o-Phenylenediamine and Related Complexes of Chromium, Vanadium and Manganese†

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Using the ligands (L–L) *o*-phenylenediamine, 4,5-dimethyl-*o*-phenylenediamine and phenanthrene-9,10-diamine, anionic chromium(III) complexes of the type $[CrCl_4(L\text{–}L)]^-$, have been isolated as quaternary phosphonium salts from interaction of $CrCl_3(thf)_3$ (thf = tetrahydrofuran) and the ligand in the presence of $[PPh_4]Cl$ or $[PPh_3(CH_2Ph)]Cl$. Interaction in the absence of quaternary phosphonium salts gives $[CrCl_2(L\text{–}L)_2]Cl$. A similar tetrachloro anion has been obtained using the chelating phosphine 1,2-$(HPr^iP)_2C_6H_4$. Similar complexes obtained from $VCl_3(thf)_3$ have the form $[VCl_4(L\text{–}L)]^-$ and $[VCl_2(L\text{–}L)_2]Cl$. Use of the dihalides leads to octahedral complexes *trans*-$MCl_2(L\text{–}L)_2$ (M = V or Cr) and *trans*-$MnI_2(L\text{–}L)_2$. The interaction of $[P(CH_2Ph)Ph_3][CrCl_4\{(H_2N)_2C_6H_2Me_2\}]$ with AgO_3SCF_3 and of $[CrCl_2\{(H_2N)_2C_6H_4\}_2]Cl$ with trifluoromethanesulfonic acid and diethyl ether leads to the unusual chromium(IV) octahedral triflate compounds $Cr(NH_2)(O_3SCF_3)_3[(H_2N)_2C_6H_2Me_2]$ and $Cr(O_3SCF_3)_4[(H_2N)_2C_6H_4]$, respectively. The crystal structures of the compounds $[PPh_3(CH_2Ph)][CrCl_4\{(H_2N)_2C_6H_4\}]$, $Cr(NH_2)(O_3SCF_3)_3[(H_2N)_2C_6H_2Me_2]$, $Cr(O_3SCF_3)_4[(H_2N)_2C_6H_4]$ and $[PPh_4][VCl_4\{(H_2N)_2C_6H_2Me_2\}]$ have been determined. All have octahedral structures with chelating diamines. In the tetrachlorochromate(III) salt, the Cr–N distances are *ca.* 0.05 Å longer than those in the chromium(IV) compounds. The V^{III}–N distances [2.16(1) Å] are *ca.* 0.05 Å longer than the Cr^{III}–N distances [2.11(1) Å], as expected, but the vanadium complex shows a much greater difference in M–Cl distances *trans* to N [2.336(4) Å] or *trans* to Cl [2.381(4) Å] than in the chromium(III) complex [all 2.342–2.356(5) Å].

We have described[1] the synthesis and X-ray crystal structures of trigonal-prismatic tris(*o*-phenylenediamido) compounds of rhenium-(VII) and -(VI), the singly and doubly deprotonated derivatives[1] thereof, and the osmium(VIII) complex[1] $OsO_2[(HN)_2C_6H_4]_2$. For Group 6 elements the octahedral chromium(IV) compound[2] $CrCl_2[(HN)_2C_6H_4](PMe_2Ph)_2$ and the tungsten complex $\{WCl_3[(HN)(H_2N)C_6H_4]\}_2[\mu\text{-}1,2\text{-}(N)_2C_6H_4]$[3] have been structurally characterised by X-ray diffraction. Several chromium(II) *o*-phenylenediamine complexes and the structures of $Cr(NCS)_2[(H_2N)_2C_6H_4]_2$ and of $[Cr\{(H_2N)_2C_6H_4\}_4][CF_3SO_3]_2$ have been described.[4] We now describe further studies on chromium and some on vanadium and manganese.

Analytical and physical data for new compounds are collected in Table 1.

Results and Discussion

Chromium Complexes.—Although vast numbers of chromium(III) amine complexes are known,[5] none appears to have *o*-phenylenediamine as ligand.

The interaction of $CrCl_3(thf)_3$ (thf = tetrahydrofuran) with 1,2-diamines in the presence of a phosphonium salt $[PPh_4]Cl$ or $[PPh_3(CH_2Ph)]Cl$ in a 1:1:1 molar ratio in refluxing toluene gives good yields of the phosphonium salts of the amines $[CrCl_4(L\text{–}L)]^-$ **1**–**3**, where L–L is $C_6H_4(NH_2)_2$-1,2, 4,5-$Me_2C_6H_2(NH_2)_2$-1,2 or $C_{14}H_8(NH_2)_2$-9,10 (phenanthrene-9,10-diamine). The grey or green salts **1**–**3** are air-stable and insoluble in hydrocarbons but soluble in CH_2Cl_2 and MeCN. Their ^1H NMR spectra are broad and uninformative; the X-band EPR spectra in frozen MeCN at 77 K are sharp with *g* values typical for Cr^{III};[5,6] there is no observable hyperfine splitting.

A variety of chromium(III) complexes of chelating phosphine and arsine ligands are known and the structure of $[NPr^n{}_4][CrCl_4(cis\text{-}Ph_2PCHCHPPh_2)]$ was determined.[7] Using the ligand 1,2-$(HPr^iP)_2C_6H_4$[8] we have also made $[PPh_3(CH_2Ph)][CrCl_4\{(HPr^iP)_2C_6H_4\}]$ **4**, which is purple in the solid state and in CH_2Cl_2 or MeCN solution in which it is somewhat air sensitive. The solvated crystals tend to lose solvent readily and so far we have been unable to obtain crystals suitable for X-ray diffraction. The ^1H NMR spectrum is again broad and uninformative while the ^{31}P NMR spectrum is not detected due to the short ^{31}P relaxation time; a similar situation was reported for $VCl_3(PMe_2Ph)_3$.[9] The X-band EPR spectrum is more complex than that of the amine complexes due probably to a change in the main axis of symmetry and a large zero-field splitting (Cr^{3+}, $S = \frac{3}{2}$) resulting in both $g_\perp$ and $g_\parallel$ values (see Experimental section).

The structure of $[PPh_3(CH_2Ph)][CrCl_4\{(H_2N)_2C_6H_4\}]$ has been determined by X-ray diffraction (Fig. 1); bond lengths and angles are given in Table 2. The anion is octahedral with the diamine chelating. The Cr–N distances [2.10(1), 2.11(1) Å] are larger than those in the chromium(IV) amido compound[2] [1.943(10) Å] as expected for an amine complex. The Cr–Cl bond distances [2.341(5) to 2.356(5)] fall within the range previously observed.[4,10]

The compounds **1**–**3** on chemical reduction gave only intractable products; they were not oxidised by molecular oxygen in solution at room temperature. The cyclic voltammograms of **1**–**4** with 0.1 mol dm^{-3} $NBu^n{}_4PF_6$ as supporting electrolyte in MeCN show irreversible oxidation waves at *ca.* +0.95 and +1.60 V *vs.* Ag–$AgClO_4$.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Analytical and physical data for new compounds

