Preparation and Properties of 1-Adamantoxides, 2-Adamantoxides, and 1-Adamantylmethoxides of Ti^{IV}, V^{IV}, Nb^{IV}, Nb^{V}, Cr^{III}, Cr^{IV}, Mo^{IV}, Mn^{II}, Fe^{III}, and Co^{II}. The Crystal and Molecular Structure of Tetrakis(1-adamantoxo)dimethylaminemolybdenum(IV) †‡

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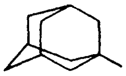
By reaction of transition-metal dialkylamides with 1-adamantanol, 2-adamantanol, and 1-adamantylmethanol, a series of first- and second-row transition-metal alkoxides has been prepared. The complexes of tetra- and penta-valent metals are monomeric (those of M^{II} and M^{III} being polymeric) mostly crystalline solids. The air-stable tetrakis(1-adamantoxo)chromium(IV) is a convenient starting material for the preparation of chromium tetra-alkyls. An *X*-ray crystallographic study of $Mo(1\text{-ado})_4(NHMe_2)$ (1-ado = 1-adamantoxo) confirms a trigonal-bipyramidal structure of the complex, with the amine and one alkoxo-ligand in the axial positions. The axial Mo–O distance [1.963(2) Å] is *ca.* 0.06 Å longer than the equatorial distances [1.888(3)—1.916(2) Å], and Mo–N is 2.321(3) Å. The compound crystallises in the triclinic space group $P\bar{1}$, with a = 13.500(1), b = 13.168(2), c = 11.646(1) Å, α = 91.034(10), β = 103.835(8), γ = 70.842(10)°, and Z = 2. The structure has been solved by Patterson and Fourier methods and refined by least squares to R = 0.041 using 5 267 observed diffractometer data.

DURING the course of studies on the co-ordinative behaviour of sterically demanding ligands, we examined the adamantyl group as a means for increasing the kinetic stability of transition-metal complexes. Compounds of ligands containing the highly symmetrical and chemically very inert adamantyl group were expected not only to be thermally stable and possibly of unusual co-ordination geometry, but also of preparative advantage. A number of complexes $M(X\text{–}ad)_n$ (M = transition metal; X = O or CH_2) [1] have been synthesised. Here we report the preparation and properties of alkoxides [2] derived from 1-adamantanol, 2-adamantanol, and 1-adamantylmethanol.

1-adamantyl =



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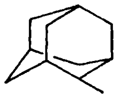

RESULTS AND DISCUSSION

A. Titanium Complexes.—The most convenient route to titanium alkoxides is by alcohol exchange of tetrakis(isopropoxo)titanium(IV) [3] and the corresponding higher-boiling alcohol in benzene.[4] The complexes $Ti(1\text{-ado})_4$ (1), $Ti(2\text{-ado})_4$ (2), and $Ti(1\text{-admeo})_4$ (3) (ado = adamantoxo, admeo = adamantylmethoxo) were prepared in this way. They are white, thermally very stable crystalline compounds. Complexes (1) and (2) reflect the excellent crystal-packing properties of the adamantyl groups in their physical behaviour; their melting points lie above 350 °C, and they are only moderately soluble in common organic solvents. The structurally similar $Ti(OBu^t)_4$ is a liquid (b.p. 107 °C, 10 Torr).[5,§]

Whereas (1) and (2) can be handled in air for short periods of time, (3) is more sensitive to hydrolysis, considerably more soluble in, *e.g.*, diethyl ether or benzene, and has a lower melting point. By comparison, $Ti(OCH_2Bu^t)_4$ is a wax-like solid, m.p. 64 °C.[3]

The i.r. spectroscopic data of these and other compounds are listed in Table 1. The most prominent features of the i.r. spectra of all alkoxides are the ν(C–O) bands found between 1 000 and 1 120 cm^{-1} (very similar values to the corresponding bands in the spectra of the free alcohol). Especially typical of adamantyl compounds are the C–H stretching bands of the bridgehead CH groups at relatively low wavenumbers (2 650 and 2 675 cm^{-1} for 1-ado).

For tetrahedral complexes, two bands due to M–O vibrations are i.r.-active, one of which (ν_3) is a stretching mode, the other (ν_4) mainly a bending mode and should therefore appear at lower energy than ν_3. This was found to be true for a very large number of tetrahedral complexes and complex anions.[6] In the range of 500—700 cm^{-1}, a complex $M(OR)_4$ should therefore exhibit only one i.r. band due to a metal–oxygen vibration. For a number of monomeric alkoxides, though, two or more bands have been found in this region and assigned as ν(M–O) modes. For $Ti(OPr^i)_4$, for example, Kriegsmann and Licht [7] found i.r. bands at 621s and 560m cm^{-1}, whereas Bradley and co-workers [8] report 619vs and 526w cm^{-1}. The increased number of bands might well be due to interaction between ν(M–O) and either δ(M–O–C) or vibrations of the alkyl substituents. The complexes

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† No reprints available.

