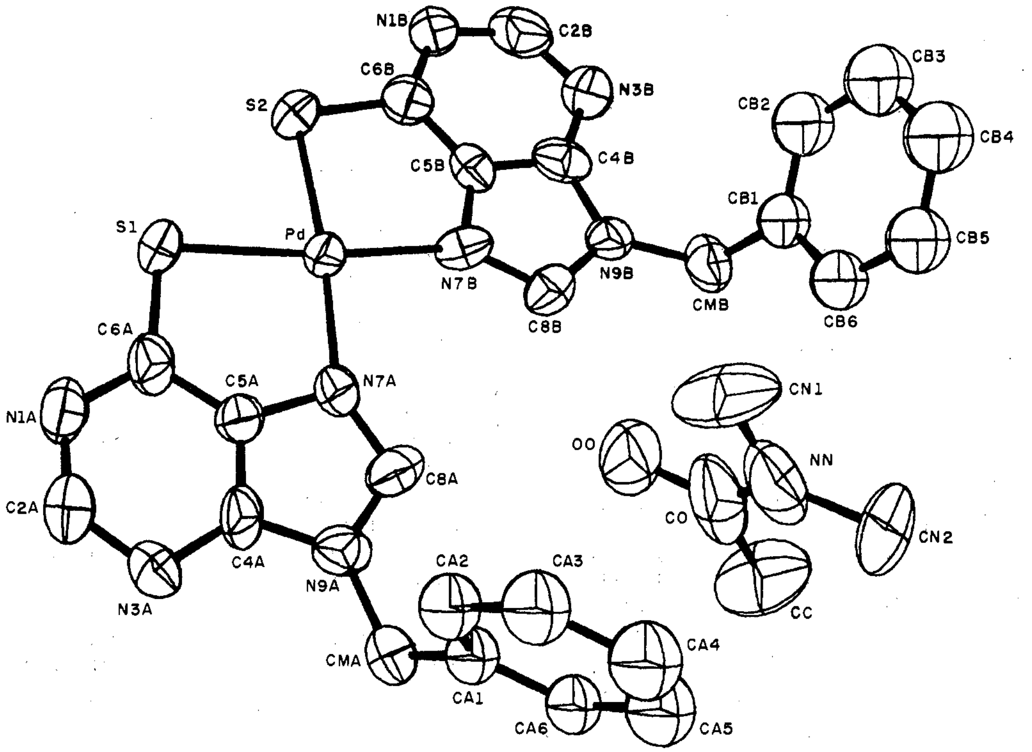
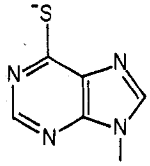


Figure 3. Bis(6-mercapto-9-benzylpurine)palladium(II)-dimethylacetamide, showing the 50% probability thermal ellipsoids and the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

small, steric factors often causing the trans form to be favored.

Another feature of the coordination geometry is the distortion of the angles around the palladium atom from the theoretical value of 90°. The best planes calculation for Pd, S1, S2, N7A, and N7B (Table V) shows little out-of-plane distortion. The H8A-H8B contact distance is 2.5 (1) Å, approximately the sum of the van der Waals radii[20] for two hydrogen atoms. Any reduction in the N7A-Pd-N7B angle of 98.7° would require a shorter H-H contact distance or an out-of-plane distortion. For example, an N7A-Pd-N7B angle of 90° would require an H-H contact of 2.0 Å, which is energetically unfavorable.