Compound	Colour	M.p./°C	Analysis (%)			
			C	H	N	Other
1 $[PPh_3(CH_2Ph)][CrCl_4\{(H_2N)_2C_6H_4\}]\cdot CH_2Cl_2$	Grey-blue	220–225	51.4	4.2	4.4	
			(51.8)	(4.3)	(3.8)	
2 $[PPh_3(CH_2Ph)][CrCl_4\{(H_2N)_2C_6H_2Me_2\}]\cdot MeCN$	Green	*ca.* 290	57.6	5.3	5.9	
			(58.0)	(5.1)	(5.8)	
3 $[PPh_3(CH_2Ph)][CrCl_4\{(H_2N)_2C_{14}H_8\}]$	Green	197–205	60.1	4.3	3.8	
			(61.9)	(4.5)	(3.7)	
4 $[PPh_3(CH_2Ph)][CrCl_4\{(HPr^iP)_2C_6H_4\}]$	Purple	*ca.* 225	57.2	5.2		Cl 19.4
			(57.5)	(5.5)		(18.4)
5 $Cr(NH_2)(OSO_2CF_3)_3[(H_2N)_2C_6H_2Me_2]\cdot Et_2O$*	Violet	*ca.* 236	25.2	3.4	5.2	
			(25.0)	(2.5)	(5.8)	
6 $Cr(OSO_2CF_3)_4[(H_2N)_2C_6H_4]\cdot 1.5Et_2O$*	Deep purple	*ca.* 312	22.4	2.6	4.3	S 14.8
			(22.1)	(2.7)	(3.3)	(14.8)
7 $[CrCl_2[\{(H_2N)_2C_6H_4\}_2]Cl$	Grey	255–259	37.8	4.5	14.0	
		(decomp.)	(38.5)	(4.3)	(15.0)	
8 $[CrCl_2\{(H_2N)_2C_6H_2Me_2\}_2]Cl$	Grey	365–370	45.0	4.7	11.8	
		(decomp.)	(44.6)	(5.6)	(13.0)	
9 $CrCl_2[(H_2N)_2C_6H_4]_2$	Sky-blue	> 150	41.2	4.2	15.5	
			(42.5)	(4.8)	(16.5)	
10 $CrCl_2[(H_2N)_2C_6H_2Me_2]_2$	Turquoise	> 150	49.1	6.6	13.6	Cl 19.5
		(decomp.)	(48.6)	(6.1)	(14.2)	(17.9)
11 $[PPh_3(CH_2Ph)][VCl_4\{(H_2N)_2C_6H_4\}]$	Pink-red	*ca.* 250	55.9	4.6	3.9	
			(56.9)	(4.6)	(4.3)	
12 $[PPh_3(CH_2Ph)][VCl_4\{(H_2N)_2C_6H_2Me_2\}]\cdot CH_2Cl_2$	Red	*ca.* 260	52.6	4.8	3.9	Cl 27.7
			(53.2)	(4.7)	(3.7)	(27.7)
13 $[VCl_2\{(H_2N)_2C_6H_4\}_2]Cl\cdot 0.14C_6H_5Me$	Purple	> 300	39.7	4.9	14.4	
			(40.3)	(4.5)	(14.5)	
14 $[VCl_2\{(H_2N)_2C_6H_2Me_2\}_2]Cl$	Purple	300	44.7	6.0	11.8	
			(44.7)	(5.6)	(13.0)	
15 $VCl_2[(H_2N)_2C_6H_4]_2\cdot 0.5CH_2Cl_2$	Pink	*ca.* 280	39.3	4.7	14.8	
		(decomp.)	(39.4)	(4.5)	(14.7)	
16 $MnI_2[(H_2N)_2C_6H_4]_2$	Green-brown	*ca.* 250	28.8	3.1	11.0	I 47.9
			(27.5)	(3.1)	(10.7)	(48.3)
17 $MnI_2[(H_2N)_2C_6H_2Me_2]_2$	Cream	300	33.8	4.2	10.2	I 43.4
			(33.1)	(4.2)	(9.6)	(43.7)

* X-Ray studies indicate $2Et_2O$ for crystals in the presence of Et_2O. Analyses are on bulk samples after evacuation for 24 h.

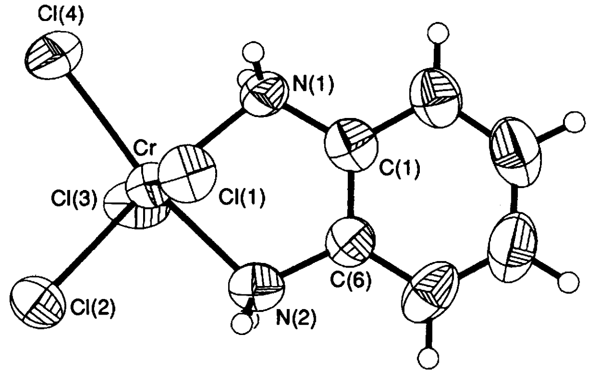


Fig. 1 The structure of the anion in the salt $[PPh_3(CH_2Ph)][CrCl_4\{(H_2N)_2C_6H_4(NH_2)_2\}]$

Attempts to isolate a chloride-free species by interaction of compound **2** with silver triflate in MeCN led, after work-up, from Et_2O to small amounts of a diamagnetic purple crystalline solid. Infrared data showed N–H stretches at *ca.* 3489 cm^{-1} while in the mass spectrum the peaks at m/z 543 and 391 corresponded to loss of the diamine and NH_2 from the parent ion; analytical data were also consistent with the stoichiometry $Cr(NH_2)(O_3SCF_3)_3[(H_2N)_2C_6H_2Me_2]$ **5**. The structure was determined by X-ray diffraction and a diagram of the molecule is shown in Fig. 2; selected bond lengths and angles are given in Table 3. The molecule has an octahedral geometry with a chelating diamine and a *mer* configuration of η^1-co-ordinated triflate groups, all of which are mutually *cis* to the NH_2 function (both hydrogens were successfully refined) which has a Cr–N distance of 1.940(9) Å. The Cr–N distances of the chelating diamino ligand [2.04(1) and 2.05(1)] are again longer than those of the chromium(IV) *o*-phenylenediamido complex;[2] however they are shorter than those of the chromium(II) *o*-phenylenedi-

Table 2 Selected bond lengths (Å) and angles (°) for the anions $[CrCl_4\{(H_2N)_2C_6H_4\}]^-$ and $[VCl_4\{(H_2N)_2C_6H_2Me_2\}]^-$

	M = Cr	M = V
Cl(1)–M	2.356(5)	2.387(4)
Cl(2)–M	2.353(5)	2.341(4)
Cl(3)–M	2.345(5)	2.375(4)
Cl(4)–M	2.341(5)	2.330(4)
N(1)–M	2.094(9)	2.159(7)
N(2)–M	2.108(10)	2.164(7)
Cl(2)–M–Cl(1)	91.8(2)	92.9(2)
Cl(3)–M–Cl(1)	171.5(1)	173.3(1)
Cl(3)–M–Cl(2)	91.8(2)	91.5(2)
Cl(4)–M–Cl(1)	94.3(2)	92.5(2)
Cl(4)–M–Cl(2)	100.5(2)	101.4(2)
Cl(4)–M–Cl(3)	99.6(2)	91.5(2)
N(1)–M–Cl(1)	84.9(3)	87.6(3)
N(1)–M–Cl(2)	172.1(3)	167.3(2)
N(1)–M–Cl(3)	90.6(3)	87.0(3)
N(1)–M–Cl(4)	87.0(3)	91.2(3)
N(2)–M–Cl(1)	87.2(3)	84.4(2)
N(2)–M–Cl(2)	90.1(3)	89.9(2)
N(2)–M–Cl(3)	85.1(3)	90.6(2)
N(2)–M–Cl(4)	169.2(2)	168.4(2)
N(2)–M–N(1)	82.6(4)	77.5(3)
C(1)–N(1)–M	110.5(7)	110.9(5)
C(6)–N(2)–M	110.0(7)	110.6(5)

Table 3 Selected bond lengths (Å) and angles (°) for $Cr(NH_2)(O_3SCF_3)_3[(H_2N)_2C_6H_2Me_2]$

N(11)–Cr	2.052(10)	N(12)–Cr	2.037(10)
O(21)–Cr	1.976(9)	O(11)–Cr	1.978(8)
N(1)–Cr	1.940(9)	O(31)–Cr	1.958(8)
N(12)–Cr–N(11)	83.7(4)	O(21)–Cr–N(11)	176.5(3)
O(21)–Cr–N(12)	92.9(4)	O(11)–Cr–N(11)	88.8(4)
O(11)–Cr–N(12)	92.7(4)	O(11)–Cr–O(21)	90.7(4)
N(1)–Cr–N(11)	91.4(4)	N(1)–Cr–N(12)	174.7(3)
N(1)–Cr–O(21)	92.1(4)	N(1)–Cr–O(11)	89.2(4)
O(31)–Cr–N(11)	89.5(4)	O(31)–Cr–N(12)	86.3(4)
O(31)–Cr–O(21)	91.0(4)	O(31)–Cr–O(11)	178.1(3)
O(31)–Cr–N(1)	91.6(4)	C(11)–N(11)–Cr	111.0(7)
C(12)–N(12)–Cr	110.5(7)	S(2)–O(21)–Cr	134.2(5)
S(1)–O(11)–Cr	142.6(4)	O(12)–S(1)–O(11)	111.9(5)
S(3)–O(31)–Cr	134.0(4)		

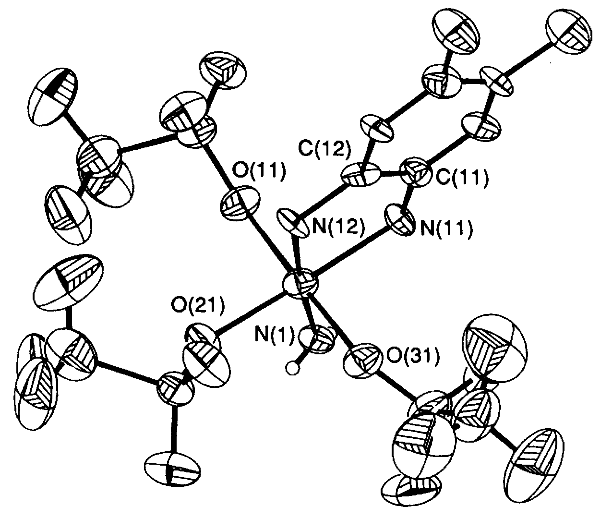


Fig. 2 The structure of $Cr(NH_2)(O_3SCF_3)_3[(H_2N)_2C_6H_2Me_2]$ in the diethyl etherate