‡ Dimethylaminetetrakis(tricyclo[3.3.1.1^{3,7}]dec-1-yloxo)-molybdenum(IV).

§ Throughout this paper: 1 Torr = (101 325/760) Pa; 1 B.M. = 9.274 × 10^{-24} A m^2.

TABLE 1

Magnetic moments and i.r. spectroscopic data

Compound	Colour	$\mu_{\text{eff.}}$ [a]	C–O stretching modes (cm^{-1})	M–O stretching [b] modes (cm^{-1})
(1) Ti(1-ado)_4	White	dia.	1 110vs 1 085vs 1 037w 1 000vs 957s	690s 641w 488s
(2) Ti(2-ado)_4	White	dia.	1 095vs 1 060vs 1 030vs	655s 622m 476s
(3) Ti(1-admeo)_4	White	dia.	1 058vs 1 023vs	690s 670s 645w 621w 608w 588m 525m 489m
(4) V(1-ado)_4	Dark green	1.75	1 102s 1 070vs 1 035w 978vs 946s	688s 639w 504w
(5) V(2-ado)_4	Blue	1.57	1 096s 1 080m 1 046s 1 006vs	656s 618m 486s 460w
(6) V(1-admeo)_4	Brown	1.71	1 067s 1 028vs	695s 679s 645m 616w 583m 544m 488m
(7) Nb(1-ado)_4	Olive green	1.40	1 107s 1 079vs 986vs 950s	667m 660s 640w 473s
(8) Nb(1-ado)_5	White	dia.	1 105vs 1 023vs 1 035w 1 010m 985vs 948s	670 (sh) 660s 640w 472s
(9) Nb(2-ado)_5	White	dia.	1 096s 1 083s 1 054vs 1 023vs 1 005s, (sh)	641s 618s 469s 448s
(10) $\text{Nb(1-admeo)}_4\cdot 0.5\text{NHEt}_2$	Blue	*ca.* 0	1 070vs,br 985m	652s 641s 600m 596w 565m 549s 450m
(11) $[\text{Cr(1-ado)}_3]_n$	Grey-green		1 108s 1 083s 1 074s 978s 432s	680m 667m 608m 597w 563s
(12) $\text{LiCr(1-ado)}_3\text{Cl}$	Pink		1 110s 1 080vs 980s 940s	676m 646w 625s 580s, br 459m
(13) $[\text{Cr(1-ado)}_3]_4(\text{LiCl})_3$	Purple	3.20	1 110vs 1 083vs 1 057s	676m 643m 624s 577m
(14) Cr(1-ado)_4	Peacock blue	2.68	1 100s 1 065vs 975s 945s	691m 685m 640w 512m
(15) $\text{Mo(1-ado)}_4(\text{NHMe}_2)$	Green	2.62	1 104s 1 090s 1 070vs	664s 643m 633m

TABLE 1 (*Continued*)

Compound	Colour	$\mu_{\text{eff.}}$ [a]	C–O stretching modes (cm^{-1})	M–O stretching [b] modes (cm^{-1})
(16) Mo(2-ado)$_4$(NHMe$_2$)	Pale blue	2.72	1 097s 1 079w 1 046s 1 007s	647s 627m 612m
(17) [Mo(1-admeo)$_4$]$_n$	Blue	1.58	1 033vs 1 010s 985s	687s 674s 647m 639m 579m 568m 550m
(18) Mo(1-ado)$_4$(PMe$_3$)	Blue		1 104m 1 089w 1 068s 1 063s 977s 944s	666m 641w 628w 490m
(19) [Mn(1-ado)$_2$]$_n$	Pale beige	5.44	1 117s 1 089s 987s 944s	594s 520s,br 445m 402w 336m 280m
(20) [Mn(1-admeo)$_2$]$_n$	Pale beige		1 060vs 1 050 (sh) 1 040 (sh)	608s 499s 420s 327m
(21) [Fe(1-ado)$_3$]$_n$	Yellow	4.69	1 116vs 1 085vs 987s 943s	673w 642m 627s 510s,br 458m
(22) [Fe(1-admeo)$_3$]$_n$	Pale beige		1 055vs 1 030s, (sh) 1 003m	670s,br 613s,br 565m 476m
(23) [Co(1-ado)$_2$]$_n$	Pale purple	5.09	1 112vs 1 081vs 980s 940vs	598s 570vs 447m 405w 346m 287m
(24) [Co(1-admeo)$_2$]$_n$	Pale pink		1 064vs	613s 500s,br 480s 328m

[a] Measured in the solid state at room temperature in Bohr Magnetons (B.M.); dia. = diamagnetic. [b] As Nujol mulls between KBr or CsI plates.

