Inorganica Chimica Acta, 63 (1982) 189–195

Reactions of Co(II) Cobaloximes with Organohaloarsines and the Crystal Structure of an Arsine Derivative of a Co(III) Cobaloxime

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Received April 20, 1982

The Co(II) cobaloximes (B)Co(dmgH)$_2$ *(B = phosphine or phosphite; dmgH = dimethylglyoximato monoanion) react with* $(R_1)(R_2)AsX$ *(X = Cl:* $R_1=R_2=CH_3$*;* $R_1=CH_3$*,* $R_2=C_6H_5$*;* $R_1=R_2=C_6H_5$*. X = I:* $R_1=R_2=CH_3$*) to give in all cases XCo(dmgH)*$_2$*B. In addition, for X = Cl,* $R_1=CH_3$*,* $R_2=C_6H_5$ *and X = Cl,* $R_1=R_2=C_6H_5$*, compounds of the formulae* $C_{15}H_{23}AsClCoN_4O_5\cdot H_2O$ *and* $C_{20}H_{25}AsClCoN_4O_5$*, respectively, were obtained. A crystal structure analysis of the former shows it to be either* $(CH_3)(C_6H_5)As(OH)Co(dmgH)_2Cl\cdot H_2O$ *or* $(CH_3)(C_6H_5)As(O)Co(dmgH)(dmg)Cl\cdot H_2O$*. The crystals (at −100 °C) are orthorhombic, space group* Pnam, a = *14.273(3),* b = *11.154(3),* c = *12.995(4) Å. The structure is disordered, but the molecule can be identified from its superimposed images. It consists of a Co atom bonded equatorially to two bidentate dmgH ligands (av. Co–N = 1.90(2) Å) with a Cl atom above this plane (Co–Cl = 2.286(3) Å) and the As atom of the* $(CH_3)(C_6H_5)$*As (O or OH) group below it (Co–As = 2.311 or 2.320(2) Å).*

Introduction

We have recently been interested in compounds containing arsenic σ-bonded to transition metals, as these systems are not well documented [1–3]. Of particular interest are derivatives containing the Co–ÄsR$_2$ moiety as there is virtually no information available concerning this system; in addition, it has been suggested that the cobaloxime compounds containing σ-bonded –ÄsR$_2$ may have some relevance to models for the biological methylation of arsenic [4].

We have previously reported the reactions of the Co(I) cobaloxime $[(C_4H_9)_3PCo(dmgH)_2]^-$, (dmgH = dimethylglyoximato monoanion), with a variety of organohaloarsines [5]. Our present work involved reacting the Co(II) cobaloximes (B)Co(dmgH)$_2$ $\{B = P(C_4H_9)_3, P(C_6H_5)_3, P(OCH_3)_3, P(OC_6H_5)_3\}$ with organohaloarsines.

Experimental

All reactions were carried out under a nitrogen or argon atmosphere. PMR spectra were run on a Varian T-60 instrument using $CDCl_3$ as solvent. Chemical shifts are given in ppm downfield from internal TMS. Microanalyses were performed by Mr. R. Teed and Mr. E. Bailey (University of Saskatchewan). Magnetic susceptibilities were measured at room temperature by the Gouy method. Arsenic compounds were prepared by using methods described in the literature: $(CH_3)_2AsCl$ [6], $(CH_3)_2AsI$ [7], $(CH_3)(C_6H_5)AsCl$ [8]. $(C_6H_5)_2AsCl$, $P(C_6H_5)_3$, $P(C_4H_9)_3$, $P(OCH_3)_3$, $P(OC_6H_5)_3$, cobalt acetate tetrahydrate and dimethylglyoxime were commercial products.

Preparation of the Cobaloxime(II) Base Adducts

The following general procedure was used for the preparation of the cobaloxime base adducts [9].