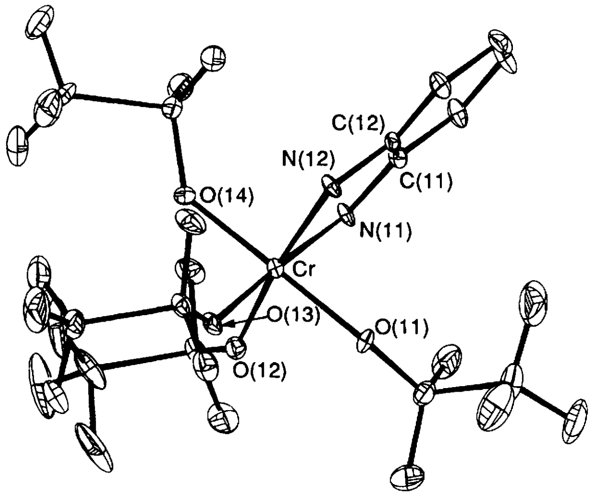


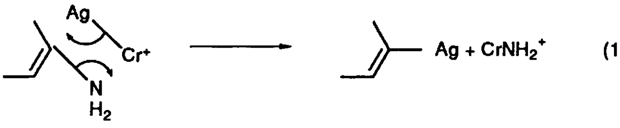
Fig. 3 The structure of $Cr(O_3SCF_3)_4[(H_2N)_2C_6H_4]$ in the diethyl etherate

Table 4 Selected bond lengths (Å) and angles (°) for $Cr(O_3SCF_3)_4[(H_2N)_2C_6H_4]$

Molecule 1		Molecule 2	
N(11)–Cr(1)	2.050(13)	N(21)–Cr(2)	2.035(13)
N(12)–Cr(1)	2.057(13)	N(22)–Cr(2)	2.005(12)
O(11)–Cr(1)	1.934(13)	O(21)–Cr(2)	1.963(12)
O(12)–Cr(1)	1.961(12)	O(22)–Cr(2)	1.946(12)
O(13)–Cr(1)	1.967(11)	O(23)–Cr(2)	1.988(11)
O(14)–Cr(1)	1.940(13)	O(24)–Cr(2)	1.962(12)
N(12)–Cr(1)–N(11)	83.7(5)	N(22)–Cr(2)–N(21)	83.6(5)
O(11)–Cr(1)–N(11)	90.3(5)	O(21)–Cr(2)–N(21)	89.3(5)
O(11)–Cr(1)–N(12)	86.4(5)	O(21)–Cr(2)–N(22)	86.8(5)
O(12)–Cr(1)–N(11)	90.0(5)	O(22)–Cr(2)–N(21)	94.4(5)
O(12)–Cr(1)–N(12)	172.5(5)	O(22)–Cr(2)–N(22)	175.2(5)
O(12)–Cr(1)–O(11)	89.4(5)	O(22)–Cr(2)–O(21)	88.8(5)
O(13)–Cr(1)–N(11)	177.7(4)	O(23)–Cr(2)–N(21)	175.2(4)
O(13)–Cr(1)–N(12)	96.1(5)	O(23)–Cr(2)–N(22)	92.2(5)
O(13)–Cr(1)–O(11)	87.4(5)	O(23)–Cr(2)–O(21)	88.3(5)
O(13)–Cr(1)–O(12)	90.0(5)	O(23)–Cr(2)–O(22)	89.7(5)
O(14)–Cr(1)–N(11)	92.6(5)	O(24)–Cr(2)–N(21)	90.6(5)
O(14)–Cr(1)–N(12)	91.4(5)	O(24)–Cr(2)–N(22)	90.8(5)
O(14)–Cr(1)–O(11)	176.2(4)	O(24)–Cr(2)–O(21)	177.6(4)
O(14)–Cr(1)–O(12)	93.1(5)	O(24)–Cr(2)–O(22)	93.6(5)
O(14)–Cr(1)–O(13)	89.7(5)	O(24)–Cr(2)–O(23)	91.7(5)
C(11)–N(11)–Cr(1)	109.3(8)	C(21)–N(21)–Cr(2)	111.1(9)
C(12)–N(12)–Cr(1)	110.5(9)	C(22)–N(22)–Cr(2)	111.7(9)
S(11)–O(11)–Cr(1)	139.5(6)	S(21)–O(21)–Cr(2)	136.4(6)
S(12)–O(12)–Cr(1)	140.2(6)	S(22)–O(22)–Cr(2)	145.5(7)
S(13)–O(13)–Cr(1)	138.0(7)	S(23)–O(23)–Cr(2)	137.5(6)
S(14)–O(14)–Cr(1)	137.4(8)	S(24)–O(24)–Cr(2)	134.3(7)

amine complex described earlier.[4] This could in part be due to the higher oxidation state of the metal centre or simply due to the greater steric constraints of three triflate groups. The Cr–O distances, 1.958(8) to 1.978(8) Å and the Cr–O–S angle indicate Cr–O π bonding; *cf.* 2.028(7) Å and Cr–O–S 137.3(3)° in $[Cr(NBu^t)_2(C_5H_5N)_2(\eta^1\text{-}O_3SCF_3)]CF_3SO_3$.[11]

The mechanism for the formation of the Cr–NH_2 group in this compound is not clear. The NH_2 group can come only from an NH_2 group of co-ordinated diamine in other anions but we are unaware of any C–NH_2 cleavage reactions of aromatic amines. A possible route involves attack of Ag^+ on a chromium atom in the complex anion to give a Cr–Ag bond as suggested previously in the oxidation of $Cr(CO)_2(dmpe)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) by AgO_3SCF_3;[12a] there are numerous examples of electrophilic additions of Ag^+ to metal atoms in complexes giving M–Ag bonds.[12b] Such an attack could be followed by the reaction (1) leading to a silver aryl which would be doubtless polymeric and insoluble.



(1)

A second, unusual, octahedral chromium(IV) compound, $Cr(\eta^1\text{-}O_3SCF_3)_4[(H_2N)_2C_6H_4]$ **6**, also deep purple, was obtained by interaction of the complex $[CrCl_2\{(H_2N)_2C_6H_4(NH_2)_2\}_2]Cl$ **7** described below with neat trifluoromethanesulfonic acid followed by addition of Et_2O. Since the acid is non-oxidising the oxidation of Cr^{III} to Cr^{IV} is presumably connected with the acid cleavage of diethyl ether,[12c] possibly involving radicals, since on stirring **7** with acid for *ca.* 12 h a deep red-orange solution is obtained that has a characteristic chromium(III) EPR spectrum. On addition of Et_2O there is an exothermic reaction and the solution immediately develops the deep purple colour of **6**. From this solution, on cooling, purple crystals of the etherate can be obtained; alternatively, evaporation gives a purple solid (see Experimental section). The ^1H NMR spectra of both crystals and solid in $(CD_3)_2CO$ are very sharp and are identical.

A crystal structure determination shows the above formulation to be correct. The structure contains two independent complex molecules, a diagram of one of which is given in Fig. 3. Selected bond lengths and angles for both are given in Table 4. The Cr–N distances at 2.01(1)–2.05(1) Å are similar to those

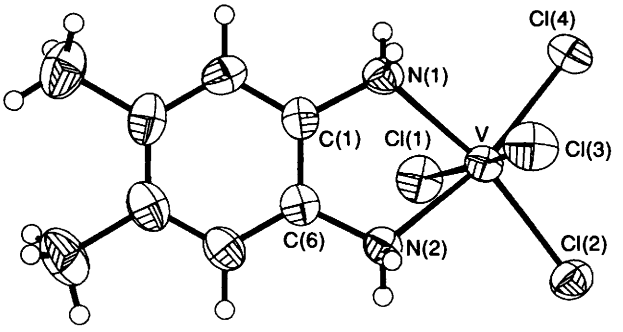


Fig. 4 The structure of the anion in the salt $[PPh_3(CH_2Ph)][VCl_4\{(H_2N)_2C_6H_2Me_2\}]\cdot CH_2Cl_2$

in the tris(triflate) described above. The lower precision of the present structure masks any indication of differences in Cr–O(triflate) distances arising from the disposition of the oxygens in the *cis*-CrN_2O_4 system. The range of Cr–O distances 1.94–1.99(1) Å, however, is again similar to that found for the tris(triflate).