Ti(1-ado)$_4$ and Ti(2-ado)$_4$ too show more than one band in the region in question at somewhat higher wavenumbers than found for Ti(OPr^i)$_4$. Assignments for Ti(1-admeo)$_4$ are not possible due to the presence of CH$_2$ deformation modes.

A diagnostically useful observation is that mononuclear 1- and 2-adamantoxides show no absorptions between 500 and 600 cm^{-1}, whereas bridging alkoxide ligands usually give rise to intense and broad bands in this region. We therefore suggest that (1) and (2) are monomeric in the solid state. The i.r. spectrum of (3) is less easily interpreted.

Molecular-weight determinations of all three compounds in benzene confirm that they are monomeric.

The complex Ti(1-ado)$_4$ has ^{1}H n.m.r. absorptions (in C$_6$D$_6$; relative to hexamethyldisiloxane) at $\delta = 1.65$ (CH) and 2.16 (CH$_2$) p.p.m; both are slightly broadened multiplets. Resonances for Ti(2-ado)$_4$ occur at $\delta = 1.7$ (t, broad), 2.22 (br), 2.57 (br), 2.70 (br), and 4.81 p.p.m. (t, CH–O–; ^3J *ca.* 3.5 Hz). The spectrum of Ti(1-admeo)$_4$ is characterised by signals at 1.45 (m), 1.87 (s,br), and 3.8 (br, –CH$_2$O–) p.p.m.; the latter show a shift of *ca.* 0.7 p.p.m. to higher field compared to unco-ordinated 1-adCH$_2$OH.

Molecular ions are observed in the mass spectra of all three complexes, accompanied by peaks reflecting the loss of one alkoxide group.

Compound (1) shows additional peaks due to disruption of a C$_{10}$H$_{15}$ skeleton (loss of C$_4$H$_9$ and C$_7$H$_{10}$) as well as for loss of this unit as a whole. For (2) stepwise loss of one, two, and three alkoxy substituents is observed. The fragmentation pattern of (3) differs in so far as not only peaks due to loss of a C$_{10}$H$_{15}$ unit, but also due to elimination of formaldehyde can be identified.

B. Vanadium Complexes.—The interaction, in diethyl ether, of vanadium tetrakis(diethylamide) with 1-adamantanol, 2-adamantanol, or 1-adamantylmethanol at room temperature over a period of 12—18 h produces the complexes V(1-ado)$_4$ (4), V(2-ado)$_4$ (5), and V(1-admeo)$_4$ (6), respectively. Compound (4) crystallises from the reaction mixture in dark green plates which are only sparingly soluble in hexane, diethyl ether, or benzene. This has precluded molecular-weight determinations. The crystals decompose slowly in a sealed tube under argon above 250 °C without melting. Complex (5) is obtained as a pale blue microcrystalline solid which demonstrates the same physical properties.

To obtain (6), the reaction mixture is taken to dryness and the residue recrystallised from light petroleum (b.p. 40—60 °C). The fine crystalline brown solid dissolves in benzene to give a green-brown colour. Molecular-weight determinations in this solvent have shown the complex to be monomeric. In light petroleum solution it undergoes a reversible colour change from brown at room temperature and below to olive green at *ca.* 40 °C. This phenomenon can be explained by assuming a monomer–oligomer equilibrium which is shifted to the monomer side by weakly co-ordinating solvents or temperature increase. It has been argued that vanadium alkoxides of primary alcohols are brown due to their oligomeric nature, whereas the alkoxides of secondary and most tertiary alcohols are monomeric and green. A significant exception amongst the primary alkoxides is $V(OCH_2Bu^t)_4$ which is a green solid and monomeric in solution.[9] This assumption of a monomer–dimer equilibrium for (6) is not fully supported. Even at −120 °C e.p.r. spectra of light petroleum solutions of (6) show that, despite the brown colour, a monomeric species is present. The eight lines of the spectrum at ambient temperature, caused by isotropic coupling of a single unpaired electron with the spin of a ^{51}V nucleus ($I = \frac{7}{2}$), split into components parallel and perpendicular to the direction of the applied magnetic field. The resulting anisotropic spectrum of two superimposed sets of eight lines is typical in its appearance for a series of vanadium(IV) compounds. The *g* values and coupling constants found for (4) and (6) agree well with those reported for $V(OBu^t)_4$[10] and $V(NR_2)_4$ (R = Me[11] or Et[12]). In contrast to the behaviour of frozen solutions of (6), no hyperfine splitting is found in clearly oligomeric compounds due to spin–spin interaction, as observed for $[V(OMe)_4]_3$ and $[V(OEt)_4]_2$.[11] The room temperature e.p.r. spectrum of (4) in diethyl ether is nearly identical to that described for (6) (see Table 2).