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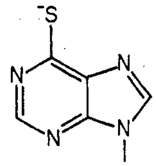

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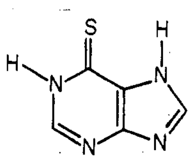

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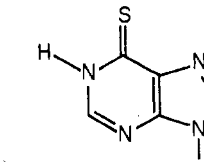
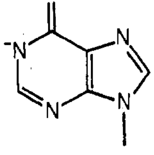


6

A comparison of the average geometry for the ligand in the complex with that observed in the free ligand 6-mercaptopurine monohydrate[21,22] or 6-thioguanosine monohydrate[23] (Table VI) shows only very small differences in bond lengths. Most of these are not significant within experimental error (three standard deviations), which is large because of the limited data set available. A few semiquantitative observations are possible, however. The range of C-N distances in the pyrimidine ring of the complexed ligand (1.34-1.36 Å) is less than the range observed in the free ligand (1.301-1.393 Å). This result indicates more aromatic character in the complexed ligand with approximately equal contributions from the two resonance forms 3 and 4. The bond distances of the free ligand, by contrast, show the predominance of the thione canonical structure,[21] 5 for 6-mercaptopurine or 6 for the riboside. The slightly longer C-S distance (1.72 Å, compared to 1.68 Å) in the complex indicates less double-bond character than in the free ligand. However, the C-S distance is shorter than that observed in metal-alkyl mercaptide complexes of *ca.* 1.80-1.85 Å. The intermediate value observed in the palladium compound, therefore, reveals a measurable contribution from resonance forms of the type with the negative charge delocalized onto the pyrimidine ring, 7 and 8.



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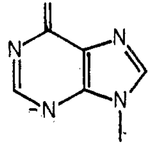

8

There are several significant differences in bond angles (Table VI). The first is the decrease in the C2-N1-C6 angle from 125-126° for the free ligand to 117 (1)° in the complex. This change is consistent with the empirical rule for six-membered nitrogen heterocycles put forth by Singh.[24] The rule states that the angle around nitrogen will fall in the

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[20] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

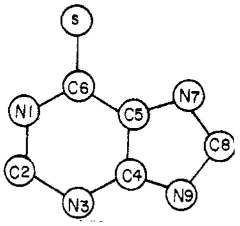
[21] E. Sletten, J. Sletten, and L. H. Jensen, *Acta Crystallogr., Sect. B*, 25, 1330 (1969).

[22] G. M. Brown, *Acta Crystallogr., Sect. B*, 25, 1338 (1969).

[23] U. Thewalt and C. E. Bugg, *J. Amer. Chem. Soc.*, 94, 8892 (1972).

[24] C. Singh, *Acta Crystallogr.*, 19, 861 (1965).

Table VI. Comparison of Geometry of 6-Mercaptopurine[a] and 6-Thioguanosine[b] with the Average Ligand Geometry of Bis(6-mercapto-9-benzylpurine)palladium(II)-Dimethylacetamide[c]



	Distance, Å		
Atoms	6-Mercaptopurine	6-Thioguanosine	Av complex distance, Å
C6–S	1.6786 (09)	1.679 (8)	1.72 (1)
C6–N1	1.3720 (13)	1.393 (8)	1.34 (1)
N1–C2	1.3583 (13)	1.343 (8)	1.36 (2)
C2–N3	1.3088 (16)	1.352 (8)	1.36 (1)
N3–C4	1.3609 (19)	1.365 (8)	1.34 (1)
C4–C5	1.3939 (11)	1.387 (8)	1.38 (1)
C5–C6	1.4050 (14)	1.415 (8)	1.37 (1)
C5–N7	1.323 (15)	1.362 (8)	1.36 (1)
N7–C8	1.3523 (15)	1.301 (8)	1.34 (1)
C8–N9	1.3326 (14)	1.394 (8)	1.36 (1)
N9–C4	1.3676 (14)	1.360 (8)	1.38 (1)