Compound **6** is a 1:1 electrolyte in MeCN, evidently giving the cation $[Cr(\eta^1\text{-}O_3SCF_3)_3\{(H_2N)_2C_6H_4\}(MeCN)]^+$. It provides a useful starting material for synthesis of other chromium(IV) complexes that will be reported separately. It may be noted finally that few octahedral chromium(IV) complexes have been made and structurally characterised.[2,13]

Bis(chelate) Compounds.—The cationic chromium(III) complexes $[CrCl_2(L\text{–}L)_2]Cl$, L–L = $C_6H_4(NH_2)_2$ **7** or $Me_2C_6H_2(NH_2)_2$ **8**, have been prepared from $CrCl_3(thf)_3$ and the appropriate diamine in refluxing toluene in essentially quantitative yield. The compounds were characterised by microanalysis, IR and EPR spectroscopy. Both have IR spectra with no strong bands above 3300 cm^{-1} for co-ordinated NH_2, but with strong CN bands in the region 1260–1230 cm^{-1} consistent with the observations of Larkworthy and co-workers.[4] In addition the compounds have a ν(Cr–Cl) stretch[10] in the characteristic region 300–450 cm^{-1}.

Interaction of the solvate $CrCl_2(thf)$[14] with a slight excess of amine $[C_6H_4(NH_2)_2$ or $Me_2C_6H_2(NH_2)_2]$ in refluxing toluene gives the neutral bis(diamine) compounds $CrCl_2(L\text{–}L)_2$, **9** and **10**, that are very air sensitive, turning dark green. Larkworthy and co-workers[4] have reported $CrBr_2[(H_2N)_2C_6H_4]_2$ and $CrI_2[(H_2N)_2C_6H_4]_2$ but their attempts to make $CrCl_2[(H_2N)_2C_6H_4]_2$ in aqueous solution were unsuccessful. The IR spectra suggest bidentate ligands and since there is only one Cr–Cl stretch {except for $CrCl_2[(H_2N)_2C_6H_4]_2$ that has a split band at *ca.* 340 cm^{-1} and hence may have *cis* and *trans* isomers} the compounds are hence considered to have the *trans* dihalide geometry that has been confirmed for the chelating complexes $MCl_2(dmpe)_2$ of the first-row elements M = Ti, V, Cr, Mn[15a] and Fe[15b] and for $Cr(NCS)_2[(H_2N)_2C_6H_4]_2$.[4] The low solubility of the compounds in organic solvents, even at elevated temperatures, precludes crystallisation and further characterisation.

Vanadium and Manganese Complexes.—Complexes of vanadium-(II) and -(III) with amine ligands are well known[16] except for those with $C_6H_4(NH_2)_2$. However, from reactions of various aromatic amines and diamines L–L [including $C_6H_4(NH_2)_2$] with VCl_4 the compounds $V^{IV}Cl_4(L\text{–}L)$ were isolated.[17a,b]

In the presence of $[PPh_3(CH_2Ph)]Cl$, $VCl_3(thf)_3$ reacts with the diamines giving the salts of the anions $[VCl_4\{(H_2N)_2C_6H_4\}]^-$ **11** and $[VCl_4\{(H_2N)_2C_6H_2Me_2\}]^-$ **12** that have ν(V–Cl) at *ca.* 310 cm^{-1} and $\nu(NH_2)$ at *ca.* 3160 cm^{-1} in the IR spectra; use of PPh_4Cl gives similar salts. In CH_2Cl_2 the compounds are EPR silent as is usually the case for the $S = 1$ system.[18] These red salts are moderately air stable, insoluble in hydrocarbons, but 1:1 electrolytes in CH_2Cl_2 and MeCN.

The structure of the $Me_2C_6H_2(NH_2)_2$ complex anion as the $[PPh_3(CH_2Ph)]^+$ salt has been determined, Fig. 4; bond lengths and angles are given in Table 2. The anion is isostructural with its chromium *o*-phenylenediamine analogue described above. Interestingly, the internal $V\text{–}N(H)_2\text{–}C$ angles are again close to 110°. It appears that the nature of the co-ordinating nitrogen can be inferred from the angle formed by the metal centre, nitrogen and the carbon of the aromatic ring; the angles for $M \leftarrow N(H)\text{–}C$ and $M{=}N\text{–}C$ are correspondingly larger.[3] One additional point of interest is that the chlorines *trans* to N or *trans* to Cl show markedly different distances in this vanadium complex, 2.375(4) and 2.387(4) Å *trans* to each other and 2.330(4) and 2.341(4) Å *trans* to the amine nitrogens, whereas the Cr–Cl distances are 2.345, 2.356(5) *trans* to each other and 2.341, 2.353(5) Å *trans* to the amines.

In the absence of phosphonium salt and using 2 equivalents of diamine per $VCl_3(thf)_3$, complexes of stoichiometry $[VCl_2(L\text{–}L)_2]Cl$ **13** and **14** are formed. Again the absence of any strong NH_2 stretches above 3300 cm^{-1} together with the presence of strong bands in the CN region (1260–1230 cm^{-1}) is consistent with bidentate chelating amine ligands and *trans* chlorides. For vanadium(II), the reaction of '$VCl_2(thf)_2$', properly $[V_2(\mu\text{-}Cl)_3(thf)_6]_2[Zn_2Cl_6]$,[19] with slightly greater than 2 equivalents of $C_6H_4(NH_2)_2$ in dichloromethane at room temperature yields an insoluble pink-red complex of stoichiometry $VCl_2[(H_2N)_2C_6H_4]_2$ **15**. The IR spectrum suggests bidentate $C_6H_4(NH_2)_2$ ligands and since there is only one V–Cl stretch the complex is considered to have the *trans* dichloride geometry found for $VCl_2(dmpe)_2$.[15a] The X-band EPR spectrum of **15** as a solid at room temperature comprises poorly defined broad low-field features but similar to those of $VCl_2(dmpe)_2$.[15a]

The corresponding manganese compounds $MnI_2(L\text{–}L)_2$, for $C_6H_4(NH_2)_2$, **16** and $Me_2C_6H_2(NH_2)_2$, **17** were made in a similar way to the above from MnI_2 and the diamines in CH_2Cl_2. The spectra are consistent with *trans* iodides. The X-band EPR spectra (solid, room temperature) have *g* values typical for octahedral Mn^{II}.[20]

Experimental

General procedures and instrumentation have been described.[1] Microanalyses were by Pascher, Remagen, University College, London, and Medac Ltd., Brunel University.

The precursors $CrCl_3(thf)_3$[21] and $VCl_3(thf)_3$[22] were prepared as described. All operations were carried out under oxygen-free nitrogen or argon. Spectra: ^1H NMR (250 MHz) referenced to $SiMe_4$; IR in Nujol mulls; mass by fast atom bombardment (matrix, *m*-nitrobenzyl alcohol) unless otherwise stated; EPR (X-band, g_{iso}) at 77 K in MeCN unless otherwise stated. Cyclic voltammetry measurements were made in MeCN with 0.1 mol dm^{-3} $[NBu^n{}_4][PF_6]$ as supporting electrolyte and referenced to $Ag\text{–}Ag^+$; the scan range was −2.0 to +2.0 V.

Commercial chemicals were from Aldrich; $C_6H_4(NH_2)_2$-1,2 was recrystallised from toluene prior to use.

*Benzyltriphenylphosphonium Tetrachloro(*o*-phenylenediamine)chromate*(III) **1**.—To a solution of $CrCl_3(thf)_3$ (1.0 g, 2.67 mmol) and $[PPh_3(CH_2Ph)]Cl$ (1.04 g, 2.6 mmol) in toluene (*ca.* 40 cm^3) was added, while stirring, $C_6H_4(NH_2)_2$ (0.29 g, 2.68 mmol). The resulting mixture was refluxed for 12 h, the precipitate collected, washed with toluene (2 × 20 cm^3) and recrystallised from $CH_2Cl_2\text{–}Et_2O$ as the CH_2Cl_2 solvate. Yield: 60–70%. IR: 3298m, 3192s, 3164s, 3090m, 3055s, 2728w, 2675w, 1713w, 1626w, 1599w, 1586w, 1556s, 1498s, 1438s, 1403m, 1288w, 1262w, 1241w, 1193w, 1158w, 1144w, 1133s, 1112s, 1066w, 1030w, 995m, 964w, 923w, 840m, 787w, 753s, 722s, 699s, 691s, 611w, 584m, 518s, 505s, 495s, 454w, 436m, 382w, 348m, 332s, 322s and 260w cm^{-1}. EPR (MeCN): $g = 1.99$. Conductivity (MeCN, 20 °C): $\Lambda_M = 88.1\ ohm^{-1}\ cm^2\ mol^{-1}$.