TABLE 2

E.p.r. data for some alkoxides

Compound	Solvent	T/K	
(4)	Benzene	295	$\langle g \rangle = 1.9863$, $A_{iso.} = -70$ G
(6)	Benzene	295	$\langle g \rangle = 1.9835$, $A_{iso.} = -71$ G
	Light petroleum	295	$\langle g \rangle = 1.9856$, $A_{iso.} = -71$ G
	Light petroleum	120	$g_{\parallel} = 1.9669$, $A_{\parallel} = -145$ G
			$g_{\perp} = 1.9627$, $A_{\perp} = -50$ G
(13)	thf	120	$g_{\perp}$ *ca.* 3.54, $g_{\parallel}$ *ca.* 1.96

Bulk magnetic susceptibilities of solids (4), (5), and (6) were measured. Although provision of diamagnetic corrections for the large ligands is likely to introduce errors, the magnetic moments so obtained compare satisfactorily with the spin-only value expected for a single unpaired electron (Table 1).

The i.r. spectra of the vanadium alkoxides are remarkably similar to those of the titanium complexes, in accord with a high degree of structural similarity. The i.r. spectrum of (6), when compared to (3), shows no additional absorption in the region between 700 and 450 cm^{-1} which might indicate a dimeric or oligomeric structure in the solid state.

In the mass spectra of (4) and (5), the molecular peaks are noted, though less intense than in the case of titanium. They are accompanied by peaks due to loss of one and two adamantyl groups as well as of adamantanol molecules. The highest peak in the spectrum of (6) can be explained as loss of methyladamantane from the molecular ion.

Complex (4) fails to react with PMe_3 in OEt_2, but with an excess of NO it forms light beige, thf-soluble VO(1-ado)$_3$ [ν(V=O) 1 003 cm^{-1}] (thf = tetrahydrofuran).

C. Niobium Complexes.—On treatment with 1-adamantanol in diethyl ether at room temperature, $Nb(NEt_2)_4$ forms olive green solutions of Nb(1-ado)$_4$ (7) which can be recovered in good yield as a fine crystalline solid. It is considerably more soluble than the vanadium analogue, presumably because the Nb centre is less shielded by its ligands than the smaller V ion and can therefore form labile solvate complexes, but in contrast to its molybdenum analogue, it does not retain co-ordinated dialkylamine (see below). Its monomeric character is supported by molecular-weight determinations in benzene, by the i.r. spectrum which largely resembles that of (1) and (4), and by the magnetic moment which agrees well with values found for NbX_4L_2 (X = Cl, Br, or I; L = pyridine or tetrahydrothiophen) where L inhibits metal–metal interactions.[13] It decomposes in a sealed tube under argon at 140 °C to give a colourless material which does not melt up to 350 °C. To our knowledge, the only other niobium(IV) alkoxide is the polymeric $Nb(OEt)_4$, a diamagnetic red oil, which is thermally stable, but extremely readily oxidised.[14] Other attempts to prepare niobium(IV) alkoxides were unsuccessful.[15] Compound (7) is air-sensitive, but significantly less so than its molybdenum analogue (16) from which it also differs in its reactivity towards Lewis bases. No reaction was observed between (7) and PMe_3 in refluxing diethyl ether, or with dimethylamine or tetrahydrothiophen at room temperature. The reaction with $LiCH_2SiMe_3$ proceeds only very slowly. No e.p.r. signal is observed using diethyl ether solutions of the complex either at room temperature or at −150 °C.

In refluxing benzene, $Nb(NEt_2)_4$ reacts with 1-adamantanol to give an off-white to greenish solid. After washing with diethyl ether, colourless Nb(1-ado)$_5$ (8) is obtained. The compound does not melt or decompose on heating up to 350 °C, is only sparingly soluble in light petroleum or diethyl ether, but slightly more so in aromatic solvents in which it is monomeric. The i.r. spectrum is very similar to that of (7).

In a similar reaction with 2-adamantanol in diethyl ether, oxidation to Nb^{V} occurs even at room temperature, and Nb(2-ado)$_5$ (9) is found. It exhibits the same physical properties as (8).

The existence of Nb(NMe$_2$)$_5$ on one hand and Nb(NEt$_2$)$_4$ on the other demonstrates the sensitive dependence of the metal oxidation state on the steric requirements of the ligands. This would explain the preference of Nb^{V} over Nb^{IV} in the presence of secondary alkoxo-ligands. With primary alcohols the formation of a niobium(v) complex might therefore be expected. The reaction of Nb(NEt$_2$)$_4$ with 1-adamantylmethanol shows that this is not the case. Instead, a deep blue light petroleum solution is obtained from which blue air-sensitive Nb(1-admeo)$_4$·0.5NHEt$_2$ (10) crystallises. The compound is diamagnetic in the solid state. In fresh benzene solutions, the monomeric complexes Nb(1-admeo)$_4$ and Nb(1-admeo)$_4$(NHEt$_2$) appear to be present, so that an average molecular weight is found. On ageing, a blue solid precipitates, which is probably the amine-free polymeric niobium alkoxide.

