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Coordination Chemistry of Higher Oxidation States. 20.¹ Synthesis and Cobalt-59 NMR Studies of [Co(diphosphine)₃]³⁺, [Co(diarsine)₃]³⁺, and Related Complexes. Crystal Structure of Tris[*o*-phenylenebis(dimethylarsine)]cobalt(III) Tetrafluoroborate-2-Water

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The syntheses of [Co(L-L)₃](BF₄)₃ (L-L = *o*-C₆H₄(PMe₂)₂, *o*-C₆H₄(PMe₂)(AsMe₂), *o*-C₆H₄(AsMe₂)₂, *o*-C₆H₄(PPh₂)₂, Me₂PCH₂CH₂PM₂) are described. The complexes are characterized by ¹H, ³¹P{¹H}, and ⁵⁹Co NMR and electronic spectroscopy. The ⁵⁹Co NMR shifts for the CoP₆³⁺ species are at the lowest frequencies yet observed for Co(III) complexes. ⁵⁹Co NMR data are also reported for a range of related complexes including [Co(L-L)₂X₂]⁺ and [Co(PhP(CH₂CH₂PPh₂)₂)X₃] (X = Cl or Br or sometimes I) and typical chemical shift ranges for the various donor sets identified. The X-ray structure of [Co(*o*-C₆H₄(AsMe₂)₂)₃](BF₄)₃·2H₂O has been determined. Crystals belong to the monoclinic system, space group P2₁/n with *a* = 15.560 (3) Å, *b* = 24.126 (5) Å, *c* = 11.845 (3) Å, β = 106.27 (2)°, and Z = 4. The structure was refined to an *R* value of 0.066 from 4467 observed reflections. The cobalt atom is octahedrally coordinated (Co-As = 2.365 (2)-2.395 (2) Å), and the cation has approximate D₃ symmetry. The detailed conformation of the ligands is dictated by the interligand Me...Me contacts in this crowded ion.

Introduction

Examples of metals in high or medium oxidation states coordinated *only* to phosphorus or arsenic donor ligands are rare.^{2,3} In the case of cobalt(III), despite the very large number of CoN₆³⁺ species, the only examples with heavier donors are a series of phosphites,⁴ [Co(P(OR)₃)₆]³⁺, and the briefly described compounds [Co(*o*-C₆H₄(AsMe₂)₂)₃](ClO₄)₃,⁵ [Co-(Me₂PCH₂CH₂PM₂)₃](ClO₄)₃,⁶ and [Co(MeAs(*o*-C₆H₄AsMe₂)₂)₂](ClO₄)₃.⁷ Here we report a detailed study of a series of these complexes, the X-ray structure of a typical example, and in particular ⁵⁹Co NMR data upon these and related halo complexes. In contrast to extensive studies of cobalt amines, ⁵⁹Co NMR data on complexes containing heavier donor atoms are extremely limited.^{4,8-10}

Experimental Section

Physical measurements were made as described in previous parts of the series. Cobalt(II) acetate hydrate (East Anglia Chemicals) was used as received. ⁵⁹Co NMR spectra were recorded for concentrated solutions of the complexes in the solvents indicated in Table III. Spectra were recorded on a Bruker AM-360 spectrometer at 85.2 MHz at 25 °C, with shifts reported with the high-frequency-positive convention, relative to external aqueous K₃[Co(CN)₆] (δ 0). Aqueous [Co(en)₃]Cl₃ was used as a secondary reference (δ 7130). Spectra were recorded with use of broad-band proton decoupling conditions.

The complexes of the air-sensitive ligands were prepared under a dinitrogen atmosphere, except where described otherwise, with use of Schlenk equipment.

Caution! Many apparently safe perchlorate complexes of cobalt(III) are known, but the safer BF₄⁻ salts are to be preferred. One sample of [Co(Me₂PCH₂CH₂PM₂)₃](ClO₄)₃ prepared in this work exploded violently when touched with a nickel spatula.

Tris(1,2-bis(dimethylphosphino)ethane)cobalt(III) Tetrafluoroborate. Cobalt(II) chloride hexahydrate, CoCl₂·6H₂O (0.13 g, 0.55 mmol), was

dissolved in deoxygenated methanol and the ligand (0.17 g, 1.1 mmol) added. After the mixture was stirred for 20 min, the solvent was removed in vacuo, the residue dissolved in dichloromethane (30 cm³), and chlorine bubbled in for a few minutes. The solvent was again removed in vacuo, the residue dissolved in methanol, and a solution of NaBF₄ (0.2 g) in methanol added. The green precipitate of [Co-(Me₂PCH₂CH₂PM₂)₂Cl₂]BF₄ was dried in vacuo. This product (0.19 g, 0.36 mmol) was dissolved in deoxygenated methanol (30 cm³) to give a green solution, and the diphosphine (0.1 g, 0.66 mmol) was syringed in. After 4 h the yellow solution was treated with excess NaBF₄ (~0.5 g) in methanol to give a yellow precipitate, which was filtered off and dried in vacuo. Anal. Calcd for C₁₈H₄₈B₃CoF₁₂P₆: C, 28.1; H, 6.2; Co, 7.7. Found: C, 28.0; H, 6.2; Co, 7.1.

Tris(*o*-phenylenebis(dimethylarsine))cobalt(III) Tetrafluoroborate. Cobalt(II) acetate hydrate, Co(OAc)₂·H₂O (0.13 g, 0.5 mmol), was dissolved in distilled water (10 cm³)/acetic acid (17 M, 2 drops) and the ligand (0.51 g, 1.8 mmol) in ethanol (20 cm³) added. The resulting brown solution was heated to boiling, cooled, and stirred in air for 24 h. Fluoboric acid (40% aqueous, 5 cm³) was added; the solution was heated to boiling and concentrated in a stream of air. The orange-yellow precipitate was filtered off and dried in vacuo. Anal. Calcd for C₃₀H₄₈As₃B₃CoF₁₂: C, 30.6; H, 4.1; Co, 5.0. Found: C, 30.4; H, 4.2; Co, 4.9.

