The Synthesis and Properties of Tris(diphosphine)- and Bis(triphosphine)-chromium(III) Cations and Analogues with Arsenic and Sulphur Donor Ligands

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The reaction of $[Cr(thf)_6][BF_4]_3$ (thf = tetrahydrofuran) with bidentate (L^2) and tridentate (L^3) ligands in thf produces $[Cr(L^2)_3][BF_4]_3$ [L^2 = $Ph_2PCH_2CH_2PPh_2$, $Me_2PCH_2CH_2PMe_2$, o-$C_6H_4(PMe_2)_2$, o-$C_6H_4(AsMe_2)_2$, *cis*-$Ph_2AsCH{=}CHAsPh_2$, or *cis*-$MeSCH{=}CHSMe$] and $[Cr(L^3)_2][BF_4]_3$ [L^3 = $PhP(CH_2CH_2PPh_2)_2$, $MeAs(CH_2CH_2CH_2AsMe_2)_2$, $MeC(CH_2PPh_2)_3$, $MeC(CH_2AsMe_2)_3$, or $S(CH_2CH_2CH_2SMe)_2$] respectively. On the basis of their i.r. and electronic spectra all contain octahedral chromium(III) $CrE_6{}^{3+}$ (E = P, As, or S) type cations. $[Cr(Me_2PCH_2CH_2PMe_2)_3][BF_4]_3$ undergoes a reversible electrochemical one-electron reduction in dimethyl sulphoxide solution.

Chromium(III) complexes of types $[Cr(L^1)_6]Y_3$, $[Cr(L^2)_3]Y_3$, and $[Cr(L^3)_2]Y_3$, where L^1, L^2, and L^3 are respectively mono-, bi-, and tri-dentate nitrogen donor ligands and Y = ClO_4, BF_4, or halide, are readily prepared.[1] Typical examples are those with L^1 = MeCN or $MeNH_2$, L^2 = $H_2NCH_2CH_2NH_2$ or 2,2′-bipyridyl (bipy),[2] and L^3 = $HN(CH_2CH_2NH_2)_2$ [3] or $EtC(CH_2NH_2)_3$.[4] Analogues with phosphorus, arsenic, or sulphur ligands have not been reported, and attempts [5] to prepare, for example, $[Cr\{o\text{-}C_6H_4(AsMe_2)_2\}_3][ClO_4]_3$ directly from $[Cr(H_2O)_6][ClO_4]_3$ and the diarsine have failed. Indeed, chromophores of the type $[ME_6]^{n+}$ (M = 3*d* metal, E = P, As, or S) are generally rare, although, a limited number of rather unstable complexes have been obtained with the other common trivalent ions Fe^{III} and Co^{III}, *e.g.* $[Fe(L^2)_3][ClO_4]_3$ [L^2 = o-$C_6H_4(AsMe_2)_2$ or *cis*-$Me_2AsCH{=}CHAsMe_2$ [6]], $[Co(L^2)_3][ClO_4]_3$ [L^2 = $Me_2PCH_2CH_2PMe_2$ [7] or o-$C_6H_4(AsMe_2)_2$ [8]], and $[Co(L^3)_2][ClO_4]_3$ [L^3 = $MeAs(o\text{-}C_6H_4\text{-}AsMe_2)_2$].[9]

Chromium(0) complexes $[Cr(L^2)_3]$ are known, the most studied being $[Cr(Me_2PCH_2CH_2PMe_2)_3]$, originally made by $LiAlH_4$ or sodium dihydronaphthylide reduction of a mixture of $[Cr(thf)_3Cl_3]$ (thf = tetrahydrofuran) and the diphosphine,[10] and more recently obtained by co-condensation of chromium metal vapour and the ligand.[11] Other examples with L^2 = $Ph_2PCH_2CH_2PPh_2$ and $Ph_2AsCH_2CH_2AsPh_2$ were obtained from L^2 and $K_6[Cr(CN)_6]$ in liquid ammonia.[12] Here we describe the preparation and properties of examples of the elusive $[Cr(L^2)_3][BF_4]_3$ and $[Cr(L^3)_2][BF_4]_3$ types with heavy donor ligands.