	Angle, deg		
Atoms	6-Mercaptopurine	6-Thioguanosine	Av complex angle, deg
C6–N1–C2	124.74 (10)	125.8 (6)	117 (1)
N1–C2–N3	124.97 (10)	123.2 (6)	130 (1)
C2–N3–C4	113.52 (08)	112.1 (6)	110 (1)
N3–C4–C5	123.91 (09)	128.2 (6)	124 (1)
C4–C5–C6	121.65 (09)	117.8 (6)	121 (1)
C5–C6–N1	111.18 (08)	112.9 (6)	116 (1)
C5–C6–S	126.64 (08)	126.7 (6)	116 (1)
C6–C5–N7	132.52 (08)	130.9 (6)	128 (1)
C4–C5–N7	105.83 (09)	111.3 (6)	112 (1)
N1–C6–S	122.18 (08)	120.5 (6)	124 (1)
C5–N7–C8	106.17 (08)	104.7 (6)	104 (1)
N7–C8–N7	113.46 (10)	112.8 (6)	112 (1)
C8–N9–C4	104.16 (09)	105.7 (6)	108 (1)
N9–C4–C5	110.38 (09)	105.5 (6)	105 (1)
N9–C4–N3	125.75 (08)	126.3 (6)	110 (1)

[a] Reference 22. [b] Reference 23. [c] Values in parentheses represent standard deviations in last significant figure.

range 125 ± 3° if there is a proton on the nitrogen atom and in the range 116 ± 3° if there is no proton. Therefore, the change in this angle confirms that the proton on N(1) is lost when the complex is formed.

Two other significant angle changes between the free and coordinated ligand are the decreases in the C5-C6-S and C6-C5-N7 angles of *ca.* 10 and 4°, respectively. These changes reflect the distortion of the ligand to give a shorter "bite" distance when the chelate ring is formed. The observed "bite" (S-N7) distances are 3.06 (1) and 3.03 (1) Å. The value calculated from the results[22,23] for the free ligand is 3.352 Å for 6-mercaptopurine and 3.323 Å for the riboside. The decreased "bite" allows better overlap of metal orbitals with the orbitals of N7 by increasing the Pd-N7-C5 angle. The observed values for this angle are 109.3 (8) and 110.0 (9)° (*cf.* Figure 1). The best planes calculation (Table VII) indicates little distortion of the purine ring from planarity.

Table VII. Best Planes Calculation for Purine Ligand[a]

Ligand A: $2.446X + 10.84Y - 9.085Z = 1.378$
Ligand B: $1.377X + 10.56Y - 9.812Z = 1.306$

	Distance from best plane,[b] Å			Distance from best plane,[b] Å	
Atom	A	B	Atom	A	B
S	−0.0001 (35)	+0.002 (3)	C4	−0.02 (1)	−0.02 (1)
C6	−0.01 (1)	−0.008 (11)	C5	−0.02 (1)	+0.006 (1)
N1	+0.02 (1)	−0.003 (10)	N7	−0.002 (8)	−0.022 (9)
C2	+0.01 (1)	−0.002 (13)	C8	+0.03 (1)	+0.02 (1)
N3	−0.008 (10)	+0.01 (1)	N9	+0.005 (9)	+0.006 (9)

[a] Monoclinic coordinates. [b] Figures in parentheses represent standard deviations in the last significant figures cited.

The dimethylacetamide geometry is summarized in Table VIII. The agreement with the bond distances observed in the related compound *N*-methylacetamide[25] is not good. Attempts to correct the bond distances by averaging over thermal motion using both "riding" and "independent" models did not result in any more reasonable bond distances. A rigid-body refinement using an idealized geometry based on *N*-methylacetamide did, however, show that the solvent geometry did not have any significant effect on the remainder of the structure. For this reason the anomalous results can be minimized in importance if not ignored in terms of the reliability of the overall structure determination. A best planes calculation (Table VIII) did show a chemically reasonable result. The planarity of dimethylacetamide is similar to that observed in other amides, such as acetamide.[26]

A major intermolecular feature of the structure is the stacking of the planar purine rings (Figure 4). Such stacking is found in many crystals of nucleic acid bases such as purine[27] and 6-mercaptopurine.[21,22] The overlap is only partial with a six-membered (pyrimidine) ring stacked on a five-membered (imidazole) ring at a distance of *ca.* 3.4 Å. The symmetry positions for one pair of molecules are x, y, z, and $^1/_2 - x$, $^1/_2 - y$, $-z$. The closest approach between atoms is 3.33 Å (N9A-C2B). An energy of 4.9 kcal/mol has been calculated for complete overlap of purines.[28] The interaction energy comes primarily from dispersion forces. Because the overlap in this structure is only partial, the energy of association is probably less. However, the self-association of the complex in the solid state is probably responsible for the low solubility of the crystalline complex.