Tris(*o*-phenylenebis(dimethylphosphine))cobalt(III) tetrafluoroborate was made similarly, except that the product was isolated by removing the solvents in vacuo and crystallizing the orange oil from ethanol/diethyl ether (1:1 v/v) at 0 °C. Anal. Calcd for C₃₀H₄₈B₃CoF₁₂P₆: C, 39.4; H, 5.3. Found: C, 40.0; H, 5.3.

Tris(*o*-(dimethylphosphino)phenyl)dimethylarsine)cobalt(III) tetrafluoroborate was made by a similar route and crystallized after trituration with diethyl ether. Anal. Calcd for C₃₀H₄₈As₃B₃CoF₁₂P₃: C, 34.45; H, 4.6; Co, 5.6. Found: C, 34.6; H, 4.7; Co, 5.9.

Tris(*o*-phenylenebis(diphenylphosphine))cobalt(III) Tetrafluoroborate. [Co(*o*-C₆H₄(PPh₂)₂)₂Cl₂]BF₄¹² (0.14 g, 0.125 mmol) in MeCN (20 cm³) was treated with AgBF₄ (0.050 g, 0.25 mmol) and the ligand (0.058 g, 0.13 mmol), and the mixture was stirred overnight. The solvent was removed in vacuo, the residue extracted with CH₂Cl₂, filtered, and the filtrate pumped down to leave a yellow solid. Anal. Calcd for C₉₀H₇₂B₃CoF₁₂P₆: C, 65.2; H, 4.3; Co, 3.55. Found: C, 65.0; H, 4.2; Co, 3.4.

Most of the cobalt(III) halo complexes were prepared by literature methods,¹¹⁻¹⁶ in several cases as the tetrafluoroborates rather than the

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Table I. Atomic Coordinates for $[\text{Co}(\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2)_3](\text{BF}_4)_3 \cdot 2\text{H}_2\text{O}^a$

atom	x	y	z	atom	x	y	z
Co	2702 (1)	3674 (1)	6094 (1)	C(31)	222 (10)	3876 (7)	4886 (12)
As(1)	4231 (1)	3602 (1)	6099 (1)	C(32)	876 (11)	4092 (7)	7453 (13)
As(2)	3272 (1)	3978 (1)	8077 (1)	C(33)	921 (9)	2934 (5)	6610 (10)
As(3)	2203 (1)	3412 (1)	4065 (1)	C(34)	55 (10)	2785 (7)	6603 (12)
As(4)	2523 (1)	4604 (1)	5373 (1)	C(35)	-71 (11)	2258 (7)	6990 (13)
As(5)	1208 (1)	3677 (1)	6246 (1)	C(36)	598 (10)	1880 (7)	7356 (13)
As(6)	2750 (1)	2740 (1)	6712 (1)	C(37)	1469 (10)	2029 (7)	7340 (12)
C(11)	4724 (10)	4047 (6)	5087 (12)	C(38)	1595 (9)	2548 (5)	6965 (11)
C(12)	4757 (10)	2890 (6)	5888 (12)	C(39)	2796 (9)	2159 (6)	5613 (11)
C(13)	4970 (8)	3789 (5)	7657 (10)	C(310)	3653 (9)	2482 (6)	8115 (11)
C(14)	5894 (10)	3795 (6)	7908 (12)	B(1)	3941 (12)	877 (7)	6694 (14)
C(15)	6409 (11)	3921 (7)	9030 (13)	F(11)	4452 (7)	1352 (5)	7041 (9)
C(16)	6011 (10)	3999 (6)	9915 (12)	F(12)	3761 (8)	862 (5)	5529 (11)
C(17)	5070 (10)	4001 (6)	9666 (12)	F(13)	3147 (8)	937 (5)	6964 (10)
C(18)	4556 (8)	3912 (5)	8520 (10)	F(14)	4371 (8)	438 (5)	7283 (9)
C(19)	2906 (10)	3603 (6)	9329 (11)	B(2)	4128 (11)	4619 (7)	2109 (13)
C(110)	3157 (10)	4744 (6)	8451 (12)	F(21)	4087 (6)	4917 (4)	3067 (7)
C(21)	3532 (10)	5098 (7)	5646 (13)	F(22)	4916 (10)	4714 (6)	1897 (12)
C(22)	1645 (10)	5093 (7)	5722 (13)	F(23)	4029 (8)	4059 (5)	2278 (9)
C(23)	2046 (9)	4566 (6)	3677 (11)	F(24)	3479 (7)	4755 (5)	1139 (9)
C(24)	1864 (10)	5065 (7)	3041 (12)	B(3)	2589 (19)	1718 (12)	854 (23)
C(25)	1512 (12)	5024 (8)	1845 (15)	F(31)	3048 (15)	1415 (9)	349 (18)
C(26)	1296 (11)	4532 (7)	1267 (14)	F(32)	2870 (12)	1674 (8)	1985 (16)
C(27)	1492 (11)	4038 (7)	1906 (13)	F(33)	1744 (11)	1550 (7)	432 (13)
C(28)	1859 (9)	4073 (6)	3146 (11)	F(34)	2757 (10)	2249 (6)	505 (12)
C(29)	2993 (9)	3089 (6)	3275 (12)	O(1)	1151 (10)	3020 (7)	-117 (13)
C(210)	1178 (10)	2934 (6)	3519 (13)	O(2)	4293 (9)	1682 (6)	4063 (11)

^a Carbon atoms are labeled C(*IJ*) where *I* (1–3) indicates the arsine ligand and *J* (1–10) gives the atoms within the ligand. Standard deviations are in parentheses. All values are multiplied by 10⁴.

perchlorates, using cobalt(II) tetrafluoroborate hydrate. Satisfactory analytical data were obtained for all samples.