D. Chromium Complexes.—The reaction of 1-adamantanol with Cr[N(Pr^i)$_2$]$_3$ in diethyl ether at room temperature yields grey-green, insoluble Cr(1-ado)$_3$ (11). The i.r. spectrum of the air-sensitive compound indicates a polymeric structure, and we propose the presence of CrO$_6$ octahedra as in the pale green Cr(OEt)$_3$.[16] The size of adamantyl groups does not appear to be sufficient to reduce the preferred co-ordination number of a trivalent metal ion. No reaction takes place between 1-adamantanol and Cr[N(SiMe$_3$)$_2$]$_3$ in boiling toluene.

Complex (11) reacts with an excess of NO to give a red-brown thf- and OEt$_2$-soluble adduct Cr(1-ado)$_3$(NO) [ν(NO) 1 715 cm^{-1}; *cf*. orange-red Cr(OBu^t)$_3$(NO): ν(NO) 1 707 cm^{-1}].[17]

When 1-adamantanol is added to a diethyl ether solution of Cr(NEt$_2$)$_3$ at −70 °C [prepared *in situ* by adding CrCl$_3$(thf)$_3$ to LiNEt$_2$ at low temperature] the solution turns red-purple during a period of several hours, and a purple solid precipitates. From the filtrate, a thf-soluble pale purple solid is obtained. The elemental analysis is consistent with the formula LiCr(1-ado)$_3$Cl (12). It is very air-sensitive and is reminiscent in colour of the pink polymeric LiCr(OBu^t)$_4$, obtained under similar conditions with t-butanol.[18]

The precipitate from the reaction is only very sparingly soluble in thf, though small quantities can be recrystallised from a thf–OEt$_2$ mixture. The bright purple crystals analyse for [Cr(1-ado)$_3$]$_4$(LiCl)$_3$ (13). This species could not be obtained chloride-free after repeated crystallisation. No melting or decomposition was observed up to 350 °C. The compound is extremely sensitive towards oxygen and water, and turns grey-green immediately on exposure to air. With traces of oxygen in solution, however, the blue, air-stable Cr(1-ado)$_4$ is formed (see below).

A comparison of the i.r. spectrum of (13) with that of (1) or (4) shows an increased number of bands between 500 and 700 cm^{-1}, with a slightly broadened band at 577 cm^{-1}, suggesting bridging alkoxo-groups; similar bands are found in the i.r. spectra of Mn(OBu^t)$_2$, Mn(1-ado)$_2$, and Co(1-ado)$_2$. The low volatility and insolubility of (13) have precluded mass-spectrometric identification or cryoscopic molecular-weight determination.

The magnetic moment in the solid state is consistent with three unpaired electrons. The e.p.r. spectrum of (14) in frozen thf solution (150 °C) consists of a sharp signal at g *ca*. 3.5 and a broad absorption at g *ca*. 2, and is typical for a d^3 species in a trigonal crystal field (C_{3v} or D_{3h}) in the case of large zero-field splitting. Similar signals have been reported for Cr[CH(SiMe$_3$)$_2$]$_3$ [19] and Cr[N(SiMe$_3$)$_2$]$_3$.[20]

Treatment of Cr(NEt$_2$)$_4$ in light petroleum (b.p. 40—60 °C) with an excess of 1-adamantanol afforded peacock blue crystals of Cr(1-ado)$_4$ (14). This compound is virtually insoluble in diethyl ether, hydrocarbon, or chlorocarbon solvents at room temperature, but may be recrystallised from hot toluene. The crystals are unaffected by temperatures up to 310 °C *in vacuo*. In contrast to its Ti and V analogues, solid (14) remains unaffected by air over several days. Solutions appear to be susceptible to hydrolysis. The enhanced stability may be ascribed to the (relative to Ti^{IV} and V^{IV}) smaller covalent radius of Cr^{IV}, allowing more effective protection by the encroaching ligands, as well as the effective crystal packing of adamantyl groups. This stability and the easy preparation render (14) an attractive precursor to organic derivatives of Cr^{IV} and give it great advantage over, for example, Cr(OBu^t)$_4$. Treatment of (14) with LiCH$_2$SiMe$_3$ in light petroleum affords Cr(CH$_2$SiMe$_3$)$_5$ in >80% yield. The transalkylation proceeds very cleanly as no redox or disproportionation reactions are involved [21] and the only by-product, 1-adamantoxolithium, is precipitated from hydrocarbon solvents.

Complex (14) can also be prepared, though in inferior yield, by successive treatment of CrCl$_3$(thf)$_3$ with 1-adamantoxolithium and CuCl.

