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Crystal Structure of Dichlorobis(6-mercaptopurine)mercury(II)

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Crystals of the title compound belong to space group *Pbcn*, $a = 9.543$ (9) Å, $b = 7.996$ (8) Å, $c = 21.10$ (2) Å, and $Z = 4$. The structure was solved by the heavy-atom method and refined on 911 nonzero reflections to $R = 0.029$. Mercury occupies crystallographic twofold axes and forms discrete monomeric molecules in which mercaptopurine is not chelated but acts as a monodentate ligand through sulfur. Two chlorine and two sulfur atoms define a highly distorted tetrahedron around the metal. The Hg–S bonds (2.460 (3) Å) are shorter and the Hg–Cl bonds (2.622 (3) Å) are longer than expected for tetrahedral species. Displacement of hydrogen from N7 in solid mercaptopurine to N9 in the complex is accompanied by characteristic changes in the geometry of the imidazole ring. Each mercaptopurine ligand participates in one intramolecular N1–H1···Cl and two intermolecular N9–H9···N7 hydrogen bonds (N–Cl and N–N distances of 3.120 (9) and 2.737 (12) Å, respectively). Complex molecules, held by hydrogen bonds, form infinite puckered sheets perpendicular to the *b* axis. Purine rings from adjacent sheets are stacked parallel at a distance of 3.4 Å. Very long intersheet contacts (3.740 (3) Å) exist between mercury and two chlorine atoms.

Introduction

6-Mercaptopurine is currently used as a chemotherapeutic agent, e.g., for the treatment of leukemia. In some cases, metal complexes have been shown to be more active than the free ligand.[1] At the present time, little is known about the structures of such complexes. Pt(II) and Pd(II) form various solid compounds in which formation of five-membered rings via S and N7 and/or four-membered rings via N3 and N9 was assumed.[2] A recent crystallographic study has proved the existence of chelate rings involving S and N7 in bis(6-mercapto-9-benzylpurinato)palladium(II) dimethylacetamide and in the isostructural platinum(II) compound.[3] For silver complexes, unidentate sulfur bonding and bidentate bridging via S and N9 were suggested.[4] The infrared spectrum of bis(6-mercaptopurinato)cobalt(II) has been interpreted in terms of unidentate S-bonded ligands.[5]

We investigated the reaction of mercuric chloride with 6-mercaptopurine and a crystalline 1:2 adduct was obtained from acidic solution. The compound was studied in order to determine the mode of attachment of mercury to the ligand.

Experimental Section

Preparation. Mercuric chloride was added to a suspension of 6-mercaptopurine in water (1:2 ratio) and the mixture was stirred at room temperature for 1 hr. The insoluble colorless powder of bis(6-mercaptopurinato)mercury(II) was obtained in quantitative yield. The same compound had been previously prepared in methanol.[6] This starting compound (0.30 g) was dissolved in boiling 0.58 *N* aqueous hydrochloric acid (300 ml). The hot mixture was filtered and left to crystallize. Yellow needles of the title compound formed overnight. Anal. Calcd for $C_{10}H_8Cl_2HgN_8S_2$: C, 20.86; H, 1.40; Cl, 12.31; Hg, 34.83; N, 19.46; S, 11.14. Found (Schwarzkopf Lab.): C, 20.86; H, 1.67; Cl, 12.33; Hg, 34.77; N, 19.68; S, 10.92.

Crystal Data. Formula $C_{10}H_8Cl_2HgN_8S_2$: fw = 575.85; orthorhombic crystals; space group *Pbcn*; $a = 9.543$ (9) Å; $b = 7.996$ (8) Å; $c = 21.10$ (2) Å; $V = 1610$ Å^3, $Z = 4$; $d_c = 2.374$ g/cm^3; d_o (flotation in s-$C_2H_2Br_4/CCl_4$ mixtures) = 2.38 (1) g/cm^3; μ(Mo Kα) = 105.7 cm^{-1}; $t = 23$°C; λ(Mo Kα) (graphite monochromator) = 0.71069 Å.