Diiodobis(o-phenylenebis(dimethylarsine)cobalt(III) iodide. An MeCN solution (10 cm³) of CoI₂·6H₂O (0.1 g, 0.24 mmol) was treated with the ligand (0.14 g, 0.5 mmol) and stirred for 0.5 h. Hydriodic acid (2 cm³, 65%) was added and the solution stirred in air for 2 h. The reddish black precipitate was filtered off and dried in vacuo. Anal. Calcd for C₂₀H₃₂As₄CoI₃: C, 23.7; H, 3.2; Co, 5.8. Found: C, 23.9; H, 3.2; Co, 5.2.

[Co(Me₂PCH₂CH₂PMe₂)₂I] was prepared similarly. Anal. Calcd for C₁₂H₃₂CoI₃P₄: C, 19.5; H, 4.3; Co, 8.0. Found: C, 19.8; H, 4.2; Co, 7.0.

[Co(o-C₆H₄(PMe₂)(AsMe₂)₂)Cl₂]BF₄ was made as described for the diphosphine analogue.¹⁶ Anal. Calcd for C₂₀H₃₂As₂BCl₂CoF₄P₂: C, 34.3; H, 4.6. Found: C, 35.1; H, 4.6.

X-ray Data and Structural Solution. Orange crystals of [Co(o-C₆H₄(AsMe₂)₂)₃](BF₄)₃·2H₂O were grown from a hot saturated aqueous solution by slow cooling. Photographic X-ray examination established the crystal system and approximate cell dimensions. Anal. Calcd: C, 29.7; H, 4.3. Found: C, 29.5; H, 4.3. Accurate cell dimensions were obtained from 25 accurately centered reflections on an Enraf-Nonius CAD-4 diffractometer and with Mo K α radiation.

The crystals are monoclinic, *a* = 15.560 (3) Å, *b* = 24.126 (5) Å, *c* = 11.845 (3) Å, β = 106.27 (2)°, *V* = 4268.5 Å³, mol wt = 1213.6 for C₃₀H₅₂As₆B₃CoF₁₂O₂, *D*_{calcd} = 1.888 g cm⁻³, *D*_{measd} = 1.88 (2) g cm⁻³, and *Z* = 4, space group *P*2₁/*n* (No. 14) (systematic absences: *h*0*l*, *h* + *l* ≠ 2*n*; 0*kl*, *k* ≠ 2*n*), *F*(000) = 2384, μ (Mo K α) = 50.59 cm⁻¹.

Data were collected from a room-temperature crystal (0.55 × 0.25 × 0.07 mm) mounted in a thin-wall capillary with Mo K α radiation (λ = 0.7107 Å) and graphite monochromator. A total of 7969 reflections were recorded (1.5 < θ < 25°) for *hkl* (*h* (0–18), *k* (0–28), *l* (–14 to +14)). There was no change in the three check reflections during the experiment. A ψ scan empirical absorption correction was applied (transmission: max, 100.0%; min, 42.8%) together with the usual *Lp* factor, and after removal of systematically absent reflections and averaging (*R*_{int} = 0.057) there remained 7477 unique reflections. Omitting reflections with *F* < 3 σ (*F*) (3010) left 4467 measurements used in the analysis.

E statistics supported the centrosymmetric space group, and the centrosymmetric direct-methods strategy in SHELX¹⁷ (EES) yielded the positions of Co and As from the *E* map of the most probable solution. Repeated structure factor and electron density syntheses located the

Table II. Selected Bond Distances (Å) and Angles (deg)

Co–As(1)	2.384 (2)	As(1)···As(2)	3.240 (2)
Co–As(2)	2.381 (2)	As(3)···As(4)	3.238 (2)
Co–As(3)	2.395 (2)	As(5)···As(6)	3.230 (2)
Co–As(4)	2.388 (2)		
Co–As(5)	2.382 (2)	As···As (interligand)	3.332 (2)–3.515 (2)
Co–As(6)	2.365 (2)		
As–C min	1.91 (1)	C–C min	1.34 (2)
max	1.96 (1)	max	1.42 (2)
mean	1.93 (1)	mean	1.38 (2)
As(1)–Co–As(2)	85.7 (1)	As(2)–Co–As(6)	91.0 (1)
As(1)–Co–As(3)	91.5 (1)	As(3)–Co–As(4)	85.2 (1)
As(1)–Co–As(4)	94.9 (1)	As(3)–Co–As(5)	91.6 (1)
As(1)–Co–As(6)	89.1 (1)	As(3)–Co–As(6)	91.8 (1)
As(2)–Co–As(4)	92.2 (1)	As(4)–Co–As(5)	90.3 (1)
As(2)–Co–As(5)	91.5 (1)	As(5)–Co–As(6)	85.8 (1)
Co–As–C(H ₃) min	113.5 (4)	Co–As–C(phenyl) min	107.4 (4)
max	122.1 (4)	max	108.8 (4)
mean	120 (2)	mean	108.1 (4)
As–C–C min	117 (1)	C–C–C min	117 (2)
max	122 (1)	max	124 (2)
mean	120 (1)	mean	120 (2)
B–F min	1.28 (3)	F–B–F min	102 (2)
max	1.39 (3)	max	117 (2)
mean	1.35 (4)	mean	109 (3)