The low solubility of (14) does not permit of molecular-weight determination but the i.r. spectrum is in accord with a monomeric species (Table 1), and a molecular ion is observed in the mass spectrum.

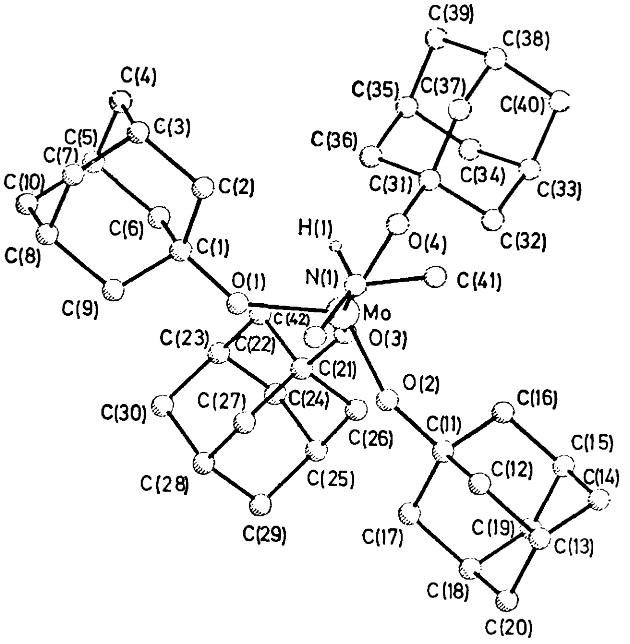
No e.p.r. signal was detectable, either in mobile or in frozen solutions, down to −120 °C. This behaviour is analogous to that of Cr(OBu^t)$_4$.[22]

E. Molybdenum Complexes.—When a light petroleum solution of Mo(NMe$_2$)$_4$ is added to 1-adamantanol in diethyl ether at room temperature, the deep purple colour of the molybdenum amides gives way immediately to green. On standing, dark green crystals of Mo(1-ado)$_4$(NHMe$_2$) (15) separate. The compound is extremely air-sensitive and once crystallised, insoluble in OEt$_2$. It begins to decompose at *ca*. 160 °C and melts with decomposition at 184—185 °C. The magnetic moment in the solid state approximates to the spin-only value for a d^2 system.

In the i.r. spectrum of (15) the N–H stretching frequency occurs at 3 300 cm^{-1}. The absence of bands between 500 and 630 cm^{-1} corroborates the monomeric nature of the complex. The highest peak observed in the mass spectrum corresponds to $MoO_2(1\text{-ado})_2^+$. The molecular structure has been determined by *X*-ray diffraction methods.

The molecular structure and atom-numbering scheme are shown in the Figure. Important bond lengths and angles relating to the metal co-ordination are given in Table 3; data for the adamantyl skeleton are normal (mean C–C 1.524 and mean O–C 1.427 Å) and are available in the Supplementary Publication (See Experimental section).

The metal co-ordination geometry is most conveniently described as a distorted trigonal bipyramid with the $NHMe_2$ ligand and one alkoxo-group occupying axial sites. The difference (0.066 Å) between the Mo–O (axial) distance (1.963 Å) and the mean Mo–O (equatorial) distance (1.897 Å) is slightly smaller than that (0.1 Å) found between the terminal axial and equatorial Mo–O distances in $Mo_2(OPr^i)_8$,[23] but in the latter compound the dimerisation and metal-to-metal bonding present will obviously have affected the bonding parameters in the co-ordination sphere.



Structure of $Mo(1\text{-ado})_4(NHMe_2)$ showing the atom-numbering system

The Mo–N bond to the amine (2.321 Å) is rather longer than the corresponding bonds in the related amine adducts $Mo_2(OSiMe_3)_6(NHMe_2)_2$ [2.278 and 2.285(6) Å][24] and $Mo(OSiMe_3)_4(NHMe_2)_2$ [2.219(4) Å],[25] but is comparable to the presumably '*trans*-influenced' W–N(py) distance of 2.32 Å in the trigonal-bipyramidal compounds $[W(OCMe_3)_3(NO)(py)]$ (py = pyridine).[26]

The lengthening of the molybdenum–amine bond is probably a consequence of steric crowding by the bulky adamantoxo-groups, and indeed the $NHMe_2$ ligand appears to be under pressure with several short contacts between its hydrogen atom and methyl groups and alkoxo-oxygen atoms (see Table 4). The distribution of the ligand atoms in the co-ordination sphere, in which the equatorial Mo–O bonds are all pushed away from the axial Mo–O(3) bond with O(3)–Mo–O (equatorial) angles of 95—100°, is also a reflection of the steric crowding.