Crystallographic Measurements. A crystal of dimensions 0.030 mm × 0.52 mm × 0.054 mm (perpendicular to the {001}, {010}, and {100} faces, respectively) was used for the present work. Space group *Pbcn* was established from a set of Weissenberg photographs. Accurate cell parameters were obtained by refinement of the setting angles 2θ, ω, and χ of 12 reflections automatically centered in the counter aperture of a Picker FACS-1 diffractometer.

Intensities of 1421 independent *hkl* reflections within a sphere $2\theta \leq 50°$ were measured with the FACS-1 difractometer using the $\theta/2\theta$ scan technique. The scan rate was 1°(2θ)/min and the 2θ range was 1.60° plus a correction for the $\alpha_1\alpha_2$ separation. Stationary background counts ($B1$ and $B2$) of 20 sec each were taken at the limits of the scan. Three standard reflections (023, 004, 400) showed maximum fluctuations of ±4% during data collection.

Net intensities I were obtained from $I = I_t - T(B1 + B2)/40$, where I_t is the total scan count and T the scan time. A total of 507 reflections with $I/\sigma(I) < 2.5$, where $\sigma(I) = [I_t + T^2(B1 + B2)/1600 + 0.0004I^2]^{1/2}$, were considered as unobserved. An absorption correction based on the crystal geometry was applied (NRC-3 Program, Ahmed and Singh). A grid of 10 × 10 × 10 was used and the transmission factor ranged from 0.55 to 0.73. Lorentz and polarization corrections were finally applied. The 911 nonzero reflections were used to solve and refine the structure.

Solution and Refinement. The structure was solved by the heavy-atom method and refined by full-matrix least squares. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$.

The unit cell contains only four mercury atoms, which must be placed in special positions of group *Pbcn*.[7] From the Patterson map, mercury was found to be located on equipoint **4c** and the molecule thus has crystallographically imposed C_2 symmetry.

Structure factors signed on mercury were calculated for all reflections with $h + k = 2n$. The signs of the remaining reflections were undefined at that stage because the Hg only model has *Cmcm* symmetry. The Fourier map calculated from the available signs showed, as expected, two superimposed images related by false mirrors at $c = {}^1/_4$ and ${}^3/_4$. One of the two possible locations for chlorine was arbitrarily selected and structure factors were calculated for all reflections. A subsequent Fourier map revealed the position of the remaining nonhydrogen atoms. Isotropic refinement with unit weights of all nonhydrogen atoms converged to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.089$. The real and imaginary parts of anomalous dispersion[8] were subsequently taken into account and the nonhydrogen atoms were anisotropically refined. On the ΔF map, peaks slightly above background were found for H1, H2, and H8 (0.5–0.6 e/Å^3). Ambiguity remained concerning the fourth hydrogen atom, which is attached to N7 in 6-mercaptopurine.[9] Although a peak of 0.54 e/Å^3 was present near N7, a higher peak (0.70 e/Å^3) was found near N9. The ΔF map obtained after refining on weighted data (individual weights $w = 1/\sigma_F{}^2$ [10]) showed essentially the same features. At that stage, it was noticed that $|F_c| > 3\,|F_o|$ for reflections 020, 040, and 060. Since there were no other abnormal residuals in the set of data, those three reflections were assigned zero weight in subsequent cycles on the basis of suspected extinction effects. The three known hydrogen atoms were fixed at the calculated positions and anisotropic refinement was continued. The next ΔF map showed residual electron density of 0.75 e/Å^3 for H9, but no significant peak was found near N7. This was considered as conclusive evidence for N9 protonation. This conclusion is consistent with the geometry of the imidazole ring (see discussion).

Anisotropic refinement of nonhydrogen atoms and isotropic refinement of hydrogen atoms converged to $R = 0.029$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.028$. In the final ΔF map, residual peaks of ∓0.75 e/Å^3 were found at ≤1.1 Å from Hg; all the remaining peaks were lower than ∓0.45 e/Å^3. The final coordinates are listed in Table I.