Table 5 Crystal data and details of refinement

Compound	**1**	**5**	**6**	**12**
Formula	$[C_{25}H_{22}P]^+$- $[C_6H_8Cl_4CrN_2]^-\cdot CH_2Cl_2$	$C_{11}H_{14}CrF_9N_3O_9S_3\cdot$ $2C_4H_{10}O$	$2[C_{10}H_8CrF_{12}N_2O_{12}S_4\cdot$ $2C_4H_{10}O]$	$[C_{25}H_{22}P]^+$- $[C_8H_{12}Cl_4N_2V]^-\cdot CH_2Cl_2$
M	740.306	789.53	1809.330	747.305
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/Å	17.198(1)	15.461(5)	24.230(5)	16.459(1)
b/Å	11.234(1)	14.273(4)	12.872(2)	9.981(2)
c/Å	18.348(2)	15.647(4)	24.175(1)	23.146(1)
α,γ/°	90	90	90	90
β/°	110.46(1)	93.66(2)	103.97(1)	107.50(1)
U/Å^3	3574.34	3499.03	7320	3632.35
Z	4	4	8	4
D_c/g cm^{-3}	1.376	1.499	1.642	1.403
F(000)	1516	1600	3664	1576
μ/cm^{-1}	8.327	5.855	6.392	7.790
Crystal size/mm	0.05 × 0.25 × 0.10	0.25 × 0.35 × 0.60	0.25 × 0.50 × 0.80	0.08 × 0.30 × 0.2
Total data measured *	16 729	6664	11 391	15 042
No of unique reflections	6198	4075	10 168	5335
No. of observed reflections $[F_o > 3\sigma(F_o)]$	2778	2340	3943	3905
No. of parameters	335	434	833	391
ρ_{min}, ρ_{max}/e Å^{-3}	−0.743, 0.668	−0.778, 0.789	−0.409, 0.722	−0.267, 0.385
Maximum least-squares shift-to-error ratio	−0.97	0.28	1.414	0.81
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0	0.0007	0.003 61	Unit weights
Final R	0.0653	0.0682	0.0791	0.0572
Final R'	0.0682	0.0700	0.0836	0.0572

* Maximum 2θ/°: 26 (**1**), 25 (**5**), 23 (**6**) and 24 (**12**).

Table 6 Fractional atomic coordinates (× 10^4) for $[PPh_3(CH_2Ph)][CrCl_4\{(H_2N)_2C_6H_4\}]\cdot CH_2Cl_2$

Atom	x	y	z	Atom	x	y	z
Cr	2817(1)	634(1)	1929(1)	C(22)	4592(4)	3683(5)	1237(4)
Cl(1)	3848(2)	−66(2)	1257(2)	C(23)	4333(4)	4166(5)	1878(4)
Cl(2)	2631(2)	2276(2)	1155(2)	C(24)	4845(4)	4277(5)	2493(4)
Cl(3)	1930(2)	1367(2)	2739(2)	C(25)	5616(4)	3903(5)	2467(4)
Cl(4)	1900(2)	−672(2)	1388(2)	C(26)	5875(4)	3420(5)	1826(4)
N(1)	3133(5)	−727(6)	2658(4)	C(31)	4998(5)	2587(5)	−317(3)
N(2)	3660(5)	1575(6)	2575(4)	C(32)	4263(5)	2108(5)	−226(3)
C(1)	3827(7)	−404(9)	3111(6)	C(33)	3709(5)	2071(5)	−812(3)
C(2)	4213(7)	−1243(10)	3569(6)	C(34)	3890(5)	2514(5)	−1491(3)
C(3)	4853(8)	−830(11)	4011(7)	C(35)	4625(5)	2993(5)	−1583(3)
C(4)	5101(8)	317(11)	3992(7)	C(36)	5179(5)	3030(5)	−996(3)
C(5)	4705(7)	1118(11)	3555(6)	C(40)	5907(6)	1022(7)	639(5)
C(6)	4090(7)	752(9)	3104(5)	C(41)	6404(4)	809(6)	1331(5)
P	5708(2)	2586(2)	422(2)	C(42)	6051(4)	468(6)	1963(5)
C(11)	6556(4)	3379(5)	181(4)	C(43)	6503(4)	278(6)	2609(5)
C(12)	6646(4)	4569(5)	357(4)	C(44)	7309(4)	429(6)	2623(5)
C(13)	7304(4)	5179(5)	156(4)	C(45)	7662(4)	770(6)	1991(5)
C(14)	7872(4)	4598(5)	−220(4)	C(46)	7210(4)	960(6)	1345(5)
C(15)	7782(4)	3408(5)	−396(4)	Cl(11)	873(3)	−469(5)	9441(3)
C(16)	7124(4)	2799(5)	−195(4)	Cl(12)	1340(4)	2003(4)	9345(3)
C(21)	5363(4)	3309(5)	1211(4)	C(10)	1158(14)	933(14)	9905(9)

Benzyltriphenylphosphonium Tetrachloro(4,5-*dimethyl*-o-*phenylenediamine*)*chromate*(III) **2**.—This was prepared as for compound **1** from $[PPh_3(CH_2Ph)]Cl$ (2.44 g, 6.27 mmol), $CrCl_3(thf)_3$ (2.35 g, 6.27 mmol) and $Me_2C_6H_2(NH_2)_2$ (0.85 g, 6.27 mmol) in toluene (*ca.* 40 cm^3). Recrystallisation from CH_2Cl_2 or MeCN–Et_2O at −20 °C gave a green crystalline solid. Yield *ca.* 90%. IR: 3279w, 3147m, 2728w, 2683w, 1714w, 1616w, 1601w, 1585m, 1557s, 1505s, 1495s, 1438s, 1317s, 1184m, 1167m, 1134m, 1109s, 1025m, 996s, 952s, 921w, 876w, 860w, 830m, 808m, 786s, 753s, 721s, 703s, 692s, 641w, 611w, 581m, 511s, 495s, 471w, 446m, 346s, 319s and 305s cm^{-1}. Mass spectrum: m/z 653.9 (M^+). EPR (MeCN): g = 2.00. Conductivity (CH_2Cl_2, 20 °C): Λ_M = 27.1 ohm^{-1} cm^2 mol^{-1}.

Benzyltriphenylphosphonium Tetrachloro(*phenanthrene*-9,10-*diamine*)*chromate*(III) **3**.—This was prepared as for compound **1** but from $[PPh_3(CH_2Ph)]Cl$ (0.67 g, 1.73 mmol), $CrCl_3(thf)_3$ (0.65 g, 1.73 mmol) and phenanthrene-9,10-diamine (0.36 g, 1.73 mmol) in toluene (*ca.* 40 cm^3). Recrystallisation from CH_2Cl_2–Et_2O afforded green prisms. Yield *ca.* 40%. Mass spectrum: m/z 544.88 (anion + matrix) and 401.87 (anion). IR: 3295w, 3240w, 3146m, 3140m, 3075m, 2731w, 2700w, 1601w, 1586w, 1552s, 1492m, 1439s, 1347w, 1326m, 1262m, 1237m, 1186w, 1111s, 1081m, 1032m, 997m, 919w, 827m, 811m, 786m, 752s, 724s, 691s, 650w, 616w, 582m, 513s, 497s, 437w, 348s and 312s cm^{-1}. EPR (MeCN): g = 1.98. Conductivity (CH_2Cl_2, 20 °C): Λ_M = 28.3 ohm^{-1} cm^2 mol^{-1}.

