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Cobalt-59 NMR Spectra of some Cobalt(III) Complexes of Bi- and Poly-arsines

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Cobalt-59 NMR spectra for a variety of cobalt(III) complexes of bi and polydentate phosphorus, arsenic and antimony ligands have recently been reported, and approximate chemical shift ranges characteristic of the various donor sets established [1, 2]. The value for the $CoAs_6{}^{3+}$ moiety was based upon the single example available $[Co\{o\text{-}C_6H_4(AsMe_2)_2\}_3](BF_4)_3$ ($\delta = -320$ ppm relative to $K_3Co(CN)_6$), and was *ca.* 5000 ppm to low frequency of the only previous report [3] in $[Co(triars)_2]I_3$**. As pointed out at the time data on further examples are desirable, and these are provided below.

Experimental

Physical measurements were carried out as described previously [1, 2]. ^{59}Co NMR data were obtained as before [1], and shifts were reported relative to external aqueous $K_3Co(CN)_6$ ($\delta = 0$), using the high frequency positive convention. The following complexes were made by literature methods and had satisfactory analyses: $[Co\{o\text{-}C_6H_4AsMe_2)_2\}_2I_2]I$ [4], $[Co\{o\text{-}C_6H_4(AsMe_2)_2\}_3](BF_4)_3$ [1], $[Co\{MeAs(o\text{-}C_6H_4AsMe_2)_2\}I_3]$ [6], $[Co\{As(CH_2CH_2CH_2AsMe_2)_3\}I_2]ClO_4$ [5].

Bis(1,1,1-tris(dimethylarsinomethyl)ethane)cobalt(III) Tetrafluoroborate

Cobalt(II) acetate hydrate (0.062 g, 0.32 mmol) was dissolved in water (5 cm^3), two drops of glacial acetic acid added and the solution deoxygenated. The ligand (0.29 g, 0.76 mmol) was dissolved in deoxygenated ethanol (15 cm^3) and added to the cobalt acetate solution. The resulting pale orange solution was heated to reflux, cooled and stirred in air overnight. Fluoroboric acid (5 cm^3, 40%) was added, and the solution concentrated at 60 °C *in vacuo,* and the product finally precipitated by adding diethyl ether (15 cm^3). This was collected, washed with ether and dried *in vacuo. Anal.* Calc. for $C_{22}H_{54}As_6B_3CoF_{12}$: C, 24.3; H, 5.0. Found: C, 24.1; H, 5.1%.

Bis(bis(o-dimethylarsinophenyl)methylarsine)cobalt(III) Tetrafluoroborate

Cobalt(II) tetrafluoroborate hydrate (0.41 g, 1.2 mmol) and the ligand (1.1 g, 2.4 mmol) were refluxed in a 1:1 mixture of acetone/water (150 cm^3) for two hours. The yellow–green solution was cooled and then treated with fluoroboric acid (50 cm^3, 45%). Air was bubbled through the solution overnight and the yellow precipitate which formed (0.90 g, 60%) was collected, washed with ether and dried *in vacuo. Anal.* Calc. for $C_{34}H_{46}As_6B_3CoF_{12}$: C, 33.37; H, 3.79. Found: C, 33.24; H, 3.83%.

Trans-bis(2,2'-biphenyldiyl(dimethylarsine)diiodocobalt(III) Iodide

Cobalt(II) iodide hydrate (0.70 g, 2.2 mmol) was dissolved in hot ethanol (40 cm^3) and added to a hot ethanol solution (20 cm^3) of the ligand (0.80 g, 2.2 mmol). The resulting deep red–brown solution was cooled and treated with a slight excess of hydroiodic acid. A dark brown powder formed on standing overnight. The powder was collected and crystallized by slow evaporation from 1:1 ethanol/dichloromethane to yield deep red–brown needles (0.90 g, 70%). *Anal.* Calc. for $C_{32}H_{40}As_4CoI_3$: C, 33.02; H, 3.46; I, 32.71. Found: C, 33.03; H, 3.94; I, 34.64%.

o-Phenylenebisdimethylarsinetris(3-dimethylarsinopropyl)arsinecobalt(III) Tetrafluoroborate

$[Co\{As(CH_2CH_2CH_2AsMe_2)_3\}I_2]ClO_4$ (0.247 g, 0.27 mmol) was dissolved in a 1:1 mixture of ethanol/dichloromethane and the solution deoxygenated. Diarsine (0.076 g, 0.27 mmol) was added and the red–brown solution was refluxed for two hours. The solution was cooled and treated with an excess of fluoroboric acid (25 cm^3, 45%). An orange–brown powder formed on standing overnight. The powder was collected and crystallized by slow evaporation from ethanol to yield dark orange–brown crystals. *Anal.* Calc. for $C_{25}H_{52}As_6B_3CoF_{12}$: C, 26.77; H, 4.67. Found: C, 26.9; H, 4.7%.

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**The formula of the triarsine is unclear due to a typographical error in ref. 3. We assumed in ref. 1 that the complex was $[Co\{MeAs(C_6H_4AsMe_2)_2\}_2]I_3$ the only example described in the literature at that time. However it may have been a complex of $MeAs(CH_2CH_2CH_2AsMe_2)_2$ (personal communication to L.R.H. from Dr R. G. Cunninghame). Since ^{59}Co NMR shifts are relatively insensitive to ligand structure, the conclusions in ref. 1 are unaffected.