The programs used are listed elsewhere.[11] The form factors for nonhydrogen atoms were those of Cromer and Waber.[12] The

Table I. Refined Atomic Coordinates ($\times 10^4$ and $\times 10^3$ for H) and Temperature Factors ($\times 10^3$ and $\times 10^4$ for Hg)[a]

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	5000	5797 (1)	2500	469 (3)	545 (4)	366 (3)	0	−138 (3)	0
Cl	2731 (3)	7514 (4)	2759 (1)	56 (2)	49 (2)	48 (1)	−9 (2)	−6 (1)	4 (1)
S	4646 (3)	4741 (4)	1417 (1)	31 (1)	64 (2)	39 (1)	−3 (1)	−4 (1)	−8 (1)
N1	1849 (9)	5288 (10)	1612 (4)	43 (5)	32 (5)	41 (5)	−0 (4)	−1 (4)	−0 (4)
N3	−51 (9)	4354 (11)	974 (3)	34 (4)	53 (5)	42 (4)	5 (6)	3 (4)	6 (4)
N7	3114 (8)	2934 (12)	251 (4)	30 (4)	53 (7)	40 (5)	3 (4)	−4 (4)	−3 (5)
N9	822 (8)	2787 (12)	67 (4)	28 (6)	51 (6)	50 (5)	−10 (5)	−7 (4)	−2 (4)
C2	458 (10)	5158 (14)	1467 (5)	40 (5)	48 (7)	32 (5)	0 (5)	−1 (4)	0 (5)
C4	974 (10)	3700 (14)	614 (4)	31 (5)	44 (6)	33 (5)	1 (5)	−1 (4)	5 (5)
C5	2392 (10)	3790 (12)	720 (4)	31 (5)	31 (5)	34 (5)	9 (4)	1 (4)	9 (4)
C6	2897 (9)	4607 (12)	1257 (4)	32 (5)	38 (6)	30 (5)	4 (4)	−2 (4)	4 (4)
C8	2112 (11)	2368 (18)	−130 (5)	41 (7)	57 (8)	39 (7)	−1 (7)	−1 (5)	−11 (7)
H1	193 (11)	593 (15)	213 (5)	60 (15)[b]					
H2	−25 (10)	562 (12)	184 (4)	40 (12)					
H8	232 (11)	193 (14)	−54 (4)	43 (18)					
H9	−10 (11)	242 (12)	−3 (4)	19 (15)					

[a] The form of the anisotropic temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] Isotropic U,

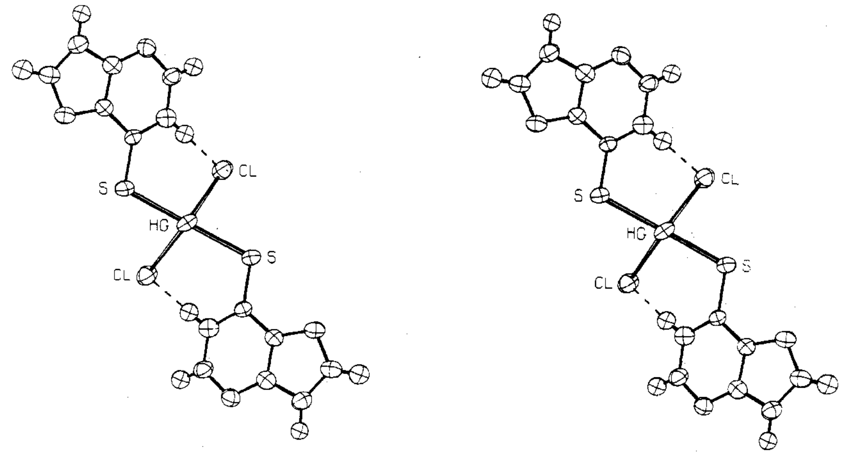


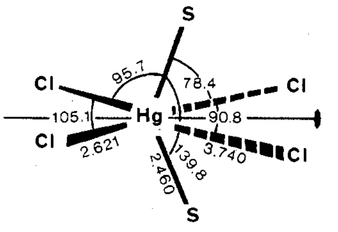
Figure 1. Stereoscopic view of the $HgCl_2(6\text{-mercaptopurine})_2$ molecule. Intramolecular hydrogen bonds are shown as dashed lines.

scattering curve of hydrogen was taken from Stewart et al.[13]

Description of the Structure and Discussion

The crystal consists of discrete monomeric molecules (Figure 1). Bond lengths and angles are shown in Figure 2.