remaining atoms (C, B, F), at which stage the oxygen atoms were identified. An electron density synthesis at a later stage of refinement showed the positions of a number of H atoms of the cation, and these were introduced into the model in calculated positions (*d*(C–H) = 1.0 Å). All methyl H atoms were given a common refined temperature factor as were the aromatic protons. Full-matrix least-squares refinement converged to *R* = 0.066 (*R*_w = 0.076) (*R* = $\sum ||F_o| - |F_c|| / \sum |F_o|$, *R*_w = $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, 290 parameters, anisotropic (Co, As) and isotropic (F, O, C, B, H) thermal parameters, $w = 1/(\sigma^2(F) + 0.0005F^2)$, maximum shift/error = 0.8, reflections/parameters = 15.4). The isotropic temperature factors on some of the F atoms were rather large, suggesting either large librational motion in the solid or some positional disorder. A final difference electron density synthesis showed all features in the range 1.41 to –0.98 e Å⁻³, with the largest peaks close to F atoms of the BF₄⁻ groups. This represents a small fraction of an F atom, and attempts to find other (disordered) BF₄⁻ anions from among these small

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Table III. NMR and UV-Visible Spectroscopic Data

complex	$\delta(^1\text{H})^a$	$\delta(^{31}\text{P}\{^1\text{H}\})^b$	$\delta(^{59}\text{Co})^{c,d}$	$E_{\text{max}}/10^3 \text{ cm}^{-1}$ ($\epsilon_{\text{mol}}/\text{dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$)	solvent ^e
[Co(<i>o</i> -C ₆ H ₄ (PMe ₂) ₂) ₃](BF ₄) ₃	2.0, 2.3	38.8	-2600 (9000)	27.6 (810)	Me ₂ SO
[Co(<i>o</i> -C ₆ H ₄ (PMe ₂)(AsMe ₂) ₂) ₃](BF ₄) ₃	1.6-2.0 ^f	50.0, 51.0, 52.1 ^f	-910 (14 000)	23.4 (575)	Me ₂ SO
[Co(<i>o</i> -C ₆ H ₄ (AsMe ₂) ₂) ₃](BF ₄) ₃	1.95 (s), 2.25 (s)		-520 (6000)	23.6 (412)	H ₂ O
[Co(Me ₂ PCH ₂ CH ₂ PMe ₂) ₃](BF ₄) ₃	1.90, 1.95	45.0	-320	23.6 (470)	Me ₂ SO
[Co(<i>o</i> -C ₆ H ₄ (PPh ₂) ₂) ₃](BF ₄) ₃		36.8	-2530 (10 000)	26.3 (690)	Me ₂ SO
<i>trans</i> -[Co(<i>o</i> -C ₆ H ₄ (PMe ₂) ₂) ₂ Cl ₂](BF ₄) ₃	1.85	53.1	-2120 (11 000)	25.6 (1000)	CH ₂ Cl ₂
<i>trans</i> -[Co(<i>o</i> -C ₆ H ₄ (PMe ₂)(AsMe ₂) ₂) ₂ Cl ₂](BF ₄) ₃	1.7 vbr	60.9	+1710 (16 500)	17.8 (63), 26.9 (3530)	Me ₂ SO
<i>trans</i> -[Co(<i>o</i> -C ₆ H ₄ (PMe ₂) ₂) ₂ Cl ₂](ClO ₄) ₃	1.8	62.0	+2490 (19 500)	16.4 (76), 26.3 (2750)	Me ₂ SO
<i>trans</i> -[Co(<i>o</i> -C ₆ H ₄ (PPh ₂) ₂) ₂ Cl ₂](ClO ₄) ₃		47.4	+1740 (14 000)	17.9 (102), 27.2 (3240)	MeCN
<i>trans</i> -[Co(<i>o</i> -C ₆ H ₄ (PPh ₂) ₂) ₂ Cl ₂](ClO ₄) ₃		47.4	+2220 (15 000)	16.0 (155), 25.3 (34 000)	CH ₂ Cl ₂
<i>trans</i> -[Co(Ph ₂ PCH=CHPPh ₂) ₂ Cl ₂](ClO ₄) ₃		32.2	+2250 (20 000)	15.9 (130), 22.7 (7800), 25.8 (25 000)	CH ₂ Cl ₂
<i>trans</i> -[Co(Me ₂ PCH ₂ CH ₂ PMe ₂) ₂ Cl ₂](BF ₄) ₃	1.5	53.3	+1660 (14 000)	17.5, 25.6	Me ₂ SO
<i>trans</i> -[Co(<i>o</i> -C ₆ H ₄ (PPh ₂) ₂) ₂ Br ₂](ClO ₄) ₃		42.2	+2750 (14 000)	14.95 (135), 25.3 (19 000)	CH ₂ Cl ₂
<i>trans</i> -[Co(Me ₂ PCH ₂ CH ₂ PMe ₂) ₂ I ₂](ClO ₄) ₃	1.9	49.2	+2830 (13 000)	15.6 (45), 21.6 (9910), 27.9 (17 360)	Me ₂ SO
<i>cis</i> -[Co(P(CH ₂ CH ₂ PPh ₂) ₃)Cl ₂](ClO ₄) ₃		116.3, 49.0, 46.6	+2360 (16 000)	19.45 (2025)	CH ₂ Cl ₂
[Co(PhP(CH ₂ CH ₂ PPh ₂) ₂)Cl ₃](ClO ₄) ₃		89.2, 44.0	+2100 (16 000)	15.3 (sh), 19.1 (1425), 22.5 (sh)	CH ₂ Cl ₂
[Co(PhP(CH ₂ CH ₂ PPh ₂) ₂)Br ₃](ClO ₄) ₃		100.0, 54.2	+2430 (16 000)	14.45 (sh), 18.05 (1670), 24.5 (sh)	CH ₂ Cl ₂
<i>trans</i> -[Co(<i>o</i> -C ₆ H ₄ (AsMe ₂) ₂) ₂ Cl ₂](ClO ₄) ₃	1.9 (s)		+2830 (15 000)	16.4 (300), 26.0 (5210)	Me ₂ SO
<i>cis</i> -[Co(<i>o</i> -C ₆ H ₄ (AsMe ₂) ₂) ₂ Cl ₂](ClO ₄) ₃	2.0 (s), 1.8 (s), 1.4 (s), 1.2 (s)		+2860 (12 000)	20.3 (630), 25.0 (sh)	Me ₂ SO
<i>trans</i> -[Co(<i>o</i> -C ₆ H ₄ (AsMe ₂) ₂) ₂ Br ₂](ClO ₄) ₃	1.9 (s)		+2880 (14 000)	15.7 (70), 23.7 (750)	Me ₂ SO
<i>trans</i> -[Co(<i>o</i> -C ₆ H ₄ (AsMe ₂) ₂) ₂ I ₂](ClO ₄) ₃	1.8 (s)		+4370 (15 000)	14.8 (126), 18.0 (sh), 21.0 (5750)	Me ₂ SO
<i>cis</i> -[Co(As(CH ₂ CH ₂ CH ₂ AsMe ₂) ₃)Cl ₂](ClO ₄) ₃	1.70 (s), 1.67 (s), 1.55 (s)		+2820 (14 500)	18.4 (740)	H ₂ O