Table 7 Fractional atomic coordinates (× 10^4) for $Cr(NH_2)(O_3SCF_3)_3[(H_2N)_2C_6H_2Me_2]\cdot 2Et_2O$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cr	4219(1)	2520(1)	731(1)	N(1)	3375(5)	1920(4)	1409(4)
N(11)	5197(6)	1708(5)	1265(5)	O(31)	4473(5)	3445(4)	1624(4)
N(12)	5191(6)	3112(5)	103(5)	S(3)	4482(3)	3432(2)	2563(2)
C(11)	6025(9)	1997(6)	991(6)	O(32)	3722(8)	3779(9)	2913(7)
C(12)	6024(8)	2723(6)	397(6)	O(33)	4844(7)	2605(6)	2916(5)
C(13)	6784(8)	3001(6)	126(6)	C(3)	5327(14)	4296(11)	2795(10)
C(14)	7561(9)	2631(7)	410(7)	F(31)	5099(8)	5066(6)	2427(7)
C(15)	7551(9)	1905(7)	1006(7)	F(32)	5370(10)	4434(8)	3625(7)
C(16)	6779(9)	1629(6)	1295(7)	F(33)	6019(8)	4027(10)	2528(9)
C(40)	8395(9)	2956(9)	65(9)	C(2)	2777(13)	4365(10)	−1046(11)
C(50)	8385(9)	1473(9)	1327(8)	F(21)	2081(8)	3900(7)	−1141(7)
O(21)	3327(5)	3329(4)	165(4)	F(22)	2640(8)	5235(6)	−1250(6)
S(2)	3233(3)	4339(2)	61(2)	F(23)	3307(9)	4031(7)	−1540(6)
O(22)	4035(6)	4809(5)	43(6)	C(1X)	153(13)	5063(12)	1676(10)
O(23)	2600(7)	4712(6)	544(6)	C(2X)	1030(10)	5437(10)	1886(8)
O(11)	4002(5)	1571(4)	−165(4)	O(3X)	1258(6)	5378(6)	2829(6)
S(1)	4248(2)	1292(2)	−1014(2)	C(4X)	1610(10)	4515(8)	3097(10)
O(12)	4517(6)	355(5)	−1029(5)	C(5X)	1926(11)	4588(9)	4029(9)
O(13)	4761(6)	1962(5)	−1409(9)	C(6X)	1694(12)	1727(13)	2774(10)
C(1)	3199(11)	1267(10)	−1635(9)	C(7X)	1154(13)	1861(15)	1982(13)
F(13)	2850(6)	2089(6)	−1626(6)	O(8X)	1680(7)	2080(8)	1331(7)
F(11)	2675(6)	692(6)	−1296(7)	C(9X)	1234(17)	1876(18)	178(16)
F(12)	3311(8)	1011(8)	−2397(5)	C(10X)	1051(19)	2611(20)	371(19)

Benzyltriphenylphosphonium Tetrachloro[o-*phenylenebis*(*isopropylphosphine*)]*chromate*(III) **4**.—This was prepared as for compound **1** but from $[PPh_3(CH_2Ph)]Cl$ (0.34 g, 0.87 mmol), $CrCl_3(thf)_3$ (0.33 g, 0.88 mmol) and $C_6H_4(PPr^iH)_2$-1,2 (0.2 cm^3, 0.88 mmol). Yield: 0.65 g, 96%. Mass spectrum: *m*/*z* 570.95 (anion + matrix) and 419.91 (anion). IR: 3382w, 2727m, 2671w, 1713w, 1586w, 1574w, 1308m, 1261w, 1245w, 1188w, 1163w, 1112s, 1063m, 1029w, 997m, 969w, 922w, 891w, 836w, 808m, 782m, 753s, 743s, 722s, 700m, 688m, 638w, 583w, 515m, 498w, 384w, 336m, 324m, 279w and 260w cm^{-1}. EPR (MeCN): *g* = 3.53 and 1.12. Conductivity (MeCN, 20 °C): Λ_M = 98.7 ohm^{-1} cm^2 mol^{-1}.

Amido(4,5-*dimethyl*-o-*phenylenediamine*)*tris*(*trifluoromethanesulfonato*-κO)*chromium*(IV) **5**.—To a solution of the diamine complex **2** (0.32 g, 0.47 mmol) in MeCN (20 cm^3) was added AgO_3SCF_3 (0.49 g, 1.91 mmol) in MeCN (15 cm^3). The resulting mixture was stirred at room temperature overnight and filtered. The purple filtrate was evaporated and the residue extracted with Et_2O (20 cm^3) and cooled (−20 °C) to give purple-black crystals. Yield: *ca.* 10%. Mass spectrum (electron impact, EI): *m*/*z* 543 (M^+) and 391 [$M - NH_2 - Me_2C_6H_2(NH_2)_2$]. IR: 3489s, 3235s, 1625m, 1575m, 1510m, 1339m, 1281s, 1113m, 1030s, 874m, 805m, 765m, 722m, 642s, 580m, 515m, 445w and 375w cm^{-1}. ^1H NMR (CD_3CN): δ 1.4, 3.4 (m, Et_2O), 2.2 (m, Me), 2.25–3.0 (br, m, 2 × aromatic NH_2), 4.6–4.7 (m, $CrNH_2$) and 7.0–8.0 (aromatic CH).

(o-*Phenylenediamine*)*tetrakis*(*trifluoromethanesulfonato*-κO)*chromium*(IV) **6**.—A suspension of $[CrCl_2\{(H_2N)_2C_6H_4\}_2]Cl$ (1.0 g) in CF_3SO_3H (*ca.* 5 cm^3) was stirred for 24 h at room temperature. To the resulting deep red-orange solution was rapidly added *via* a syringe degassed Et_2O (*ca.* 50 cm^3). A purple solution which instantaneously formed in an exothermic reaction was stirred at −20 °C for 12 h. A pale precipitate, probably a salt of the diamine removed in the reaction, was filtered off and the filtrate cooled for several days at −20 °C to give purple needles of the etherate of X-ray quality in *ca.* 40% yield. The residual solution was red and some red crystals, still under investigation, were obtained on cooling.

If hexane is added to the initial purple Et_2O solution a purple oil is formed. Removal of Et_2O and washing of the oil with *ca.* 30 cm^3 each of toluene and hexane left a purple solid that was dried in vacuum (80 °C). The solid was washed with Et_2O (2 × 30 cm^3 at 0 °C) and again dried. Yield: 55–60% based on Cr. This solid is insoluble in CH_2Cl_2 and hydrocarbons and sparingly soluble in Et_2O, but readily soluble in MeCN giving a purple solution. Conductivity (MeCN, 20 °C): Λ_M = 101.14 ohm^{-1} cm^2 mol^{-1}. The following data refer to the etherate. Mass spectrum: *m*/*z* 755.68 (AB_2^-), 605.77 ($AB^- - BH$), 455.84 ($AB_2^- - 2BH$), 298.88 (BH^-) and 148.95 (B^-); A = $Cr[C_6H_4(NH_2)_2](OSCF_3)_2$, B = CF_3SO_3. IR: 3248s, 3210s, 3181s, 3116s, 2718m, 1713m, 1604m, 1574s, 1505s, 1315s, 1264s, 1156s, 1006s(br), 765s, 723m, 627s, 599s, 574m, 528s, 439m, 384w, 368w, 350w, 333m and 287m cm^{-1}. ^1H NMR [$(CD_3)_2CO$]: δ 1.1, 3.4 (Et_2O) and 8.0 [m, $C_6H_4(NH_2)_2$]; NH_2 groups not observed.

Dichlorobis(o-*phenylenediamine*)*chromium*(III) *Chloride* **7**.—The compounds $CrCl_3(thf)_3$ (1.0 g, 2.67 mmol) and $C_6H_4(NH_2)_2$ (0.57 g, 5.34 mmol) were refluxed in toluene (*ca.* 50 cm^3) for 12 h. The precipitate was collected, washed with toluene (2 × 2 cm^3) and hexane (*ca.* 30 cm^3) and dried *in vacuo*. Yield: essentially quantitative. IR: 3200s, 3158s, 1622w, 1601w, 1562s, 1500s, 1300w, 1261w, 1239m, 1116s, 1034m, 943w, 861w, 803m, 758s, 723m, 696w, 525w, 497w, 431m, 355m, 348m and 338m cm^{-1}. EPR (solid): *g* = 1.99.

Dichlorobis(4,5-*dimethyl*-o-*phenylenediamine*)*chromium*(III) *Chloride* **8**.—This was prepared as for compound **7** but from $CrCl_3(thf)_3$ (1.46 g, 3.90 mmol) and $Me_2C_6H_2(NH_2)_2$ (1.1 g, 8.08 mmol). IR: 3291m, 3187s, 3142s, 3077s, 1622w, 1569s, 1558s, 1508m, 1495w, 1302m, 1276m, 1209m, 1183w, 1153m, 1105s, 1056m, 1020w, 900w, 871m, 856w, 804w, 738s, 722m, 698w, 680w, 544w, 479w, 444m, 361w, 343s, 319m, 305s and 288m cm^{-1}. EPR (solid): *g* = 1.98.

Dichlorobis(o-*phenylenediamine*)*chromium*(II) **9**.—To a suspension of $CrCl_2(thf)$ (2.0 g, 10.3 mmol) in toluene (*ca.* 40 cm^3) was added $C_6H_4(NH_2)_2$ (2.22 g, 20.51 mmol). After refluxing (*ca.* 12 h) the precipitate was washed with toluene (2 × 30 cm^3) and hexane (*ca.* 40 cm^3) and dried *in vacuo*. Yield: 1.44 g, 42%. IR: 3418w, 3257w, 3223w, 3196w, 3172w, 1564w, 1499w, 1261s, 1233w, 1193w, 1155w, 1125m, 1096s, 1019s, 918w, 864w, 800s, 760m, 722w, 594w, 442w, 402w, 348w, 341w, 311w and 285w cm^{-1}. EPR (solid): silent.