Mercury Coordination. Two types of coordination are commonly found for Hg(II) in the solid state: tetrahedral 4-coordination and octahedral (2 + 4)-coordination (i.e., two short axial bonds and four intermolecular contacts or weak bonds in the equatorial plane).[17] In the present compound, two sulfur and two chlorine atoms are close enough to be considered as bonded to mercury. The tetrahedron is highly distorted, however, and the presence of an extra pair of chlorine atoms at 3.740 (3) Å from mercury (formula I and Figure 3)



I

suggests that a description in terms of (2 + 4)-coordination would also be possible. The S–Hg–S angle (139.8 (1)°) and the Hg–S distances (2.460 (3) Å) are half-way between the values expected for (2 + 4)-coordination (180°, 2.38 Å [14]) and 4-coordination (109°, 2.55 Å [15]). Furthermore, the two Hg–Cl bonds (2.622 (3) Å), which would be equatorial, are much

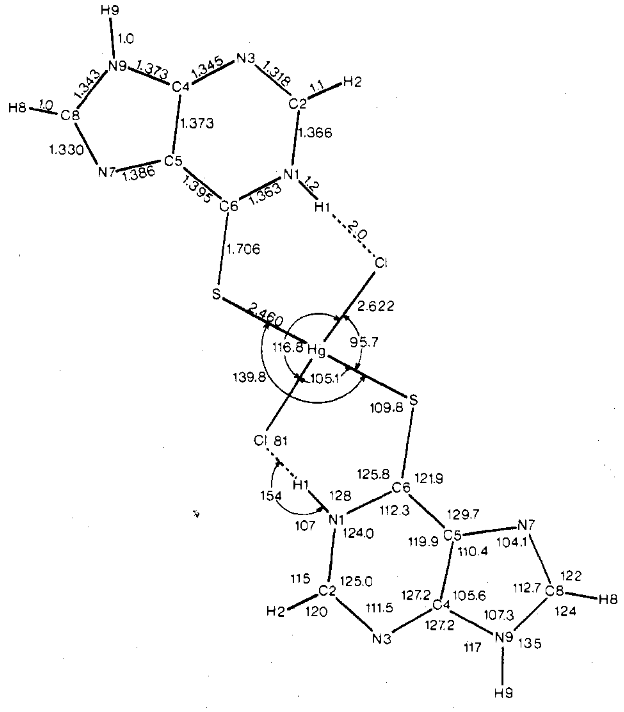


Figure 2. Bond lengths (Å) and angles (deg) in the $HgCl_2(6\text{-mercaptopurine})_2$ molecule. The esd's are: Hg–S(Cl), 0.003 Å; S(Cl)–C(N), 0.009 Å; C–C(N), 0.012–0.014 Å; H–C(N), 0.1 Å; angles at Hg, 0.1°; at S, 0.3°; at C or N, 0.7–1.0°, except for those involving H, 3–6°. This also applies to formula I.