Results and Discussion

The reaction of $[Cr(thf)_3Cl_3]$ with three equivalents of $AgBF_4$ in dry thf solution gives, after removal of the AgCl by filtration, a bright green moisture-sensitive solution which probably contains [13] $[Cr(thf)_6][BF_4]_3$. The solution decomposes on concentration and hence was prepared and used *in situ*. This solution was treated with three equivalents of the bidentate ligands $Me_2PCH_2CH_2PMe_2$, o-$C_6H_4(PMe_2)_2$, $Ph_2PCH_2CH_2PPh_2$, o-$C_6H_4(AsMe_2)_2$, *cis*-$Ph_2AsCH{=}CHAsPh_2$, or *cis*-$MeSCH{=}CHSMe$, or two equivalents of the tridentate ligands $PhP(CH_2CH_2PPh_2)_2$, $MeAs(CH_2CH_2CH_2AsMe_2)_2$, $MeC(CH_2PPh_2)_3$, $MeC(CH_2AsMe_2)_3$, or $S(CH_2CH_2CH_2SMe)_2$, under anhydrous oxygen-free conditions. The reaction of $[Cr(thf)_6]^{3+}$ with monodentate phosphines gave green oils, and the tetradentate ligand $P(CH_2CH_2PPh_2)_3$ produced an insoluble blue solid which has not been characterised. The complexes $[Cr(L^2)_3][BF_4]_3$ and $[Cr(L^3)_2][BF_4]_3$ are moisture-sensitive blue-green or yellow-green solids (Table), and are generally insoluble in non-polar solvents, although both $[Cr(Ph_2PCH_2CH_2PPh_2)_3][BF_4]_3$ and $[Cr\{PhP(CH_2CH_2PPh_2)_2\}_2][BF_4]_3$ dissolve slightly in halogenocarbons. The complex $[Cr(Me_2PCH_2CH_2PMe_2)_3][BF_4]_3$ dissolves readily in dry dimethyl sulphoxide (dmso) in which it is a 3 : 1 electrolyte (Λ_M = 109 Ω^{-1} cm^2 mol^{-1}),† but the other complexes decompose rapidly in dmso or nitromethane solutions. Instability in solution is also a characteristic of the Co^{III} and Fe^{III} analogues,[6–8] although unlike these, the Cr^{III} complexes are stable with respect to reduction. In contrast to the amine complexes where $CrN_6{}^{3+}$ type cations are often obtainable in the presence of halide ions, the complexes of the heavier donor ligands react rapidly with LiX or $NBu^n{}_4X$ (X = Cl or Br) in solution, or suspension in thf or CH_2Cl_2, with partial displacement of the neutral ligand(s). For example, $[Cr\{PhP(CH_2CH_2PPh_2)_2\}Cl_3]$ [14] is formed readily from $[Cr\{PhP(CH_2CH_2PPh_2)_2\}_2][BF_4]_3$ and LiCl in CH_2Cl_2 at room temperature. The i.r. spectra of all the complexes contain broad unsplit absorptions at *ca.* 1 050 cm^{-1} due to non-co-ordinated $BF_4{}^-$ ions.

Cyclic voltammograms were recorded for a series of the complexes at a hanging mercury drop electrode in aprotic solvents (acetonitrile, dmso, or CH_2Cl_2 depending upon stability and solubility). While all the Cr^{III} complexes showed reduction processes, in most cases the current *vs.* potential curves were complex and showed only irreversible processes. The cyclic voltammogram for $[Cr(Me_2PCH_2CH_2PMe_2)_3][BF_4]_3$ in dmso–$[NBu^n{}_4][BF_4]$ (0.1 mol dm^{-3}), however, showed a reversible one-electron transfer process [E^0 = −0.87 *vs.* s.c.e., $\Delta E_p \simeq$ 70 mV] even at slow potential scan rates, and it may therefore be concluded that in this solvent $[Cr(Me_2PCH_2CH_2PMe_2)_3]^{2+}$ is stable on the time-scale of the experiment ($t_{\frac{1}{2}}$ > 100 s). Attempts to synthesise the Cr^{II} complex, however, were not successful.

Electronic Spectra.—The electronic spectra were recorded by the diffuse reflectance technique. The spectra are consistent with octahedral Cr^{III} (Table),[15] consisting of two main absorptions at *ca.* 15 000—17 000 cm^{-1} and 22 000—24 000 cm^{-1} assignable to the spin-allowed transitions ${}^4A_{2g} \longrightarrow {}^4T_{2g}$ (ν_1) and ${}^4A_{2g} \longrightarrow {}^4T_{1g}(F)$ (ν_2) respectively. Weaker, often ill defined absorptions were also present in most of the spectra which are attributable to the spin-forbidden transitions to the spin-doublet states. Broad absorptions were present at > *ca.* 25 000 cm^{-1} due to charge transfer and internal ligand bands, and ν_3 [${}^4A_{2g} \longrightarrow {}^4T_{1g}(P)$] was not identified. The solution

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† 3 : 1 electrolytes in dmso have Λ_M = *ca.* 110 Ω^{-1} cm^2 mol^{-1} (W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81).