Cobalt acetate tetrahydrate (1.0 g; 0.004 mol), dimethylglyoxime (0.93 g; 0.008 mol) and the corresponding base (0.004 mol) were added successively into 25 ml of degassed absolute methanol. The reaction mixture was stirred under nitrogen for 4 h. The brown precipitate was collected by filtration under nitrogen, washed with absolute methanol and dried at 25 °C under vacuum (0.1 mm Hg). Yield: 50–70%. Analytical and magnetic susceptibility data for the complexes are given in Table I.

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0020-1693/82/0000-0000/$02.75

TABLE I. Analytical and Magnetic Data for the Cobaloxime(II) Base Adducts.

Compound	Calcd. %			Found, %			μ_{eff}, B.M.
	C	H	N	C	H	N	
$Co(dmgH)_2PPh_3$	56.62	5.26	10.16	56.40	5.35	9.88	1.7
$Co(dmgH)_2P(C_4H_9)_3$	48.88	8.35	11.41	48.70	8.18	11.25	2.4
$Co(dmgH)_2P(OCH_3)_3$	31.96	5.57	13.56	32.06	5.33	13.19	2.3
$Co(dmgH)_2P(OPh)_3$	52.09	4.84	9.35	52.28	5.10	9.17	2.3

TABLE II. Analytical Data for the Halobasecobaloximes.

Compound	Calcd, %					Found, %				
	C	H	N	Cl	I	C	H	N	Cl	I
$ClCo(dmgH)_2PPh_3$	53.20	4.94	9.55	6.05		53.00	4.81	9.40	5.87	
$ICo(dmgH)_2PPh_3$	46.02	4.28	8.26		18.73	46.05	4.60	8.52		18.40
$ClCo(dmgH)_2P(C_4H_9)_3$	45.58	7.79	10.63	6.74		45.78	7.60	10.51	6.50	
$ICo(dmgH)_2P(C_4H_9)_3$	38.83	6.63	9.06		20.55	38.61	6.50	9.00		20.33
$ClCo(dmgH)_2P(OCH_3)_3$	29.43	5.13	12.49	7.92		29.40	5.00	12.30	7.99	
$ICo(dmgH)_2P(OCH_3)_3$	22.15	3.86	9.40		21.31	22.40	3.57	9.71		21.00
$ClCo(dmgH)_2P(OPh)_3$	49.17	4.57	8.83	5.59		49.00	4.52	8.90	5.62	
$ICo(dmgH)_2P(OPh)_3$	42.99	3.99	7.71		17.49	43.35	4.23	7.35		17.15

Reactions of Cobaloxime(II) Base Adducts with $(CH_3)_2AsCl$ and $(CH_3)_2AsI$

The following general procedure was used for the reactions of the cobaloximes with $(CH_3)_2AsCl$ and $(CH_3)_2AsI$.

The arsine (0.200 mmol) was dissolved in 5 ml of degassed methanol and then added dropwise to a solution of the cobaloxime (0.400 mmol) in 50 ml of degassed methanol. The resulting brown-red solution was stirred at 20 °C under nitrogen for 1 h. The solvent was removed under reduced pressure and the oily residue chromatographed using silicic acid (200–400 mesh). Methylene dichloride eluted a dark brown band which, after solvent removal and recrystallization from a methylene dichloride/hexane mixture, afforded crystals of the halobasecobaloxime (yield: 40–60%). Analytical and PMR data for these complexes are presented in Tables II and III.

Reactions of Cobaloxime(II) Base Adducts with $(CH_3)(C_6H_5)AsCl$ and $(C_6H_5)_2AsCl$

The above reaction procedure was also used for the reactions with the phenyl-substituted arsines. An oily residue was obtained after solvent removal and chromatographed using silicic acid (200–400 mesh).

A 5% acetone/methylene dichloride mixture eluted a brown-coloured band containing the halobasecobaloxime. The species were recrystallized from a methylene dichloride/hexane mixture. Yield: ~35%.

A 20% acetone/methylene dichloride mixture eluted a rust-coloured band. Upon removal of the solvents and recrystallization from a methylene dichloride/hexane mixture, brown crystals were obtained in 15–20% yield.