Dichlorobis(4,5-*dimethyl*-o-*phenylenediamine*)*chromium*(II)

Table 8 Fractional atomic coordinates (× 10^4) for $Cr(O_3SCF_3)_4[(H_2N)_2C_6H_4]\cdot 2Et_2O$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Molecule 1				Molecule 2			
Cr(1)	1700(1)	2165(2)	4263(1)	Cr(2)	−639(1)	2111(2)	1686(1)
N(11)	1643(4)	2366(9)	3410(4)	N(21)	−1412(4)	2732(9)	1683(4)
N(12)	2318(5)	3290(9)	4354(5)	N(22)	−402(4)	2800(9)	2451(4)
C(11)	2076(6)	3077(12)	3337(6)	C(21)	−1403(6)	3247(11)	2225(6)
C(12)	2427(6)	3541(12)	3813(7)	C(22)	−881(6)	3253(12)	2620(7)
C(13)	2844(6)	4241(14)	3766(7)	C(23)	−854(7)	3751(13)	3131(7)
C(14)	2939(8)	4475(15)	3232(9)	C(24)	−1328(8)	4157(16)	3243(8)
C(15)	2587(9)	4001(17)	2768(9)	C(25)	−1839(7)	4124(16)	2863(8)
C(16)	2177(7)	3312(14)	2800(6)	C(26)	−1897(7)	3651(13)	2351(7)
O(11)	2305(4)	1167(8)	4307(4)	O(21)	−832(4)	891(7)	2090(4)
O(12)	1144(4)	1031(7)	4088(4)	O(22)	−911(4)	1368(8)	972(4)
O(13)	1780(4)	1932(7)	5082(4)	O(23)	129(3)	1502(7)	1760(4)
O(14)	1120(4)	3204(8)	4267(4)	O(24)	−435(4)	3358(7)	1313(4)
S(11)	2442(2)	263(4)	3994(2)	S(21)	−1319(2)	169(4)	2021(2)
S(12)	564(2)	821(4)	3742(2)	S(22)	−1241(2)	1444(4)	375(2)
S(13)	1996(2)	2498(4)	5621(2)	S(23)	719(2)	1818(3)	1980(2)
S(14)	968(2)	4250(4)	4023(2)	S(24)	−542(2)	4467(4)	1356(2)
O(111)	2197(7)	329(11)	3403(6)	O(211)	−1850(5)	647(10)	1757(5)
O(112)	2402(7)	−695(11)	4272(7)	O(212)	−1216(6)	−814(10)	1833(5)
O(121)	347(5)	1671(10)	3372(5)	O(221)	−1513(5)	515(9)	174(5)
O(122)	503(6)	−203(10)	3529(6)	O(222)	−1568(5)	2360(10)	264(5)
O(131)	2404(5)	1912(11)	6018(5)	O(231)	778(4)	2815(8)	2238(4)
O(132)	2111(6)	3558(10)	5527(5)	O(232)	1072(4)	1013(9)	2272(4)
O(141)	623(6)	4199(10)	3461(5)	O(241)	−241(7)	4884(10)	1886(6)
O(142)	1426(6)	4938(10)	4125(6)	O(242)	−1104(6)	4736(10)	1143(7)
C(101)	3179(14)	403(27)	4075(13)	C(201)	−1345(8)	−30(21)	2763(9)
F(111)	3382(7)	−321(13)	3789(8)	F(211)	−866(5)	−442(9)	3045(4)
F(112)	3298(7)	1319(17)	3873(11	F(212)	−1762(5)	−635(11)	2790(6)
F(113)	3437(6)	381(14)	4603(10)	F(213)	−1392(6)	897(13)	2996(6)
C(102)	160(10)	914(24)	4280(8)	C(202)	−694(10)	1585(24)	−20(8)
F(121)	−362(7)	650(18)	4089(7)	F(221)	−333(8)	890(15)	84(9)
F(122)	353(11)	79(17)	4619(11)	F(222)	−916(6)	1651(15)	−550(5)
F(123)	238(9)	1690(17)	4570(9)	F(223)	−406(6)	2463(13)	134(6)
C(103)	1387(11)	2473(22)	5906(9)	C(203)	954(7)	1983(17)	1334(8)
F(131)	1521(8)	2967(14)	6401(7)	F(231)	918(5)	1092(9)	1049(4)
F(132)	954(7)	2968(14)	5592(7)	F(232)	1503(4)	2231(10)	1464(4)
F(133)	1215(6)	1570(13)	5988(6)	F(233)	678(5)	2692(9)	1003(4)
C(104)	553(11)	4744(18)	4484(13)	C(204)	−161(12)	4978(19)	841(11)
F(141)	812(7)	4862(12)	4998(6)	F(241)	−198(7)	6019(11)	866(7)
F(142)	112(5)	4090(12)	4473(6)	F(242)	−399(7)	4666(14)	344(7)
F(143)	302(7)	5596(12)	4268(6)	F(243)	350(6)	4755(11)	958(7)
Solvent molecules							
C(1X)	251(11)	3282(21)	7047(12)	C(1B)	3867(13)	673(24)	2662(14)
C(2X)	156(16)	2509(29)	7392(16)	C(2B)	3476(14)	1230(25)	2255(14)
O(1X)	−336(8)	2242(15)	7505(8)	O(1B)	3761(11)	2092(20)	2083(12)
C(3X)	−374(14)	1217(27)	7796(16)	C(3B)	3347(17)	2504(30)	1562(19)
C(4X)	−330(12)	1423(24)	8365(14)	C(4B)	3685(20)	2583(36)	1140(21)
C(1A)	2881(13)	1129(22)	9386(13)	C(1C)	2121(15)	3220(26)	8015(16)
C(2A)	2403(15)	1140(28)	9541(14)	C(2C)	1927(16)	3588(30)	8359(17)
O(1A)	2160(8)	2209(14)	9504(7)	O(1C)	2450(18)	4043(32)	8803(18)
C(3A)	1623(18)	2397(29)	9583(17)	C(3C)	2482(12)	3528(22)	9025(13)
C(4A)	1375(22)	2451(38)	9841(23)	C(4C)	3027(12)	4295(22)	9469(12)

10.—This was prepared as for compound **7** but from $CrCl_2(thf)$ (1.0 g, 5.13 mmol) and $Me_2C_6H_2(NH_2)_2$ (1.4 g, 10.28 mmol). Yield: 1.1 g, 54%. IR: 3156m, 1713w, 1620w, 1561m, 1508m, 1298m, 1266m, 1207m, 1184m, 1102s, 1083s, 1019m, 999m, 861s, 800m, 729s, 696m, 624w, 601s, 533w, 461w, 439s, 360w, 331s and 278s cm^{-1}. EPR (solid): silent.

Benzyltriphenylphosphonium Tetrachloro(o-*phenylenediamine*)*vanadate*(III) **11**.—To a solution of $VCl_3(thf)_3$ (0.97 g, 2.6 mmol) and $[PPh_3(CH_2Ph)]Cl$ (1.01 g, 2.6 mmol) in toluene (*ca.* 40 cm^3) was added $C_6H_4(NH_2)_2$ (0.28 g, 2.6 mmol) and the mixture was refluxed for 12 h. Removal of volatiles under vacuum and extraction of the residue in MeCN, filtration, concentration and cooling (−20 °C) gave red plates. Yield: 30%. IR: 3284m, 3162s, 3048s, 2727w, 2608w, 1620w, 1603w, 1584w, 1536s, 1499s, 1340m, 1310m, 1251m, 1187m, 1166w, 1105s, 1027m, 996m, 957m, 941m, 921w, 858w, 756s, 722s, 690s, 576w, 528s, 459w, 437m, 311s and 250m cm^{-1}. EPR (CH_2Cl_2): silent. Conductivity (CH_2Cl_2, 20 °C): Λ_M = 43.8 ohm^{-1} cm^2 mol^{-1}.