Table. Electronic spectral and analytical data for $[Cr(L^2)_3]^{3+}$ and $[Cr(L^3)_2]^{3+}$

	Compound	Colour	$^2T_{1g}{}^2E_g \leftarrow {}^4A_{2g}$ [a]	$^4T_{2g} \leftarrow {}^4A_{2g}(\nu_1)$ [a]	$^2T_{2g} \leftarrow {}^4A_{2g}$ [a]	$^2T_{1g}$-$(F) \leftarrow {}^4A_{2g}(\nu_2)$ [a]	ν_2/ν_1	Dq	B	β_{35} [b]	Analysis [c] C	Analysis [c] H
	$[Cr(L^2)_3][BF_4]_3$											
L^2	$Me_2PCH_2CH_2PMe_2$	Green	14 790	17 010	21 550	24 270	1.43	1 701	740	0.80	27.6 (28.3)	6.1 (6.3)
			—	16 600 [d]	—	25 500 [d]						
	$Ph_2PCH_2CH_2PPh_2$	Green	14 080	15 530	20 160	21 830	1.41	1 553	640	0.70	63.0 (62.1)	4.9 (4.8)
	o-$C_6H_4(PMe_2)_2$	Green	14 400 (sh)	16 670	20 830	23 180	1.39	1 667	640	0.70	40.1 (39.7)	5.2 (5.3)
	o-$C_6H_4(AsMe_2)_2$	Bright green	—	16 330	21 840	23 800	1.46	1 633	775	0.85	30.0 (30.7)	4.0 (4.1)
	cis-$Ph_2AsCH{=}CHAsPh_2$	Green	14 000	15 520	20 000	21 550	1.39	1 552	615	0.67	52.1 (53.0)	3.5 (3.7)
	cis-$MeSCH{=}CHSMe$	Yellow-green	—	16 230	21 300	23 350	1.44	1 623	750	0.825	21.1 (21.4)	3.6 (3.6)
	$[Cr(L^3)_2][BF_4]_3$											
L^3	$PhP(CH_2CH_2PPh_2)_2$	Pale blue	13 970 (sh)	16 660	21 550	22 730	1.36	1 666	617	0.67	59.4 (59.0)	5.0 (4.8)
	$MeC(CH_2PPh_2)_3$	Pale green	14 400	15 430	20 300	22 300	1.45	1 543	650	0.71	62.1 (63.0)	5.0 (5.0)
	$MeC(CH_2AsMe_2)_3$	Turquoise	*ca.* 15 000 (sh)	16 450	20 800	24 300	1.47	1 645	790	0.86	24.0 (24.4)	5.3 (5.0)
	$MeAs(CH_2CH_2CH_2AsMe_2)_2$	Green	14 534 (sh)	15 625	21 460 (sh)	22 730	1.45	1 563	774	0.84	24.1 (24.4)	5.1 (4.9)
	$S(CH_2CH_2CH_2SMe)_2$	Green	*ca.* 14 500 (sh)	15 720	21 330	22 940	1.46	1 570	750	0.825	25.6 (26.2)	5.3 (4.9)
	$[Cr(H_2NCH_2CH_2NH_2)_3]^{3+}$ [e]			21 800		28 600	1.31	2 180	640	0.70		
	$[Cr(bipy)_3]^{3+}$ [f]			23 400		28 900	1.24	2 340	540	0.59		
	$[Cr(dmso)_6]^{3+}$ [e]		—	15 770	—	22 520	1.43	1 577	685	0.75		
	$[Cr(H_2O)_6]^{3+}$ [e]		15 000	17 400	—	24 600	1.41	1 740	710	0.79		
	$[CrCl_6]^{3-}$ [e]			13 180	—	18 700	1.41	1 318	549	0.59		

[a] Values in cm^{-1}. [b] Free ion, $B = 918\ cm^{-1}$. [c] Calculated values are in parentheses. [d] Solution in dmso. [e] Data from ref. 16. [f] Data from ref. 2.

spectrum of $[Cr(Me_2PCH_2CH_2PMe_2)_3][BF_4]_3$, and of several of the other complexes in freshly prepared acetonitrile solution showed only ν_1 and ν_2,* although the instability prevented measurement of ε_{mol}. The $^4A_{2g} \longrightarrow {}^4T_{2g}$ transition gives $10Dq$; the Racah parameter B was estimated using plots of ν_2/ν_1 *vs.* Dq/B, and when combined[15] with B_0 for Cr^{III} (918 cm^{-1}) gave the nephelauxetic ratio, β_{35}. The results are given in the Table along with data taken from the literature for other Cr^{III} complexes.