Another intermolecular interaction is indicated by the short distances between both C8A and C8B and the oxygen atom of the dimethylacetamide of *ca.* 3.1 Å. The spatial relationship of the dimethylacetamide molecule as a whole to the complex is seen in Figure 4. The approximate geometry of the oxygen-C8A-C8B interaction is shown in Figure 5. The interaction may be described as a type of weak hydrogen bond. Carbon is usually too electropositive to donate a proton to a hydrogen bond; however, such donation can occur when the carbon atom is activated by adjacent nitrogens. Sutor[29] has compiled a list of compounds where this type of weak, hydrogen-like bonding occurs. The acceptor atom in most of these examples is a ketonic oxygen. The observed carbon-oxygen distance is also consistent with the values tabulated by Sutor (3.0-3.24 Å). The hydrogen-oxygen distance is less than the van der Waals distance of 2.6 Å, consistent with the structural criterion for hydrogen bonding defined by Ibers and Hamilton.[30] The angle around hydrogen is *ca.* 155°. Hydro-

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(25) J. L. Katz and B. Post, *Acta Crystallogr.*, 13, 624 (1960).

(26) W. C. Hamilton, *Acta Crystallogr.*, 18, 866 (1965).

(27) D. G. Watson, R. H. Sweet, and R. Marsh, *Acta Crystallogr.*, 19, 573 (1965).

(28) P. Pullman and A. Pullman, *Progr. Nucl. Acid Res. Mol. Biol.*, 9, 328 (1969).

(29) D. J. Sutor, *Nature (London)*, 195, 68 (1962).

(30) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, p 16.

Table VIII

Dimethylacetamide Geometry[a]

	Distance, Å			Angle, deg	
Atoms	Dimethylacetamide[b]	Methylacetamide[c]	Atoms	Dimethylacetamide[b]	Methyl-acetamide[c]
CC-CO	1.63 (3)	1.54 (2)	OO-CO-CC	116 (2)	120.5
CO-OO	1.27 (2)	1.24 (1)	OO-CO-NN	128 (3)	123
CO-NN	1.18 (2)	1.29 (1)	CC-CO-NN	115 (2)	116.5
NN-CN1	1.60 (2)	1.46 (1)	CN1-NN-CN2	117 (2)	
NN-CN2	1.46 (2)	1.47 (1)	CN1-NN-CO	113 (2)	120.5
			CN2-NN-CO	130 (2)	

Best Planes Calculation for Dimethylacetamide[d] $16.55X - 3.375Y + 7.639Z = 7.796$

Atom	Distance from best plane, Å	Atom	Distance from best plane, Å	Atom	Distance from best plane, Å
CN2	+0.01 (2)	NN1	+0.004 (10)	OO	−0.006 (1)
CN1	+0.005 (20)	CO	− 0.03 (1)	CC	+0.01 (2)

[a] Values in parentheses represent standard deviations in last significant figures. [b] See Figure 3 for atom labeling. [c] Reference 25. [d] Monoclinic coordinate system.

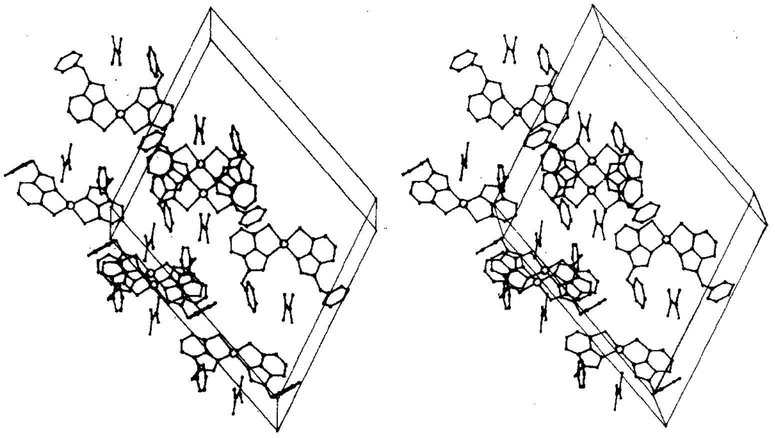

Figure 4. Stereoscopic unit cell packing diagram of bis(6-mercapto-9-benzylpurine)palladium(II)–dimethylacetamide.