^a Methyl resonances only; complex partially resolved multiplets except where marked (s) (=singlet). ^b Relative to 85% H₃PO₄. ^c ±50 ppm. Positive shifts to high frequency of K₃Co(CN)₆ in H₂O. ^d Line width at half-height given in parentheses (±500 Hz). ^e ¹H NMR run in deuterated analogue. ^f Mixture of isomers (*mer* and *fac* arrangement of Me₂P- and Me₂As-groups in the unsymmetrical ligand).

peaks were not successful. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from ref 18 (Co, As) and SHELX¹⁷ (F, O, C, B, H), and all calculations were performed with the computer programs SHELX,¹⁷ ORTEP,¹⁹ and XANADU.²⁰

The final non-hydrogen atomic positions are given in Table I, and the hydrogen positions, thermal parameters, and structure factors are available as supplementary material.

Results and Discussion

The [Co(L-L)₃]Y₃ complexes (L-L = *o*-C₆H₄(PMe₂)₂, *o*-C₆H₄(PMe₂)(AsMe₂)₂, *o*-C₆H₄(AsMe₂)₂; Y = ClO₄, BF₄) are best obtained by modification of the method of Burstall and Nyholm,⁵ which consists of the reaction of the ligand (L-L) with cobalt(II) acetate in alcohol, followed by air oxidation. The complexes were isolated as BF₄⁻ salts rather than as the potentially explosive perchlorates. If insufficient L-L is present, cobalt(III) acetate complexes are produced. The [Co(L-L)₃]³⁺ complexes are also produced by air oxidation of mixtures of [Co(H₂O)₆](BF₄)₂ and L-L in EtOH with added HBF₄, but the isolation of pure products from the mixture of complexes produced is difficult. Bosnich et al.²¹ showed that, for the *o*-C₆H₄(AsMe₂)₂-Co(ClO₄)₂·6H₂O system, a number of products including dioxygen adducts and aquo and solvent complexes could be isolated depending upon the conditions, and it is likely that some of these were produced in our reactions. [Co(Me₂PCH₂CH₂PMe₂)₃](BF₄)₃ was obtained from [Co(Me₂PCH₂CH₂PMe₂)₂Cl₂](BF₄)₃ and Me₂PCH₂CH₂PMe₂ in the absence of oxygen.⁶ A ⁵⁹Co NMR spectrum of [Co(*o*-C₆H₄(PPh₂)₂)₂Cl₂](ClO₄)₃ in CH₂Cl₂ containing excess ligand showed resonances due both to the starting material and to [Co(*o*-C₆H₄(PPh₂)₂)₃]³⁺ (below), but the latter could be isolated pure only after displacement of the equilibrium by removal of the

chloride with AgBF₄. Attempts to isolate analogues with *cis*-Ph₂PCHCHPPh₂ or PhP(CH₂CH₂PPh₂)₂ were unsuccessful, nor could we prepare [Co(*o*-C₆H₄(PMe₂)(NMe₂)₂)₃]³⁺, although [Co(H₂NCH₂CH₂PMe₂)₃]³⁺ is known.²² In the last case it is probable that the steric hindrance of the dimethylamino groups is responsible.

The [Co(L-L)₃](BF₄)₃ compounds are air-stable solids, soluble in polar solvents such as dimethyl sulfoxide (Me₂SO), less soluble in MeCN, and only slightly soluble in chlorocarbons ([Co(*o*-C₆H₄(PPh₂)₂)₃](BF₄)₃ differs in dissolving easily in CH₂Cl₂). [Co(Me₂PCH₂CH₂PMe₂)₃](ClO₄)₃ is reported⁶ to be oxygen-sensitive both in solution and in the solid state; our studies suggest that although Me₂SO solutions decompose at varying rates, probably due to Co(II) catalysis,¹⁴ the pure solid BF₄⁻ salt is air-stable. The complexes of *o*-C₆H₄(AsMe₂)₂, *o*-C₆H₄(PMe₂)(AsMe₂)₂, and Me₂PCH₂CH₂PMe₂ react rapidly with dry HCl in Me₂SO, LiBr in Me₂SO, or Cl₂ in MeCN to form *trans*-[Co(L-L)₂X₂]⁺, but [Co(*o*-C₆H₄(PMe₂)₂)₃]³⁺ is particularly robust and is only slowly attacked by these reagents at room temperature. The structure of [Co(*o*-C₆H₄(AsMe₂)₂)₃](BF₄)₃ (as the dihydrate) was confirmed by an X-ray study (below), and comparison of the spectroscopic data (Table III) shows that octahedral (CoP₆, CoAs₆, or CoP₃As₃) moieties are present in all the species.