The product, *A*, from the reaction with $(CH_3)(C_6H_5)AsCl$ analysed as $C_{15}H_{21}AsClCoN_4O_5 \cdot H_2O$. Calc.: C, 34.34; H, 4.42; As, 14.28; Cl, 6.76; N, 10.68%. Found: C, 34.45; H, 4.46; As, 13.85; Cl, 6.57; N, 10.66%. The PMR spectrum consisted of singlets at 1.58 (As-CH_3), 2.13 (dmgH-CH_3) and 2.23 (dmgH-CH_3) and a broad multiplet centered at 7.46 (As-C_6H_5).

The reaction with $(C_6H_5)AsCl$ afforded crystals which analysed as $C_{20}H_{25}AsClCoN_4O_5$. Calc.: C, 42.11; H, 4.39; As, 13.16; Cl, 6.23; N, 9.82%. Found: C, 41.95; H, 4.56; As, 13.40; Cl, 6.36; N, 9.76%. The PMR spectrum consisted of singlets at 2.00 (dmgH-CH_3) and 7.50 (As-C_6H_5).

TABLE III. PMR Data for the Halobasecobaloximes.

Compound	Chemical shift
$ClCo(dmgH)_2PPh_3$	Doublet centred at 2.00 (dmgH-CH_3, J(H,P) = 2.0 Hz). Multiplet centred at 7.4 (PPh_3).
$ICo(dmgH)_2PPh_3$	Doublet centred at 2.00 (dmgH-CH_3, J(H, P) = 2.0 Hz). Multiplet centred at 7.4 (PPh_3).
$ClCo(dmgH)_2P(C_4H_9)_3$	Doublet centred at 2.20 (dmgH-CH_3, J(H,P) = 2.0 Hz). Broad multiplets centred at 0.90 and 1.26 ($P(C_4H_9)_3$).
$ICo(dmgH)_2P(C_4H_9)_3$	Doublet centred at 2.20 (dmgH-CH_3, J(H, P) = 2.0 Hz). Broad multiplets centred at 0.92 and 1.30 ($P(C_4H_9)_3$).
$ClCo(dmgH)_2P(OCH_3)_3$	Doublet centred at 2.30 (dmgH-CH_3, J(H,P) = 2.0 Hz). Doublet centred at 3.66 ($P(OCH_3)_3$, J(H,P) = 10.0 Hz).
$ICo(dmgH)_2P(OCH_3)_3$	Doublet centred at 2.30 (dmgH-CH_3, J(H,P) = 2.0 Hz). Doublet centred at 3.68 ($P(OCH_3)_3$, J(H,P) = 10.0 Hz).
$ClCo(dmgH)_2P(OPh)_3$	Doublet centred at 2.10 (dmgH-CH_3, J(H,P) = 2.0 Hz). Multiplets centred at 6.90 and 7.30 ($P(OPh)_3$).
$ICo(dmgH)_2P(OPh)_3$	Doublet centred at 2.10 (dmgH-CH_3, J(H,P) = 2.0 Hz). Multiplets centred at 6.90 and 7.33 ($P(OPh)_3$).

Structure Determination and Refinement

Crystals of *A* appeared adequate for an X-ray structure analysis and this was supported by preliminary X-ray photographs. We had experienced some problems in collecting X-ray intensity data with a plate-like crystal of a related cobaloxime [5] so it was decided to collect the data for *A* at –100 °C. A single crystal was sealed inside a Lindemann tube which was then mounted on a Cryo-Tip single-crystal X-ray diffraction refrigerator system (Air Products and Chemicals, Inc.). Intensity data were collected on a Picker FACS-I four-circle automated diffractometer employing graphite-monochromated Mo Kα radiation ($\lambda = 0.70926$ Å). Accurate cell dimensions were obtained at room temperature by a least-squares fit of the angular parameters of 22 reflections with $2\theta > 28°$. The crystal assembly was then cooled to –100 °C and the cell dimensions redetermined. Crystal data are given in Table IV. The line profiles of 1429 unique reflections $3° < 2\theta < 45°$ were measured at this temperature with a θ–2θ scan. The scan rate was 2° min^{-1} and scan width $(1.7 + 0.692 \tan\theta)°$. Stationary-crystal stationary-counter background counts of 10% of scan time were taken at each side of the scan. Peak profile analyses were performed to determine the intensities and associated errors [10]. Two standards were measured after every 70 reflections but gave no indication of decomposition. 1186 reflections with $I > 2.3\sigma(I)$ ($\sigma(I)$ is the standard deviation in the intensity derived from counter statistics and a precision factor of 0.03) were regarded as observed and used in structure solution and refinement.