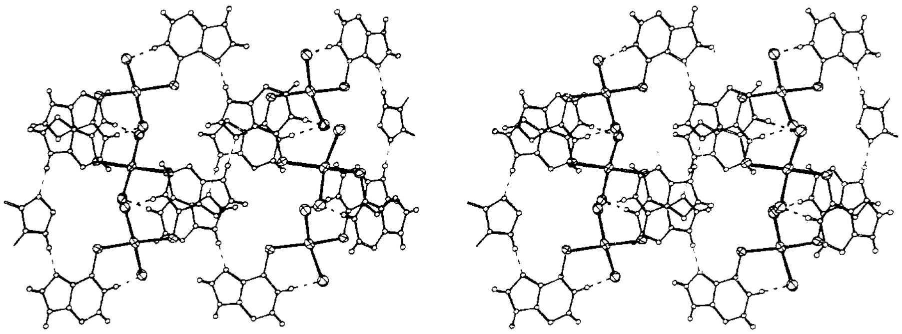


Figure 3. Stereoscopic view of the molecular packing in $HgCl_2$(6-mercaptopurine)$_2$. The direction of view of *b-c* is horizontal and *a* is vertical. Mercury, sulfur, and chlorine are represented as ellipsoids, whereas carbon, nitrogen, and hydrogen atoms are shown as small spheres. Dashed lines correspond to hydrogen bonds.

longer than observed in typical 4-coordinate molecules (2.50 Å [16]). From the above considerations only, the structure could be discussed in terms of distortions from either type of coordination. However, the distance from mercury to the third and fourth chlorine atoms (3.740 (3) Å) is so much longer than the sum of the van der Waals radii (1.50 Å for Hg,[17] 1.80 Å for Cl[18]) that they are not considered here as part of the coordination sphere. Accordingly, mercury is assumed to possess a distorted tetrahedral coordination.

The Ligand. The C–S bond (1.706 (9) Å) is slightly longer than in 6-mercaptopurine[9] and the corresponding riboside[19] (1.67–1.68 Å). This bond retains appreciable double-bond character in the complex, since a C–S distance of 1.76–1.77 Å[20] is expected for a single bond. The ligand is planar within 2σ (0.016 Å) and the pyrimidine ring is not affected by complexation. The large C6–N1–C2 angle (124.0 (8)°) confirms that a hydrogen atom is still attached to N1, for this angle is 118–119° when N1 is not protonated.[21]

In the electron density map, there were indications that the hydrogen atoms attached to N7 in mercaptopurine were displaced to N9 in the complex. This displacement, which also takes place in aqueous solution,[22] is confirmed by characteristic changes in the geometry of the imidazole ring. We have compared x-ray results for a number of purines and significant differences in interatomic distances and bond angles have been found between N7-substituted and N9-substituted molecules (designated below by N7-R and N9-R, respectively). A full report of this study will be published elsewhere, but part of the conclusions are summarized in Table II. The greatest differences in bond lengths between N9-R and N7-R are observed for N7–C8 (0.028 Å) and C8–N9 (0.042 Å). They will generally be large compared to the esd's in organic structures, but for very-heavy-atom compounds, the esd's are often too high to make such differences highly significant. In the present case, N7–C8 appears to be longer then C8–N9, as for pattern N9-R, but no clear conclusion can be drawn from bond lengths alone. On the other hand, angles N9–C4–C5 and C4–C5–N7 are more sensitive to the position of the substituent. Their respective values are 105.9 and 110.7° for N9-R, but 110.8 and 105.6° for N7-R. Our results (Table II) are obviously in good agreement with pattern N9-R and hydrogen is believed to be attached to N9 in the complex.

The molecule contains two symmetry-related intramolecular N1–H1···Cl hydrogen bonds. The N–Cl distances are short (3.120 (9) Å) and the angles are favorable (C2–N1–Cl = 118.7 (7)°, C6–N1–Cl = 117.1 (7)°). (No use is made of H1 itself in this discussion because its position is poorly defined.) Cl–Hg–S angle (105.1 (1)°) is normal. The S–C6–N1 angle (125.8 (7)°) is 3.5° greater than in free 6-mercaptopurine[2] and the riboside,[19] which may indicate a certain amount of tension to improve hydrogen-bonding efficiency.