The formation of, and bonding parameters in, this compound make an interesting comparison with the related six-co-ordinate molecule $Mo(OSiMe_3)_4(NHMe_2)_2$ mentioned previously. It is clear that the isolated $Mo(OR)_4$ system, which would probably have a tetrahedral structure, is co-ordinatively unsaturated and thus ready to accept additional ligands. The degree to which this can be achieved will depend on the bulk of the R group on the alkoxide. The formation of these di- and mono-adducts reflects the diminished crowding potential of the $OSiMe_3$ group, due in part to the relatively long O–Si bond which pushes the $SiMe_3$ umbrella outwards and thus reduces its steric 'cone angle'.

TABLE 3

Important bond lengths and angles for $Mo(1\text{-ado})_4(NHMe_2)$ with estimated standard deviations in parentheses

(*a*) Bond lengths (Å)

Mo–N(1)	2.321(3)	N(1)–C(41)	1.486(4)
Mo–O(1)	1.897(2)	N(1)–C(42)	1.485(7)
Mo–O(2)	1.916(2)	N(1)–H(1)	0.80(4)
Mo–O(3)	1.963(2)		
Mo–O(4)	1.888(3)		

(*b*) Bond angles (°)

N(1)–Mo–O(1)	90.0(1)	Mo–N(1)–C(41)	113.0(2)
N(1)–Mo–O(2)	78.6(1)	Mo–N(1)–C(42)	113.0(2)
N(1)–Mo–O(3)	173.2(1)	C(41)–N(1)–C(42)	111.4(3)
N(1)–Mo–O(4)	80.4(1)		
O(1)–Mo–O(2)	117.4(1)	Mo–O(1)–C(1)	141.7(2)
O(1)–Mo–O(3)	96.3(1)	Mo–O(2)–C(11)	136.8(2)
O(1)–Mo–O(4)	116.4(1)	Mo–O(3)–C(21)	140.3(2)
O(2)–Mo–O(3)	100.4(1)	Mo–O(4)–C(31)	137.8(2)
O(2)–Mo–O(4)	121.6(1)		
O(3)–Mo–O(4)	94.6(1)		

Upon treatment with 2-adamantanol, $Mo(NMe_2)_4$ forms $Mo(2\text{-ado})_4(NHMe_2)$ (**16**) as fine pale blue, aerobically susceptible crystals. We assume the structure to be similar to that of (**15**). The i.r. spectrum has ν(N–H) at 3 290 cm^{-1}. The analogous reaction of $Mo(NMe_2)_4$ with 1-adamantylmethanol produces a deep blue solution, and the solid obtained after evaporation of the solvent is initially very soluble in OEt_2 but on standing at room temperature, a blue, much less soluble solid precipitates.

TABLE 4

Short interatomic non-bonded contacts (Å) for $Mo(1\text{-ado})_4$-$(NHMe_2)$

(*a*) Intramolecular-interligand

C(41) · · · O(2)	3.14	H(6a) · · · H(22a)	2.52
C(41) · · · O(4)	3.04	H(6b) · · · H(36b)	2.35
C(42) · · · O(1)	3.34	H(16b) · · · H(32b)	2.54
C(42) · · · O(2)	3.03	H(17a) · · · H(27b)	2.32
H(1) · · · C(2)	2.76	H(42c) · · · H(9a)	2.41
H(1) · · · H(2b)	2.35	H(41b) · · · H(12a)	2.47
H(1) · · · O(4)	2.64		

(*b*) Intermolecular

The shortest such contact is 2.28 Å between
H(9a) · · · H(29b) $(\bar{x}, \bar{y}, \bar{z})$
All others are 2.42 and above.

It analyses for Mo(1-admeo)$_4$ (17). The compound is polymeric and does not contain amine, plausibly because the sterically less demanding adamantylmethoxo-ligands allow the individual Mo(1-admeo)$_4$ units to associate. Spin–spin interaction of the Mo centres is now possible, and a reduction in magnetic moment is observed. Similar behaviour of related molybdenum(IV) alkoxides has recently been reported. The compound Mo(OBu^t)$_4$, which was obtained by sublimation and consequently may have lost any initially co-ordinated amine, has a magnetic moment of 1.38 in solution; Mo(OPr^i)$_4$ and Mo(OCH$_2$Bu^t)$_4$ are dimeric with very low magnetic moments.[25]

Complex (15) reacts with PMe$_3$ in refluxing diethyl ether to give very air-sensitive blue crystals of Mo(1-ado)$_4$(PMe$_3$) (18). The compound is moderately soluble in diethyl ether or benzene and is presumably isostructural with (15).