The structure was solved by heavy-atom methods assuming the space group to be *Pnam* (non-standard form of *Pnma*). Full-matrix least-squares refinement of the non-hydrogen atoms with isotropic temperature factors (O(W) with occupancy 0.5) gave $R = (\Sigma \| F_o| - |F_c\| / \Sigma |F_o|) = 0.115$. A difference map at this stage indicated that many of the atoms were disordered. This led to a model in which disordered half-atoms were found for almost the entire structure, with the molecule *roughly* centered on the mirror plane $z = 0.25$ (as the ordered model had shown). An absorption correction was also applied (T = 0.42–0.81) at this time. Isotropic refinement of this model (97 variables) converged to $R = 0.059$, $R_w = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2)^{1/2} = 0.071$.

Clearly, the possibility of a lower symmetry or a larger cell should be carefully considered. We exhaustively used models in $Pna2_1$, $P2_12_12_1$ and $P2_1am$, but found that they gave higher R values and would not refine to give reasonable Co–N distances. In addition, close inspection of the origin peak of the Patterson map revealed a distinct shoulder at ~0.6 Å in the *c* direction which is consistent only with disorder as none of the interatomic vectors could be this short. Although the systematic

TABLE IV. Crystal Data.

Orthorhombic, *Pnam*[a]	$Z = 4$	
	−100 °C	20 °C
a (A)	14.273(3)	14.336(3)
b (A)	11.154(3)	11.164(2)
c (A)	12.995(4)	13.019(3)
U (A^3)	2068.8	2083.7
μ (cm^{-1})	27.1	26.9
	$C_{15}H_{23}AsClCoN_4O_6$	$C_{15}H_{25}AsClCoN_4O_6$
fw	524.68	526.70
ρ_o (gm cm^{-3})	–	1.67[b]
ρ_c (gm cm^{-3}) at 20 °C	1.672	1.679
ρ_c (gm cm^{-3}) at −100 °C	1.684	1.691

[a] See text for discussion on space group. [b] Density by flotation in $CHCl_3/CHBr_3$.

TABLE V. Final Positional and Thermal Parameters for *A*. All atoms have half-occupancy except C(23) and C(24).

Atom	x	y	z	10^3 U (A^2)
As	0.03735(7)	0.53319(10)	0.24320(34)	25.8(4)
Co	0.15357(9)	0.38910(12)	0.24043(32)	21.9(5)
Cl	0.2675(2)	0.2460(3)	0.2270(3)	31(1)
O(11)	0.1960(10)	0.4674(13)	0.0427(11)	52(4)
N(12)	0.2140(11)	0.4818(15)	0.1404(15)	29(5)
C(13)	0.2759(11)	0.5597(14)	0.1762(14)	22(4)
C(14)	0.3304(11)	0.6399(15)	0.0991(15)	35(4)
C(15)	0.3445(11)	0.6487(14)	0.3501(14)	32(4)
C(16)	0.2827(11)	0.5636(15)	0.2861(12)	29(5)
N(17)	0.2280(11)	0.4863(13)	0.3314(12)	21(5)
O(18)	0.2259(9)	0.4685(12)	0.4366(11)	37(3)
O(21)	0.0793(8)	0.3151(12)	0.0512(12)	44[a]
N(22)	0.0759(10)	0.2959(18)	0.1525(17)	25[a]
C(23)[b]	0.0312(5)	0.2128(6)	0.1945(6)	31(2)
C(24)[b]	−0.0230(5)	0.1252(7)	0.1280(7)	42(2)
N(27)	0.0929(10)	0.2933(18)	0.3396(17)	25[a]
O(28)	0.1074(8)	0.3002(12)	0.4420(12)	44[a]
C(1)	−0.0629(10)	0.5166(14)	0.3417(14)	36(4)
O(2)	−0.0220(7)	0.5387(10)	0.1247(10)	43(3)
C(71)	0.0839(7)	0.6952(9)	0.2369(18)	24(3)
C(72)	0.0982(12)	0.7411(16)	0.1416(13)	27[a]
C(73)	0.1374(12)	0.8584(17)	0.1410(12)	30[a]
C(74)	0.1639(8)	0.9211(11)	0.2295(14)	33(4)
C(75)	0.1496(13)	0.8720(17)	0.3285(13)	30[a]
C(76)	0.1075(13)	0.7562(16)	0.3328(12)	27[a]
O(W)	−0.1433(8)	0.3771(10)	0.0773(10)	59(3)