Packing. A packing diagram is shown in Figure 3. Each complex molecule is involved in four N9–H9···N7 intermolecular hydrogen bonds (twice as donor, twice as acceptor). The N7–N9 distances (2.737 (12) Å) indicate strong hydrogen bonding. This network of H bonds links the molecules together in infinite puckered sheets perpendicular to the *b* axis. There are no H bonds between the sheets. The purine moieties from adjacent sheets are stacked parallel at 3.4 Å as commonly found for this type of molecule. The long Hg···Cl intersheet contacts (3.740 (3) Å) have been discussed above.

Table II. Interatomic Distances and Bond Angles in N7- and N9-Substituted Purines[a]

	N9-R	N7-R	This work
	Distances, Å		
C4–C5	1.380	1.380	1.373
C5–N7	1.384	1.374	1.386
N7–C8	1.310	1.338	1.330
C8–N9	1.370	1.328	1.343
N9–C4	1.372	1.362	1.373
	Angles, deg		
C5–N7–C8	104.0	106.0	104.1
N7–C8–N9	113.5	113.7	112.7
C8–N9–C4	105.9	104.0	107.3
N9–C4–C5	105.9	110.8	105.6
C4–C5–N7	110.7	105.6	110.4

[a] Weighted average values obtained from 55 N9-substituted and 13 N7-substituted purines with R = H, alkyl, aryl, or ribosyl. Standard deviations for the average values are 0.008 Å and 0.6°. This work, 0.012–0.014 Å and 0.7–1.0°.

Conclusion

6-Mercaptopurine is sulfur bonded, in good agreement with the well-known affinity of mercury for sulfur donors. Chelate formation via S and N7, known to take place with Pd and Pt,[3] would have been a priori possible in an ionic complex [(6-mercaptopurine)$_2$Hg]Cl_2, but such a structure was not observed. Obviously, tetrahedral coordination would require S–M–N angles larger than square-planar coordination, but this does not seem to be the determining factor here, since the present work shows that the angles at mercury (e.g., Cl–Hg–S 95.7 (1)°) can be decreased to values not much greater than found in the palladium chelate (88°). Consequently, the monodentate character of mercaptopurine is not believed to result from geometrical constraints. It is better explained in terms of the preference for chlorine over nitrogen donors, which is considerably greater for mercury than for platinum (and presumably palladium). This was proposed[23] in order to explain that adenine is not coordinated to mercury in the compound obtained from dilute hydrochloric acid solutions, whereas coordination occurs with the platinum complex prepared under similar conditions. In the present case, sulfur and chlorine fulfill the coordination requirements of mercury and leave no coordination sites available for nitrogen. However, chelate formation appears to be possible in the absence of chlorine or other good donors toward mercury, in bis(6-mercaptopurinato)mercury (II), for instance.

Registry No. Dichlorobis(6-mercaptopurine)mercury(II), 56995-00-7.

Supplementary Material Available: A listing of structure factor amplitudes, nine pages. Ordering information is given on any current masthead page.

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Synthesis and Properties of Cobalt and Nickel Complexes with the Tripod Ligand Tris(2-diphenylarsinoethyl)amine. Structural Characterization of a σ-Phenyl Complex of Nickel(II) with the Same Ligand

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The "tripod" ligand tris(2-diphenylarsinoethyl)amine, nas3, reacts with cobalt(II) and nickel(II) salts in the presence of sodium borohydride to give complexes of cobalt(I) and nickel(I) having the general formula [MX(nas3)] (M = Co, X = Cl, Br, I; M = Ni, X = Cl, Br, I, NCS, NO_3). These compounds are assigned a trigonal-bipyramidal structure. The cobalt(I) complexes are high spin. A trigonal-pyramidal structure is suggested for the ionic compound [Ni(nas3)]BF_4. A bound halide ion can be replaced by carbon monoxide yielding cations isolated as the salts [M(CO)(nas3)]BPh_4 (M = Co, Ni); the cobalt(I) compound is low spin. The product of the reaction of nickel(II) chloride and sodium tetraphenylborate has the formula [Ni(C_6H_5)(nas3)]BPh_4. In this reaction a phenyl group is transferred from the boron to the nickel atom. An x-ray structural analysis has shown that the complex has a trigonal-bipyramidal structure with a phenyl group σ-bonded in the axial position. Analogous σ-phenyl complexes are formed with other polydentate arsenical ligands.