Benzyltriphenylphosphonium Tetrachloro(4,5-*dimethyl*-o-*phenylenediamine*)*vanadate*(III) **12**.—To a solution of $VCl_3(thf)_3$ (1.55 g, 4.15 mmol) and $[PPh_3(CH_2Ph)]Cl$ (1.61 g, 4.15 mmol) in toluene (*ca.* 35 cm^3) was added $Me_2C_6H_2(NH_2)_2$ (0.56 g, 4.15 mmol). The resulting mixture was refluxed for 12 h, the precipitate was collected, washed with toluene (2 × 20 cm^3) and recrystallised from CH_2Cl_2. Yield: *ca.* 90%. IR: 3317w, 3151m, 3062m, 1616w, 1585m, 1559s, 1506s, 1407m, 1378s, 1342w, 1332w, 1285w, 1263s, 1238w, 1200m, 1183m, 1168m,

Table 9 Fractional atomic coordinates (× 10^4) for $[PPh_3(CH_2Ph)][VCl_4\{(H_2N)_2C_6H_2Me_2\}]\cdot CH_2Cl_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
V	925(1)	8 462(1)	2 536(1)	C(17)	2 293(3)	4 051(3)	2 338(2)
Cl(1)	1 855(1)	8 773(2)	1 930(1)	C(18)	2 396(3)	2 716(3)	2 199(2)
Cl(2)	1 761(1)	6 740(2)	3 100(1)	C(19)	2 926(3)	2 388(3)	1 849(2)
Cl(3)	−132(1)	8 148(2)	3 032(1)	C(20)	3 352(3)	3 394(3)	1 640(2)
Cl(4)	1 472(1)	10 320(2)	3 135(1)	C(21)	3 061(3)	6 410(5)	722(2)
N(1)	9(3)	9 692(5)	1 892(2)	C(22)	2 211(3)	6 009(5)	564(2)
N(2)	293(3)	7 034(5)	1 845(2)	C(23)	1 664(3)	6 294(5)	−12(2)
C(1)	−269(4)	9 053(7)	1 298(3)	C(24)	1 967(3)	6 981(5)	−429(2)
C(2)	−660(4)	9 745(7)	773(3)	C(25)	2 818(3)	7 383(5)	−271(2)
C(3)	−877(4)	9 102(8)	209(3)	C(26)	3 365(3)	7 097(5)	305(2)
C(4)	−669(4)	7 768(8)	185(3)	C(27)	3 934(4)	7 468(5)	1 950(2)
C(5)	−290(4)	7 072(7)	717(3)	C(28)	4 264(3)	8 628(5)	1 668(2)
C(6)	−106(4)	7 711(7)	1 270(3)	C(29)	5 134(3)	8 892(5)	1 805(2)
C(7)	−846(6)	7 042(10)	−421(4)	C(30)	5 415(3)	9 960(5)	1 527(2)
C(8)	1 331(6)	9 887(10)	−358(4)	C(31)	4 826(3)	10 764(5)	1 113(2)
P(1)	3 747(1)	5 997(2)	1 461(1)	C(32)	3 956(3)	10 500(5)	976(2)
C(9)	4 740(2)	5 378(5)	1 407(2)	C(33)	3 675(3)	9 432(5)	1 253(2)
C(10)	4 801(2)	4 818(5)	870(2)	C(34)	−2 707(10)	7 628(16)	841(5)
C(11)	5 570(2)	4 267(5)	848(2)	Cl(5)	−2 809(3)	6 672(4)	187(2)
C(12)	6 278(2)	4 276(5)	1 364(2)	Cl(6)	−4 024(10)	7 556(21)	436(8)
C(13)	6 217(2)	4 836(5)	1 901(2)	Cl(6B)	−3 610(13)	8 208(20)	779(10)
C(14)	5 448(2)	5 387(5)	1 923(2)	Cl(6C)	−2 622(9)	8 995(18)	948(9)
C(15)	3 250(3)	4 729(3)	1 779(2)	Cl(6D)	−3 191(20)	9 039(22)	749(9)
C(16)	2 720(3)	5 057(3)	2 129(2)				

1134m, 1090s, 1032m, 1016m, 996s, 922w, 876m, 860w, 839m, 810w, 788m, 754s, 734s, 721s, 693s, 581m, 509s, 496s, 439m, 362m and 301s cm^{-1}. Conductivity (CH_2Cl_2, 20 °C): Λ_M = 53.2 ohm^{-1} cm^2 mol^{-1}. EPR (CH_2Cl_2): silent.

Dichlorobis(o-*phenylenediamine*)*vanadium*(III) *Chloride* **13**.—The compounds $VCl_3(thf)_3$ (1.08 g, 2.89 mmol) and $C_6H_4(NH_2)_2$ (0.63 g, 5.78 mmol) were refluxed for 12 h in toluene (*ca.* 40 cm^3). The precipitate was collected, washed with toluene (2 × 30 cm^3) and hexane (30 cm^3) and dried *in vacuo*. Yield: essentially quantitative. IR: 3357w, 3232s, 3163m, 3115m, 1720w, 1629w, 1601w, 1561s, 1499s, 1298m, 1241s, 1125s, 1085m, 854w, 772s, 761s, 722s, 669w, 645w, 597w, 515w, 481w, 433s, 360s, 338s, 314s and 287m cm^{-1}. EPR (solid): g = 1.97.

Dichlorobis(4,5-*dimethyl*-o-*phenylenediamine*)*vanadium*(III) *Chloride* **14**.—This was prepared as for compound **13** but from $VCl_3(thf)_3$ (1.09 g, 2.68 mmol) and $Me_2C_6H_2(NH_2)_2$ (0.73 g, 5.36 mmol). Yield: essentially quantitative. IR: 3297w, 3195s, 3155s, 3087s, 1722w, 1620w, 1563s, 1545m, 1509s, 1300w, 1280m, 1207m, 1188m, 1126s, 1106s, 1022m, 1000m, 968m, 885m, 872s, 825w, 804w, 728s, 687w, 661w, 638w, 613w, 534w, 441m, 347m, 322m and 300m cm^{-1}. EPR (solid): g = 1.97.

Dichlorobis(o-*phenylenediamine*)*vanadium*(II) **15**.—To $[V_2Cl_3(thf)_6][Zn_2Cl_6]$[19] (1.63 g, 6.14 mmol) in CH_2Cl_2 (*ca.* 40 cm^3) was added $C_6H_4(NH_2)_2$ (1.33 g, 12.3 mmol). After stirring (25 °C) for 12 h the pink-red precipitate was collected, washed with CH_2Cl_2 (2 × 40 cm^3) and dried *in vacuo*. Yield: essentially quantitative. IR: 3396w, 3191s, 1652w, 1601m, 1571s, 1498s, 1304m, 1284m, 1266s, 1248s, 1199m, 1155m, 1101s, 1075s, 941w, 926w, 898w, 867w, 857w, 753s, 743s, 701m, 623m, 591m, 567w, 546w, 477w, 462w, 438s and 287s cm^{-1}. EPR: see text.

Diiodobis(o-*phenylenediamine*)*manganese*(II) **16**.—To a suspension of MnI_2 (1.0 g, 3.24 mmol) in CH_2Cl_2 (*ca.* 40 cm^3) was added $C_6H_4(NH_2)_2$ (0.7 g, 6.48 mmol). After stirring (25 °C) for 48 h the green precipitate was collected, washed with CH_2Cl_2 (2 × 30 cm^3) and dried *in vacuo*. Yield: 1.4 g, 82%. IR: 3351w, 3317m, 3261s, 3245s, 3158s, 3120s, 1605m, 1570m, 1558s, 1497s, 1302w, 1259m, 1249m, 1207w, 1192w, 1173w, 1154w, 1100m, 1053s, 996s, 982s, 942m, 926m, 864m, 852w, 770s, 758s, 733s, 575m, 546s, 533s, 482m, 457m, 435m, 424m and 282m cm^{-1}. EPR (solid): g = 2.00.

Diiodobis(4,5-*dimethyl*-o-*phenylenediamine*)*manganese*(II) **17**.—This was prepared as for compound **16** but from MnI_2 (1.0 g, 3.24 mmol) and $Me_2C_6H_2(NH_2)_2$ (0.89 g, 6.53 mmol). Yield: 1.37 g, 73%. IR: 3267s, 3190s, 2727w, 1717w, 1619w, 1557s, 1509s, 1293m, 1219m, 1195m, 1154w, 1084m, 1033s, 995s, 883m, 872m, 824w, 722m, 583m, 517m, 440m and 357m cm^{-1}. EPR (solid): g = 2.02.

X-Ray Crystallography.—Crystals of all four compounds were sealed under argon in thin-walled glass capillaries. Cell dimensions and intensity data were recorded as previously described using a CAD4 diffractometer[23] for the two triflates and a FAST TV area detector diffractometer[24] for the chlorides. The structures were solved and developed *via* the heavy-atom method and refined by full-matrix least squares. An absorption correction *via* the DIFABS method[25] was applied. Non-hydrogen atoms were refined anisotropically. Hydrogens were included in idealised positions in all cases (aromatic and NH_2) except for the phenylenediamine hydrogens of the chromium tetrachloride complex **1** and the co-ordinated amido group of the tris(triflate) **5**, where they were experimentally located and refined with individual U_{iso} values. The CF_3 groups of the triflates in both complexes **5** and **6** showed extensive thermal motion/disorder, but no splitting of peaks occurred. The *R* values for these structures are adversely affected by this effect. Crystal data and experimental details are given in Table 6. Final fractional atomic coordinates for non-hydrogen atoms are given in Tables 7–9.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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