[a] Not refined in least-squares. [b] In subsequent tables, C(25) = C(23) transformed by (x, y, ½ − z); C(26) = C(24) transformed by (x, y, ½ − z).

extinction conditions for *Pnam* are violated by two reflections (014 and 027 and their equivalents) they are very weak, so we feel that the molecular geometry we have obtained in this space group will essentially be correct.

TABLE VI. Interatomic Distances (Å) and Angles (deg.).

Co–As	2.311 or 2.320(2)	Co–Cl	2.286(3)
Co–N(12)	1.87(2)	Co–N(22)	1.90(2)
Co–N(17)	1.92(1)	Co–N(27)	1.89(2)
As–C(1)	1.93(2)	As–O(2)	1.76(1)
As–C(71)	1.93 or 1.94(1)		
O(11)–N(12)	1.30(2)	O(21)–N(22)	1.34(2)
N(12)–C(13)	1.32(2)	N(22)–C(23)	1.25(2)
C(13)–C(14)	1.55(2)	C(23)–C(24)	1.52(1)
C(13)–C(15)	1.43(3)	C(23)–C(25)	1.44(1)
C(15)–C(16)	1.54(2)	C(25)–C(26)	1.52(1)
C(15)–N(17)	1.30(2)	C(25)–N(27)	1.33(2)
N(17)–O(18)	1.38(2)	N(27)–O(28)	1.35(3)
C(71)–C(72)	1.36(3)	C(71)–C(76)	1.46(3)
C(72)–C(73)	1.42(3)	C(76)–C(75)	1.42(3)
C(73)–C(74)	1.40(2)	C(75)–C(74)	1.41(3)
As–Co–Cl	176.5 or 179.0(3)		
As–Co–N(12)	87.6 or 90.6(5)	Cl–Co–N(12)	90.3(5)
As–Co–N(17)	89.7 or 87.1(4)	Cl–Co–N(17)	92.7(4)
As–Co–N(22)	88.3 or 91.0(5)	Cl–Co–N(22)	89.3(5)
As–Co–N(27)	93.1 or 90.1(5)	Cl–Co–N(27)	89.0(5)
N(12)–Co–N(17)	82.0(7)	N(22)–Co–N(27)	80.4(4)
N(12)–Co–N(22)	98.8(9)	N(17)–Co–N(27)	98.8(8)
N(12)–Co–N(27)	179.0(8)	N(22)–Co–N(17)	177.9(7)
Co–As–C(1)	118.5 or 113.8(5)	C(1)–As–O(2)	103.1(7)
Co–As–O(2)	110.9 or 116.7(4)	C(1)–As–C(71)	112.0 or 104.8(7)
Co–As–C(71)	113.8 or 114.0(3)	O(2)–As–C(71)	95.5 or 104.4(8)
O(11)–N(12)–Co	121(1)	O(21)–N(22)–Co	119(1)
O(11)–N(12)–C(13)	124(2)	O(21)–N(22)–C(23)	125(2)
Co–N(12)–C(13)	115(1)	Co–N(22)–C(23)	116(1)
N(12)–C(13)–C(14)	119(2)	N(22)–C(23)–C(24)	119(1)
N(12)–C(13)–C(15)	115(2)	N(22)–C(23)–C(25)	116(1)
C(14)–C(13)–C(15)	126(2)	C(24)–C(23)–C(25)	124.7(4)
C(13)–C(15)–C(16)	127(2)	C(23)–C(25)–C(26)	124.7(4)
C(13)–C(15)–N(17)	113(2)	C(23)–C(25)–N(27)	109(1)
C(16)–C(15)–N(17)	121(2)	C(26)–C(25)–N(27)	126(1)
C(15)–N(17)–Co	115(1)	C(25)–N(27)–Co	117(1)
C(15)–N(17)–O(18)	124(2)	C(25)–N(27)–O(28)	118(2)
Co–N(17)–O(18)	121(1)	Co–N(27)–O(28)	125(1)
As–C(71)–C(72)	116 or 122(1)	As–C(71)–C(76)	119 or 114(1)
C(71)–C(72)–C(73)	114(1)	C(71)–C(76)–C(75)	119(1)
C(72)–C(73)–C(74)	124(2)	C(76)–C(75)–C(74)	117(2)
C(73)–C(74)–C(75)	121(1)	C(75)–C(71)–C(72)	125(1)