The electronic spectra of [Co(L-L)₃]³⁺ exhibit the ¹A_{1g} → ¹T_{1g} band at high energy (Table III), consistent with the high ligand field strength of diphosphines and diarsines toward later transition metals.²³ All the complexes of the methyl-substituted ligands show two methyl resonances in the ¹H NMR spectra (1:1 intensity), which show further multiplet splittings in the diphosphines. The X-ray study shows that, for each EMe₂ (E = P, As) group, one Me group points into a type A face (see below) of the octahedron and the other lies over the *o*-C₆H₄ backbone of a second ligand, accounting for the different chemical shifts.

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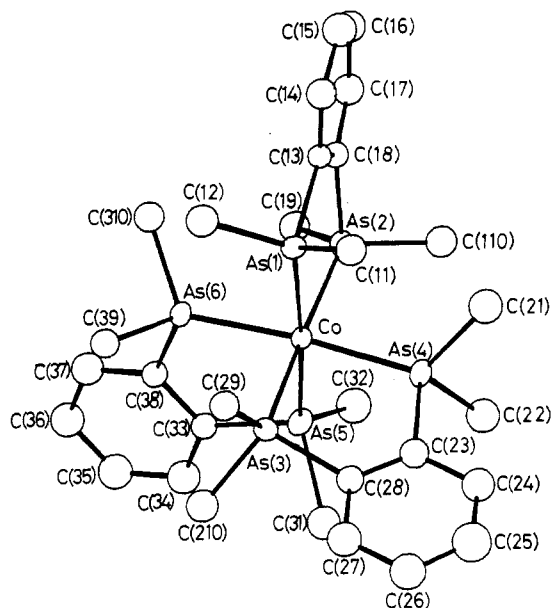


Figure 1. Cation in $[\text{Co}(\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2)_3](\text{BF}_4)_3 \cdot 2\text{H}_2\text{O}$, showing the atom-numbering scheme, with thermal ellipsoids drawn with 40% probability boundary surfaces. Hydrogen atoms have been omitted for clarity.

The $^{31}\text{P}\{^1\text{H}\}$ spectra of the diphosphine complexes show single rather broad (~ 50 Hz) resonances (Table III). Although $[\text{Co}(\text{P}(\text{OMe})_3)_6]^{3+}$ shows a clear eight-line pattern ($^1J_{\text{Co-P}} = 443$ Hz) due to coupling to ^{59}Co ($I = 7/2$, 100%),⁴ reduction of the symmetry from O_h to D_3 in the present cases is apparently sufficient to cause rapid relaxation and loss of coupling.

Structure of $[\text{Co}(\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2)_3](\text{BF}_4)_3 \cdot 2\text{H}_2\text{O}$. A view of the cation and the atom-labeling scheme used are shown in Figure 1, and selected bond distances and angles are shown in Table II. The six Co-As distances (2.365 (2)–2.395 (2) Å) are significantly longer than those in $[\text{Co}(\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2)_2(\text{ClO}_4)_2]^{24}$ (2.300 (3), 2.295 (3) Å) and $[\text{Co}(\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2)_2\text{Cl}_2]\text{X}$ (2.333 (3), 2.336 (3) Å, X = Cl;²⁵ 2.338 (3), 2.344 (3) Å, X = ClO_4).²⁶ The geometry of the arsine ligand is unexceptional and has been determined in a number of structures.²⁷ As noted before²⁵ the Co-As-C(H₃) angle is about 120° (see Table II) and the C(H₃)-As-C(H₃) angle about 100°, presumably due to steric forces. Construction of a scale model shows a very crowded cation with approximate D_3 symmetry with the detailed conformation determined by interligand contacts between the methyl groups. The intraligand C(H₃)...C(H₃) distances are 2.94 (2)–3.01 (2) Å while the shortest interligand C(H₃)...C(H₃) is 3.32 (2) Å. The As₆ octahedron has two types of triangular face: type A (three As atoms from different ligands) and type B (two As atoms from one ligand and one from another). Six methyl groups are associated with type A faces, and each has three short C...C contacts (3.46–3.76 Å). The remaining six methyl groups each have two short C...C contacts (3.32–3.72 Å). There are no further C...C distances < 4 Å. The dihedral angles between the CoAs₂ plane and the associated *o*-phenylene backbone are 4.8, 6.7, and 9.2° for the three ligands. The tetrafluoroborate anion is well characterized in many crystals and is frequently disordered. The rather large range of bond distances and F–B–F angles may result from rather large librational motion or disorder.