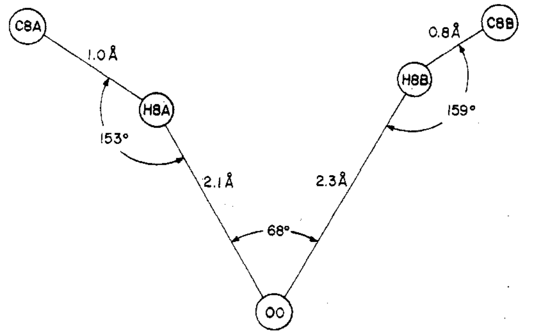

Figure 5. Hydrogen-bonding geometry of the dimethylacetamide oxygen atom with the purine rings.

gen bond angles have been observed to be as low as 140°.[31]

Other short intermolecular contacts are listed in Table IX. The contact distances here are close to the sum of van der Waals radii and represent nonbonded interactions.

Conclusions. The chief conclusion that can be drawn from the results of this structure determination is that chelation by 6-mercaptopurine and its derivatives in solution is entirely possible, if not likely. In particular, the higher formation constants observed for 6-thioguanosine compared to 8-thioguanosine[7] may be explained by chelate formation. The great affinity of sulfur for "soft" metals is sufficient to overcome any unfavorable overlap on nitrogen that might accompany chelate ring formation.[6] In fact, the ligand has been shown to be able to undergo considerable distortion to accommodate the metal ion. Finally, sulfur has been indicated as a possible binding site for metals to naturally occurring substances containing thiolated nucleosides. The structure of 1-methyl-4-thiouracilyl-*p*-mercuribenzoic acid has also established sulfur coordination.[32] These results are important to current work in which metal ions and organometallic complexes are used as probes to study the conformation of such molecules in solution. Studies of the interaction of mercury com-

Table IX. Intermolecular Contacts Other Than Stacking or Hydrogen Bonding

Atom 1[a]	Atom 2	Symmetry position[b]	Distance, Å
CA6	CO	$x, -y, \frac{1}{2} + z$	3.58
CA5	NN	$x, -y, \frac{1}{2} + z$	3.53
CN2	H2A	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$	3.00
N3B	H2B	$x, -y, \frac{1}{2} + z$	2.74
N1A	N1A	$-x, -y, -z$	3.31
H2A	HMA2	$x, -y, \frac{1}{2} + z$	3.01
CB6	NN	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$	3.63
CA5	S2	$x, -y, \frac{1}{2} + z$	3.70
CA3	N7B	$\frac{1}{2} - x, \frac{1}{2} - y, -z$	3.69
N3A	CB4	$-x, -y, -z$	3.69

[a] See Figure 3 for atom labeling. [b] Atom 1 has coordinates shown in Table I. Atom 2 has coordinates transformed by the symmetry operation shown.

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pounds with transfer RNA have already been performed,[7,8,33] and further work is in progress.

Acknowledgment. We thank the National Science Foundation for partial support of this work under Grant GP-27239X and Drs. J. J. Mayerle and T. Li for their advice.

Registry No. Bis(6-mercapto-9-benzylpurine)palladium-dimethylacetamide, 50306-73-5; bis(6-mercapto-9-benzylpurine)-platinum-dimethylacetamide, 50306-74-6.

Supplementary Material Available. A listing of structure factor amplitudes 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 $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-815.