TABLE VII. Least-squares Plane.

Atoms defining plane:	Co, N(12), N(17), N(22), N(27)
Eqn. of plane:	$0.731x - 0.679y - 0.063z + 1.547 = 0$
Deviations of atoms from plane (Å):	Co, 0.009(1); N(12), 0.020(16); N(17), −0.024(15); N(22), −0.025(17); N(27), 0.020(17)

The quantity minimized in least-squares refinement was $\Sigma w(|F_o|-|F_c|)^2$ where w is a weighting factor of the form $w = (\sigma(F))^{-2}$. Neutral scattering factors were employed [11] and anomalous dispersion corrections were applied for Co, As and Cl [12]. Computing was performed on PDP8e [13] and IBM 370/155 [14] computers at Simon Fraser University.

The atomic coordinates listed in Table V have been chosen from the equivalent positions to give the geometrically most-reasonable model of the molecule.

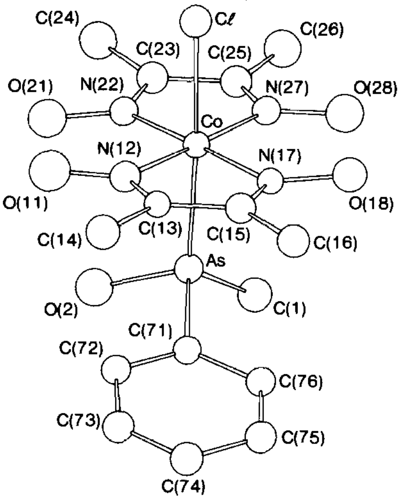

Fig. 1. Projected view of a molecule of *A* showing atomic labelling scheme. Probability ellipsoids are shown at the 50% level. Hydrogen atoms were not located.

In some cases, however, ambiguity remains, giving rise to more than one possible value for bond lengths and angles. On these occasions, both values are given in Table VI. Figure 1 shows the atomic labelling scheme for this 'best-model'. A listing of observed and calculated structure factors has been deposited with the Editor.

Description of the Structure

Even though the structure is disordered, the two images can be identified in most cases. The Co atom is coordinated by two bidentate dmgH or dmg ligands with the Co and four N atoms in one plane (Table VII). A Cl atom at 2.286(3) Å and the As atom of a $(CH_3)(C_6H_5)As$ (O or OH) group (2.311 or 2.320(2) Å) are bonded above and below this plane to complete an irregular octahedral configuration. The Co–N distances average 1.90(2) Å and the chelated N–Co–N angles average 81(1)° which are comparable with the values found for $Co^{III}(dmgH)_2XY$ compounds [5]. The bond lengths and angles within the dmgH ligands were determined with only low precision on account of the disorder, but are in agreement with previously reported dmgH complexes.