^{59}Co NMR Spectra. The ^{59}Co NMR spectra of $[\text{Co}(\text{L-L})_3]^{3+}$ consist (Table III) of very broad lines ($w_{1/2} \sim 6000$ – 14000 Hz) with no resolved coupling to the donor atoms. The lower symmetry of the halo complexes results in even broader lines, in both series the large line widths reduce the precision with which the chemical

shifts (δ) can be measured, and error limits of up to ± 50 ppm on the shifts in Table III are likely. The tris(diphosphine) complexes have the lowest frequency resonances yet reported for Co(III) complexes and lie in the range previously typical of Co(0) or Co(–1) carbonyls.^{8,9} It is well established^{8–10} that $\delta(^{59}\text{Co})$ is dominated by the paramagnetic term (σ_p)

$$\sigma_p \propto \langle r^{-3} \rangle_{3d} / \Delta E(^1A_{1g} \rightarrow ^1T_{1g}) \quad (O_h \text{ symmetry})$$

where r is the radius of the d orbitals and $\Delta E(^1A_{1g} \rightarrow ^1T_{1g})$ the energy of the lowest spin-allowed electronic spectral band. Furthermore, plots of $\delta(^{59}\text{Co})$ vs. the $^1A_{1g} \rightarrow ^1T_{1g}$ transition energy give linear regressions, the slopes differing for first-row (C, N, O) and heavier (S, Se, P, As) donors. The data in the present study combined with literature data^{8,9} for $[\text{Co}(\text{P}(\text{OR})_3)_6]^{3+}$ and CoS_6 give a slope of $\sim 260 \text{ cm}^{-1}$. The previously reported plot, necessarily using $[\text{Co}(\text{P}(\text{OR})_3)_6]^{3+}$ as the CoP_6 type, had a slope of $\sim 230 \text{ cm}^{-1}$,⁹ while with the CoS_6 and the (erroneous) CoAs_6 data, along with the zero intercept from the CoN_6 , CoO_6 , and CoC_6 data, gave a slope of $\sim 310 \text{ cm}^{-1}$.⁸ The extrapolation of these plots to yield "absolute" shieldings for the cobalt nuclei has been criticized recently,²⁸ and the procedure is clearly subject to large errors. Juranic¹⁰ has reported a different approach in which a single regression for all donors is achieved by incorporating a term reflecting the nephelauxetic parameter β_{35} . However, for phosphine and arsine complexes, the presence of low-lying charge-transfer bands prevents an analysis of the electronic spectra to obtain B (the Racah parameter), and hence β_{35} cannot be calculated. The ^{59}Co resonance of $[\text{Co}(\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2)_3]^{3+}$ (~ 320 ppm) is in fair agreement with Juranic's value (~ 100 ppm)¹⁰ but is very different from the values (4902, 5398 ppm) reported²⁹ for $[\text{Co}(\text{MeAs}(\text{o-C}_6\text{H}_4\text{AsMe}_2)_2)_2\text{I}_3]$; generally, $\delta(^{59}\text{Co})$ shifts are fairly insensitive to ligand structure or substituents. However, the value of 4370 ppm observed for *trans*- $[\text{Co}(\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2)_2\text{I}_2]^+$ strongly suggests that the reported shifts for the triarsine complex refer to a $\text{CoAs}_4\text{I}_2^+$ or a CoAs_3I_3 entity rather than CoAs_6^{3+} . In the absence of any other data the triarsine shifts were taken as typical of CoAs_6^{3+} in the standard texts,^{8,9} but it seems that the correct range is some 5000 ppm more negative, and data on further examples are desirable. The chemical shift of the $\text{CoP}_3\text{As}_3^{3+}$ group in $[\text{Co}(\text{o-C}_6\text{H}_4(\text{PMe}_2)(\text{AsMe}_2))_3]^{3+}$ (~ 910 ppm) is consistent with the lower frequency shift range for arsenic donors.

The ^{59}Co NMR data for various halo complexes also revealed characteristic ranges for different donor sets. Thus, for $\text{CoP}_4\text{Cl}_2^+$ where P_2 is a methyl-substituted diphosphine, δ is ~ 1600 – 1800 ppm, whereas phenyl-substituted diphosphines have larger chemical shifts, typically in the range 2100–2400 ppm. For complexes of type $\text{CoAs}_4\text{Cl}_2^+$ ($\text{As}_2 =$ methyl-substituted diarsine), δ is ca. 2800 ppm. The shifts of *cis*- and *trans*- $[\text{Co}(\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2)_2\text{Cl}_2]^+$ are the same within experimental error, although the *cis* complex has the smaller line width as expected. The effect of replacing chloride by bromide is less clear; in $[\text{Co}(\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2)_2\text{X}_2]^+$ (X = Cl or Br) the shifts are not significantly different (cf. $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{X}_2]^{30}$), but in $[\text{Co}(\text{o-C}_6\text{H}_4(\text{PPh}_2)_2)_2\text{X}_2]^+$ and $[\text{Co}(\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2)\text{X}_3]$, the bromides have higher frequency resonances, perhaps due to increasing steric crowding weakening the Co–P interaction. Iodo complexes have markedly higher frequency resonances.

Summary

^{59}Co NMR data have been obtained for a variety of Co(III) complexes containing phosphorus and arsenic donor ligands, and the shifts were found to be characteristic of the donor set present but insensitive to the stereochemical arrangement of the donors. Generally, the observed trends parallel those found with nitrogen donor ligands but the resonances are at substantially lower frequencies.