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TABLE I. NMR and UV–Vis Spectroscopic Data

Complex	$\delta(^{59}Co)$[a]	E_{max} ($\times 10^3$ cm^{-1})[b]	Solvent
$[Co\{o\text{-}C_6H_4(AsMe_2)_2\}_3](BF_4)_3$	−320	23.6(470)	dmso
	−120[c]	23.5(480)	H_2O
$[Co\{MeC(CH_2AsMe_2)_3\}_2](BF_4)_3$	−190	21.65(595)	dmso
	+120	21.5(530)	H_2O
$[Co\{MeAs(o\text{-}C_6H_4AsMe_2)_2\}_2](BF_4)_3$	−30	23.6(580)	dmso
	+100	23.5(640)	H_2O
$[Co\{As(CH_2CH_2CH_2AsMe_2)_3\{o\text{-}C_6H_4(AsMe_2)_2\}](BF_4)_3$	+195	14.74(119), 17.9sh(550), 20.8(4634)	dmso
'$[Co\{PhAs(CH_2CH_2CH_2AsMe_2)_2\}_2](BF_4)_3$'[d]	+160	20.1(sh)	MeCN
$[Co\{MeAs(o\text{-}C_6H_4AsMe_2)_2\}I_3]$	+4625	16.15(2750), 20.3(3050)	CH_2Cl_2
trans-$[Co\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]I$	+4370	14.8(125), 18.0sh, 21.0(5750)	dmso
	+4290	14.7(120), 17.9sh, 20.8(5100)	CH_2Cl_2
$[Co\{As(CH_2CH_2CH_2AsMe_2)_3\}I_2]ClO_4$	+4060	15.6sh(1000), 21.8(4480)	CH_2Cl_2
trans-$[Co\{2,2'\text{-}(C_6H_4AsMe_2)_2\}_2I_2]I$	+4890	13.9(237), 17.1sh, 20.0(5630)	CH_2Cl_2
	+4830	13.9(222), 17.1sh, 20.1(5500)	dmso

[a] Relative to external $K_3Co(CN)_6$ in H_2O (δ = 0), high frequency +ve convention ±50 ppm. [b] E_{mol} (dm^3 cm^{-1} mol^{-1}) in parentheses. [c] Reported in error as −520 in ref. 1. [d] Not obtained analytically pure.

Results and Discussion

The cobalt-59 NMR chemical shifts and relevant UV–Vis data for four examples of $CoAs_6$ chromophores (including the previously studied [1] $[Co\{o\text{-}C_6H_4(AsMe_2)_2\}_3]^{3+}$ are shown in Table I, and confirm the identification of the characteristic shift range as *ca.* −350 to +200 ppm from the reference $[Co(CN)_6]^{3-}$. The cobalt resonances are single broad ($W_{1/2}$ = *ca.* 12–18000 Hz) lines, the linewidth reflecting the rapid relaxation of the quadrupolar cobalt nucleus (^{59}Co, $I = 7/2$) due to the low symmetry imposed by the steric constraints of the chelate ligands and to chemical shift anisotropy effects at the high magnetic field strength (8.45 *T*) [7]. Although the major influence on $\delta(^{59}Co)$ is the donor set, studies with cobalt(III) complexes of O and N donor ligands have identified small but significant effects due to the solvent, the solute concentration and the temperature [8]. For the present $CoAs_6$ complexes the effects of concentration were negligible compared with the estimated experimental uncertainty in measuring δ (*ca.* ±50 ppm) due to the large linewidth. The complexes were insufficiently soluble in halocarbons, but data for dimethylsulphoxide and water solutions are given in Table I, which shows that δH_2O is up to *ca.* 200 ppm to high frequency of δdmso.

Such solvent dependence is reasonable in view of the 3+ charge in the cations, which is expected to lead to strong interaction with polar solvents. For cobalt(III) ammines significant differences in linewidth as a function of solvent have been ascribed to N–H–solvent H-bonding [9]. Support for this explanation comes from the similar linewidths in the two solvents for the $CoAs_6$ species, where H-bonding is not expected. An attempt to prepare $[Co\{PhAs(CH_2CH_2CH_2AsMe_2)_2\}_2](BF_4)_3$, by the route successfully used for analogues with $o\text{-}C_6H_4(AsMe_2)_2$ and $MeC(CH_2AsMe_2)_3$, produced a dull yellow powder, but this could not be obtained analytically pure. However in MeCN solution this complex had a $\delta(^{59}Co)$ resonance of +160 ppm, good evidence for a $CoAs_6$ cation, and illustrates the value [2] of the characteristic cobalt chemical shift for identifying the cobalt environment even in impure materials.

Table 1 also contains data on further examples of $CoAs_3I_3$ and $CoAs_4I_2$ entities, *cf.* 4902, 5398 ppm in '$[Co(triars)_2]I_3$' indicating that iodide coordination was present in the latter sample in solution and explaining the erroneous shift ascribed to the $CoAs_6$ type [8]. It is noticeable that solvent effects are smaller here than in the $CoAs_6$ system, probably reflecting weaker interaction with the lower charge on the ions.

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