Some doubt exists as to the nature of the As-based ligand, which can be either $(CH_3)(C_6H_5)$ As^{III}–OH or $((CH_3)(C_6H_5)As^{V}{=}O)^+$. The As–O distance of 1.76(1) Å is greater than in $[(CH_3)(C_6H_5)As(O)Co^{III}(dmgH)(dmg)P(C_4H_9)_3]_2$-$Co^{II}$, *B*, (1.68 and 1.63(3) Å) [5] and is even longer than in $(C_6H_5)_3As(OH)X$ (X = Cl, Br) (1.70(1) Å) [15] and $[(C_6H_5)_3As–OH\cdots Cl\cdots HO–As(C_6H_5)_3]^+ICl_2^-$ (1.72 Å) [16] which supports the former contention. O(W) appears to be strongly hydrogen-bonded to O(2) (2.57(2) Å) which is also consistent with $As^{III}–OH\cdots H_2O$.

The arsine methyl resonance in the PMR spectrum, however, is very similar to that found in *B* (1.58 *cf.* 1.60 ppm) suggesting that the As^V formalism may be correct. In this case either a proton is lost from one dmgH ligand or the 'water molecule' is, in fact, an hydroxide ion. The latter, however, could not occur in the diphenyl analogue where analysis indicates that there is no 'water molecule' and so can probably be discounted. The oxime O···O intramolecular distances are asymmetric (2.38(2) and 2.53(2) Å), which is what would be expected if one pair were hydrogen-bonded but the other pair were not, *i.e.* (dmgH)(dmg). The ambiguities of the disordered structure, however, preclude this from being proof of the As^V formalism. Furthermore, in the $As^{III}/(dmgH)_2$ model there is some evidence of O(W) being hydrogen-bonded to O(18) (2.78(2) Å) but not to O(11) (2.45(2) Å appears unreasonably short and probably arises from the superposition of the images of the molecule in the disordered structure) which could also account for the asymmetry of the O···O distances.

Results and Discussion

The reactions of Co(II) cobaloximes with organohaloarsines afforded different products than had been produced by Co(I) cobaloximes [5].

The solid Co(II) complexes exhibit magnetic moments in the range 1.7–2.4 B.M. (Table I), close to the values expected for a low-spin d^7 complex having one unpaired electron. Reactions of the Co(II) complexes with $(CH_3)_2AsCl$ and $(CH_3)_2AsI$ give *only* the respective halobasecobaloxime, XCo-$(dmgH)_2B$, as the major product (Tables II and III). However, $(CH_3)(C_6H_5)AsCl$ gives, in addition to the chlorobasecobaloxime, a red-brown air-stable product. Microanalysis indicates the presence of Cl and As and the PMR spectrum exhibits an As-C_6H_5 multiplet, an As-CH_3 singlet and two dmgH-CH_3 singlets. These data imply that the complex contains an -$As(CH_3)(C_6H_5)$(O or OH) moiety [5] bound to the cobalt. This has been confirmed by the X-ray structure determination. The asymmetric arsenic atom would give rise to the two ligand methyl resonances [18, 19].

The analogous reactions with $(C_6H_5)_2AsCl$ again afford the chlorobasecobaloxime and a red-brown air-stable product of formula $C_{20}H_{25}AsClCoN_4O_5$ as determined by microanalyses. The PMR spectrum exhibits singlets corresponding to As-C_6H_5 and dmgH-CH_3. These data suggest a structure for this complex similar to that of *A* with the axially bound arsenic ligand containing an -$As(C_6H_5)_2$(O or OH) moiety.

As in our earlier work [5], complexes with σ bonded organoarsine oxides were obtained *only* for the aryl substituted arsines. The present findings appear to suggest that whether an arsenic derivative is obtained depends on the nature of the arsine and not on the base axially bound to the cobaloxime. Preliminary ESR studies indicate the course of reaction is dependent upon the stability of the arsenic-centered paramagnetic species formed during the reaction.

Acknowledgements

We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this work in the form of operating grants to F.W.B.E. and L.M.M. The assistance of Miss Gaye Eatock is also acknowledged.

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