The Dq values of the complexes prepared in this study are internally consistent showing the expected trends with changes in donor and substituent, but the absolute values are surprisingly low, both in comparison with those in $[Cr(H_2NCH_2CH_2NH_2)_3]^{3+}$ and $[Cr(bipy)_3]^{3+}$ and with the Dq values observed in $[Cr(L^3)X_3]$,[14,17] $[Cr(L^2)_2X_2]^+$ (X = halide),[18] and $[Cr(NCS)_4(L^1)_2]^-$,[19] (L^3, L^2, L^1 refer to tri-, bi-, and monodentate P or As donor ligands). For the d^6 ions Co^{III} and Rh^{III} the alkyl diphosphines and diarsines[19] occupy high positions in the spectrochemical series, comparable with ethylenediamine. The relatively low Dq values produced in the Cr^{III} cations are due to both electronic and steric factors. The hard Cr^{III} centre will bind soft P or As donors less strongly than the hard N donors, and the 3+ charge on the cation will cause contraction of the chromium d orbitals, increasing the mismatch in size and energy with the P (or As) donor orbitals. It is evident from models, and also by extrapolating from the X-ray data on $[Cr\{P(CH_2CH_2PPh_2)_3\}Cl_3]$, $[Cr(Ph_2PCH{=}CHPPh_2)Cl_4]^-$,[14] and $[Cr(Me_2PCH_2CH_2PMe_2)_3]$,[11] that these cations are very sterically crowded, and this will further reduce Dq. Overall the Dq values of the phosphines and arsines are similar to those produced by oxygen donors such as H_2O or dmso. The chemistry of $[Cr(L^3)_2]^{3+}$ or $[Cr(L^2)_3]^{3+}$, for example the ready displacement of L^2 or L^3 by halide ions and the instability in solution, support the proposal that the neutral ligands are not strongly bound. The B and β_{35} values are large for heavy Group 5B donors, and although individual values are probably of relatively low accuracy, the range of β_{35} is consistent with the soft ligands being unusually ineffective at reducing electron–electron repulsions at the Cr^{3+} centre.

Experimental

Electronic spectra were measured on a Perkin-Elmer 554 spectrometer. Samples for i.r. and electronic spectra were made up in sodium-dried Nujol, in a dry-box (H_2O <5 p.p.m.) and protected from moisture throughout. The electronic spectra were run using the diffuse reflectance attachment of the above spectrometer, the Nujol-mulled samples being placed between quartz slides and backed with $BaSO_4$ using $BaSO_4$ as reference. Difficulty was experienced in obtaining good C and H analytical data unless $K_2Cr_2O_7$ or WO_3 was added as a catalyst during combustion. Other physical measurements were made as described previously.[20]

All preparations were conducted in dry solvents and under dry dinitrogen using standard Schlenk-tube and dry-box techniques. The synthesis of $[Cr(thf)_6][BF_4]_3$ has been described elsewhere.[13] Ligands were made by literature methods,[21] except for $PhP(CH_2CH_2PPh_2)_2$, $MeC(CH_2PPh_2)_3$, and $P(CH_2CH_2PPh_2)_3$ which were commercial samples (Strem Chemicals Co.). Thioethers were made by Miss R. Ali.

Bis[1,1,1-*tris*(*diphenylphosphinomethyl*)*ethane*]*chromium*(III) *Tris*(*tetrafluoroborate*), $[Cr\{MeC(CH_2PPh_2)_3\}_2][BF_4]_3$.—Addition of $MeC(CH_2PPh_2)_3$ (0.63 g, 1 mmol) to $[Cr(thf)_6][BF_4]_3$ (0.5 mmol) in thf (20 cm^3), followed by gentle refluxing, and removal of the solvent *in vacuo* gave a green solid, which was stirred under light petroleum (b.p. 40—60 °C), filtered off, and dried *in vacuo*.