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Transition Metal Hydroborate Complexes. VII.[1] Preparation, Properties, and Structure of Bis(cyanotrihydroborato)-1,1,4,7,7-pentamethyldiethylenetriaminecopper(II)

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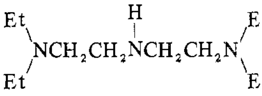
Received September 5, 1973

The compound bis(cyanotrihydroborato)-1,1,4,7,7-pentamethyldiethylenetriaminecopper(II) has been prepared and its crystal and molecular structure determined by a single-crystal X-ray diffraction study. The complex crystallizes in the space group *Pbca* of the orthorhombic system with eight monomeric molecules in the unit cell. Lattice parameters are a = 14.749 (2) Å, b = 17.604 (3) Å, and c = 13.907 (3) Å. Using 1391 unique observed reflections collected by diffractometer, the structure was solved and refined on F to a final value for the discrepancy index R_1 of 0.031. The compound is a pentacoordinate complex of copper(II). The coordination polyhedron is a distorted square-based pyramid with one of the $-NCBH_3$ ligands occupying the apical position. The two Cu-N distances to the cyanotrihydroborate ligands are 1.980 (4) and 2.153 (3) Å (apical) and the Cu-N-C bond angles are 165.0 (3) and 175.6 (3)°, respectively. The difference in bonding of the two $-NCBH_3$ ligands can account for the appearance of the two CN stretching frequencies separated by 18 cm^{-1} which are observed in the infrared spectrum of the solid. The molar conductivity of this complex at 25° in several solvents and its magnetic susceptibility as a function of temperature have been investigated and are discussed in terms of the known structure.

Introduction

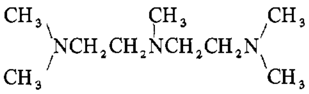
The use of the cyanotrihydroborate anion to produce complexes containing the $M-NCBH_3$ linkage has been the subject of several recent investigations.[3-7] The structure of a copper(I) complex in which H_3BCN^- acts as a bidentate bridging ligand has recently been determined in these laboratories.[1] Interest in the present compound grew out of a study, currently in progress, to prepare and characterize complexes in which the cyanotrihydroborate anion serves to bridge paramagnetic metal ions.

It is well known[8-11] that the two tridentate ligands 1,1,4,7,7-pentamethyldiethylenetriamine (Me_5dien) and 1,1,7,7-tetraethyldiethylenetriamine (Et_4dien) frequently form pentacoordinate complexes of the first-row transition elements.



$Et_2NCH_2CH_2N(H)CH_2CH_2NEt_2$

Et_4dien



$(CH_3)_2NCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)_2$

Me_5dien

Copper(II) usually prefers a coordination number of 6. The alkyl substituents on the triamine ligand cause pronounced stereochemical effects, however, and the extra bulk tends to block the sixth coordination site and produce pentacoordinate copper. The structure of the complex formed by copper(II) with Me_5dien and the cyanotrihydroborate anion was therefore anticipated to be either the dimeric cation $[Cu(Me_5dien)(NCBH_3)]_2^{2+}$ or the neutral $Cu(Me_5dien)(NCBH_3)_2$. The present investigation distinguishes between these two possibilities and provides further structural information about the cyanotrihydroborate ion as a ligand.

Experimental Section

Synthesis. A 1.59-g (9-mmol) sample of Eastman 1,1,4,7,7-pentamethyldiethylenetriamine (Me_5dien) dissolved in 50 ml of 95% ethanol was added to 2.0 g (9 mmol) of copper(II) bromide dissolved in 400 ml of 95% ethanol, with continuous stirring. On mixing, the brown cupric bromide solution darkened and then became a deep blue. A 1.49-g (>18-mmol) amount of Aldrich sodium cyanotrihydroborate was added to 250 ml of 95% ethanol and stirred for several minutes. Dissolution was incomplete and the mixture was filtered into the deep blue cupric solution while stirring continuously. A further darkening of the blue solution was observed. The solution was stirred for 2 hr at room temperature and then chilled in an ice bath. A very small amount (0.04 g) of an insoluble greenish blue

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