Introduction

Some years ago we found that the reaction of $NiBr_2$ and NiI_2 with the tetradentate ligand tris(2-diphenylarsinoethyl)amine, nas3, in the presence of $NaBPh_4$, yields five-coordinate complexes of the formula [NiX(nas3)]BPh_4.[1] The salt $NiCl_2$ yielded a different, chloride-free complex which has now been fully characterized as a five-coordinate nickel(II) complex containing a σ-bonded phenyl group. Analogous compounds incorporating a nickel–carbon σ bond can be obtained if nas3 is replaced by other polydentate ligands containing arsenic donor atoms.

Using $NaBH_4$ two series of five-coordinate cobalt(I) and nickel(I) complexes were obtained having the general formula [MX(nas3)] (M = Co, X = Cl, Br, I; M = Ni, X = Cl, Br, I, NCS, NO_3) and the two carbonyl derivatives [M(CO)-(nas3)]BPh_4 (M = Co, Ni). The nickel(II) tetrafluoroborate gave the complex [Ni(nas3)]BF_4, which has been attributed a trigonal-pyramidal geometry.

All the compounds were characterized and their physical properties studied by the usual methods. A complete x-ray determination of the complex [Ni(C_6H_5)(nas3)]BPh_4 has been carried out. Preliminary results of this structure have already appeared.[2]

Experimental Section

All solvents were purified by standard methods. Electronic and infrared spectra, molar conductivities, and other physical measurements were performed using methods described elsewhere.[3]

Synthesis of Ligands. The ligands nas3, tris(*o*-diphenylarsinophenyl)arsine, QAS, and *o*-phenylenebis(dimethylarsine), DAS, were synthetized by published methods.[4]

Tris(2-dimethylarsinoethyl)amine, Me6nas3, was prepared as follows. $N(CH_2CH_2Cl)_3$[5] (0.124 mol) in anhydrous tetrahydrofuran (50 ml) was added with stirring to $NaAsMe_2$[6] (0.37 mol) in tetrahydrofuran (300 ml). The resulting mixture was heated under reflux for 3 hr and the solvent then removed under reduced pressure. The residue was dissolved in ether, washed with water, and dried over Na_2SO_4, and the ether was then removed under reduced pressure. The ligand distills at 130°C and 0.5 Torr. The ligand was prepared and stored under nitrogen; yield 43%. Anal. Calcd for $C_{12}H_{30}As_3N$: C, 34.9; H, 7.3; N, 3.4; As, 54.9. Found: C, 34.9; H, 7.4; N, 3.6; As, 54.8.

Preparation of Complexes. All complexes were prepared and manipulated under dry nitrogen unless otherwise stated.

[NiX(nas3)], X = Cl, Br, I, NO_3, BF_4. The ligand (1 mmol) in methylene chloride (20 ml) was added to a hot solution of NiX_2 (1 mmol) in ethanol (15 ml). $NaBH_4$ (1 mmol) in ethanol (15 ml) was then added to the resulting mixture. The crystals obtained by concentrating the solution were washed with ethanol and light petroleum.

X = NCS. The complex was prepared at room temperature.

[Ni(CO)(nas3)]BPh_4. Carbon monoxide was bubbled for 30 min through a suspension of [NiBr(nas3)] (1 mmol) in dry tetrahydrofuran (20 ml). $NaBPh_4$ (1 mmol) in ethanol (10 ml) was then added. The violet-brown product which crystallized on evaporation of the solvent was filtered and washed with ethanol and petroleum ether.

[Ni(C_6H_5)(nas3)]BPh_4. A solution of $NaBPh_4$ (2 mmol) in butanol (15 ml) was added in air to a mixture of $NiCl_2$ (1 mmol) and nas3 (1 mmol) in boiling butanol (50 ml). After partial boil off of the solvent, cherry red crystals formed and were filtered hot, washed with