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Supplementary Material Available: Thermal parameters for non-hydrogen atoms (Tables S-IV and S-V), calculated atomic coordinates for

H atoms (Table S-VI), bond distances and angles for the cation and BF_4^- anions (Table S-VII), and a packing diagram (5 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (25 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

Contribution from the Laboratoire de Spectrochimie des Eléments de Transition, UA 420, Université Paris-Sud, 91405 Orsay, France

Spin State of Cobalt(II) in Five- and Six-Coordinate Lewis Base Adducts of (*N,N'*-Ethylenebis(3-carboxysalicylaldiminato))cobalt(II). New Spin-Crossover Complexes

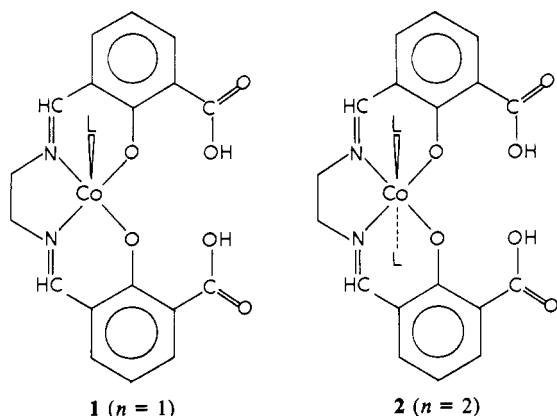
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The spin-state behavior of cobalt(II) was investigated by variable-temperature magnetic susceptibility measurements and EPR spectroscopy in a set of compounds of the type $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})\text{L}_n$, where $\text{H}_2(\text{fsa})_2\text{en}^{2-}$ is the phenolic dianion of the Schiff base *N,N'*-ethylenebis(3-carboxysalicylalimine) and L is a substituted pyridine. These complexes were found to display a wide range of magnetic properties. Concerning the five-coordinate ($n = 1$) species, the L = 2-Mepy adduct admits a spin-quartet ground state, and its magnetic behavior can be described by using a rhombic spin Hamiltonian ($(D^2 + 3E^2)^{1/2} = 16.7 \text{ cm}^{-1}$, $g = 2.04$) with additional temperature-independent paramagnetism ($N\alpha = 211 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$); the L = 3-OHpy adduct is likely to undergo a kinetically controlled $S = 3/2 \leftrightarrow S = 1/2$ crossover, while retaining an essentially high-spin character; finally, the L = 4-Mepy adduct is in the low-spin state, even at room temperature. Concerning the six-coordinate ($n = 2$) species, compounds with L = 3-Mepy, 3-NH₂py, and 3,5-Me₂py present a predominant high-spin behavior. Assuming the existence of a spin admixing between the quartet ground state ($^4A_{2g}$) and the first excited doublet state ($^2A_{1g}$), the energy gaps between these two states (Δ) and between the Kramers doublets arising from $^4A_{2g}$ (δ) could be estimated as $\Delta \sim 550\text{--}600 \text{ cm}^{-1}$ and $\delta \sim 95\text{--}115 \text{ cm}^{-1}$. Compounds with L = 4-Mepy and L = 4-*t*-Bupy exhibit a $S = 3/2 \leftrightarrow S = 1/2$ crossover. In the first case, this transition is of the continuous type and thermodynamic calculations show, as expected, that cooperative effects are negligible; an upper limit of 194 cm^{-1} is calculated for Δ , the ground state being then a spin doublet. By contrast, the spin conversion of the latter complex is one of the most abrupt ever observed in Co(II) complexes and presents a hysteresis of ca. 16 K, being centered at $T_c \downarrow = 138 \text{ K}$ and $T_c \uparrow = 154 \text{ K}$ for decreasing and increasing temperatures, respectively. The effect of the nature of apical ligands on the spin state of Co(II) is discussed in terms of σ -donor ability, orientation of the pyridine ring, and steric requirements.

Introduction

The family of solid cobalt(II) complexes of the type $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})\text{L}_n$ —where $\text{H}_2(\text{fsa})_2\text{en}^{2-}$ is the phenolic dianion of the Schiff base *N,N'*-ethylenebis(3-carboxysalicylalimine) and n the number of axial ligands L—is expected to provide the possibility, through the choice of L, for selecting the metal ion electronic ground state.



Preliminary results^{1,2} have shown that five- (see **1**) or/and six-coordinate (see **2**) adducts could be obtained, according to the nature of L. This property, owing to the fact that the square-planar complex (*N,N'*-ethylenebis(salicylaldiminato))cobalt(II),

or Co(salen), is known to never bind more than one axial Lewis base, may be accounted for by the equatorial ligand field lowering due to the presence of an electron-attracting carboxylic group on each aromatic ring of the Schiff base. The magnetic behavior of $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})\text{L}^{1,2}$ and $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})\text{L}_2^{1-3}$ species clearly suggests that, in both kinds of compounds, the lowest high-spin ($S = 3/2$) and low-spin ($S = 1/2$) states are very close in energy. Indeed, though the $\chi_M T$ products (χ_M = molar magnetic susceptibility) related to $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(\text{EtOH})^1$ and $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(4\text{-}t\text{-Bupy})^2$ (EtOH = ethanol, 4-*t*-Bupy = 4-*tert*-butylpyridine) follow, in a wide temperature range, a Curie law characteristic of the low-spin form, the slight increase of $\chi_M T$ with temperature that is observed above $\sim 200 \text{ K}$ for the former compound and $\sim 250 \text{ K}$ for the latter seems to indicate the beginning of an occupation of excited high-spin levels. Likewise, in the sixfold coordinated complexes, the ligand field appears to approximate the conditions suitable for the pairing of electrons: in $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(3\text{-Mepy})_2^2$, cobalt(II) was found to retain an essentially high-spin state from 300 to 4 K, while in $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(\text{py})_2^{1,2}$ and $\text{Co}(\text{H}_2(\text{fsa})_2\text{en})(\text{H}_2\text{O})_2^{1,3}$ it exhibits thermally induced quartet \leftrightarrow doublet spin transitions. It is worth noting that these transitions are very abrupt, in contrast with those previously reported for cobalt(II) complexes, which are generally of the continuous type.⁴⁻¹³

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