Bis[1,1,1-*tris*(*dimethylarsinomethyl*)*ethane*]*chromium*(III) *Tris*(*tetrafluoroborate*), $[Cr\{MeC(CH_2AsMe_2)_3\}_2][BF_4]_3$.—The complex was prepared as above using the ligand (0.384 g, 1 mmol) and heating the solution until it turned turquoise-blue.

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* Spin-forbidden bands in the spectra of Cr^{III} complexes are often seen for the solids but are absent in solution.[16]

After concentration *in vacuo*, the sticky turquoise solid was stirred under light petroleum until it became a powder, filtered off and dried *in vacuo*.

Bis[*bis*(2-*diphenylphosphinoethyl*)*phenylphosphine*]*chromium*(III) *Tris*(*tetrafluoroborate*), $[Cr\{PhP(CH_2CH_2PPh_2)_2\}_2][BF_4]_3$.—Addition of the ligand (0.53 g, 1 mmol) to $[Cr(thf)_6][BF_4]_3$ in thf-CH_2Cl_2 (1 : 1, 20 cm^3) and stirring at room temperature for 30 min gave a blue solution, which yielded a blue solid on concentration. This was washed with light petroleum, filtered off, and dried *in vacuo*.

Similarly prepared were bis[bis(3-dimethylarsinopropyl)-methylarsine]chromium(III) tris(tetrafluoroborate), $[Cr\{MeAs(CH_2CH_2CH_2AsMe_2)_2\}_2][BF_4]_3$, tris[1,2-bis(diphenylphosphino)ethane]chromium(III) tris(tetrafluoroborate), $[Cr(Ph_2PCH_2CH_2PPh_2)_3][BF_4]_3$, tris[1,2-bis(diphenylarsino)-ethylene]chromium(III) tris(tetrafluoroborate), $[Cr(Ph_2AsCH{=}CHAsPh_2)_3][BF_4]_3$, and tris[*o*-phenylenebis(dimethylphosphine)]chromium(III) tris(tetrafluoroborate), $[Cr\{o\text{-}C_6H_4(PMe_2)_2\}_3][BF_4]_3$.

Tris[1,2-*bis*(*dimethylphosphino*)*ethane*]*chromium*(III) *Tris*(*tetrafluoroborate*), $[Cr(Me_2PCH_2CH_2PMe_2)_3][BF_4]_3$.—A green precipitate formed immediately on adding the ligand (0.225 g, 1.5 mmol) to $[Cr(thf)_6][BF_4]_3$ (0.5 mmol) in thf. This was filtered off and dried *in vacuo*.

Tris[o-*phenylenebis*(*dimethylarsine*)]*chromium*(III) *Tris*(*tetrafluoroborate*), $[Cr\{o\text{-}C_6H_4(AsMe_2)_2\}_3][BF_4]_3$.—The reaction of the ligand (0.43 g, 1.5 mmol) and $[Cr(thf)_6][BF_4]_3$ (0.5 mmol) gave a green oil. The thf was decanted off, and the oil stirred with light petroleum (25 cm^3) containing CH_2Cl_2 (0.5 cm^3) for 1 week to produce a green solid.

Bis[*bis*(3-*methylthiopropyl*) *sulphide*]*chromium*(III) *Tris*(*tetrafluoroborate*), $[Cr\{S(CH_2CH_2CH_2SMe)_2\}_2][BF_4]_3$.—$S(CH_2CH_2CH_2SMe)_2$ (0.210 g, 1 mmol) was added to a solution of $[Cr(thf)_6][BF_4]_3$ (0.5 mmol) in thf (20 cm^3). After stirring for about 10 min, thf was removed by pumping and dichloroethane (*ca.* 25 cm^3) added under a stream of nitrogen. After overnight stirring, a green oil appeared round the base of the flask, with a brown solution above it. The latter was removed by filtration and a pale green solid isolated by vigorous stirring under light petroleum.

Tris[cis-1,2-*bis*(*methylthio*)*ethylene*]*chromium*(III) *Tris*(*tetrafluoroborate*), $[Cr(MeSCH{=}CHSMe)_3][BF_4]_3$.—The green solid was prepared as described for $[Cr\{S(CH_2CH_2CH_2SMe)_2\}_2][BF_4]_3$, but using *cis*-MeSCH=CHSMe (0.180 g, 1.5 mmol).

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