F. Manganese Complexes.—Bis(alkoxo)manganese(II) compounds Mn(1-ado)$_2$ (19) and Mn(1-admeo)$_2$ (20) precipitate quantitatively when a solution of Mn[N(SiMe$_3$)$_2$]$_2$ in light petroleum is added to a solution of the corresponding alcohol in diethyl ether at room temperature. They are air-sensitive, pale beige insoluble polymers; (19) appears to be less sensitive towards air than Mn(OBu^t)$_2$ (prepared by the same route for comparison). Neither compound melts or decomposes upon heating up to 350 °C. The magnetic moment indicates the presence of five unpaired electrons per Mn. The polymeric nature of (19) and (20) is supported by their i.r. spectra.*

G. Iron Complexes.—The iron(III) alkoxides Fe(1-ado)$_3$ (21) and Fe(1-admeo)$_3$ (22) are obtained by reacting Fe[N(SiMe$_3$)$_2$]$_3$, in refluxing benzene, with 1-adamantanol and 1-adamantylmethanol, respectively. Compound (21) is a yellow microcrystalline solid of low solubility in most organic solvents. This precludes cryoscopic molecular-weight determinations, so that it is uncertain whether it exists as a dimer, as does Fe(OSiMe$_3$)$_3$,[27] or as a trimer like the iron alkoxides of smaller alcohols.[28] The magnetic moment is low for a d^5 ion {*cf.* the moments of [Fe(OR)$_3$]$_3$ (R = Me, Et, or Bu^n)} and can be attributed to magnetic interaction with neighbouring metal ions.[28]

H. Cobalt Complexes.—On addition of Co[N(SiMe$_3$)$_2$]$_2$ to benzene solutions of 1-adamantanol and 1-adamantylmethanol, respectively, the cobalt alkoxides Co(1-ado)$_2$ (23) and Co(1-admeo)$_2$ (24) precipitate as insoluble polymers. The reaction is completed by brief refluxing. Complex (23) is a pale purple paramagnetic solid; its magnetic moment compares well with that of Co(OMe)$_2$ ($\mu_{\text{eff.}}$ = 5.46 B.M.).[16] Complex (24) is pale pink. The i.r. spectra of both these compounds are virtually identical to those of the manganese alkoxides (19) and (20) respectively. Disparities occur only below 600 cm^{-1} where manganese exhibits lower ν(M–O) values than cobalt.[29] We suggest that the manganese and cobalt complexes are isostructural with triply bridging alkoxo-ligands octahedrally surrounding the metal(II) centres.

EXPERIMENTAL

Microanalyses were by Pascher and by Butterworth Laboratories. Perkin-Elmer R32, 90-MHz (^{1}H n.m.r.), Perkin-Elmer 457 (i.r.), Varian E12 *X*-band (e.p.r.), and VG Micromass (mass) spectrometers were used. Magnetic moments were measured in sealed tubes under argon using an apparatus constructed by Dr. D. F. Evans. All operations were carried out under argon. Diethyl ether, tetrahydrofuran (thf), light petroleum (b.p. 40—60 °C), and benzene were distilled from sodium–benzophenone under nitrogen. Toluene was distilled from sodium. Melting points were determined in sealed capillaries under argon and are uncorrected. The compounds 1-adamantanol, 2-adamantanol, and 1-adamantylmethanol were used as supplied (Aldrich Chemical Co. Ltd.). The starting materials, Ti(OPr^i)$_4$,[3] V(NEt$_2$)$_4$,[15] Cr(NEt$_2$)$_4$,[30] Mn[N(SiMe$_3$)$_2$]$_2$,[31] Cr[N(Pr^i)$_2$]$_3$,[18] Fe[N(SiMe$_3$)$_2$]$_3$,[32,33] Co[N(SiMe$_3$)$_2$]$_2$,[32] Mo(NMe$_2$)$_4$,[34] Nb(NEt$_2$)$_4$,[35] and Nb(NMe$_2$)$_5$ [35] were prepared according to literature methods. The melting points and analytical data are collected in Table 5.

Titanium Compounds.—*Tetrakis*(1-*adamantoxo*)*titanium*(IV), (1). The compound Ti(OPr^i)$_4$ (1.36 g, 4.78 mmol) and 1-adamantanol (3.0 g) were refluxed in benzene for 2 h. The benzene–isopropanol azeotrope was distilled off, the residue concentrated to 10 cm^3, and allowed to crystallise. Yield 2.8 g (90%).

In an identical fashion, (2) (yield 92%) and (3) (yield 81%) were made from 2-adamantanol and 1-adamantylmethanol, respectively.

Vanadium Compounds.—The complex V(NEt$_2$)$_4$ (1.0 mmol) in light petroleum was added to a solution of 1-adamantanol (610 mg, 4 mmol) in OEt$_2$ (20 cm^3) at room temperature. The mixture was stirred briefly and left overnight to give dark green crystals of (4) (420 mg, 0.64 mmol; 64%).

From 2-adamantanol, blue (5) was obtained (60% yield).

The complex V(NEt$_2$)$_4$ (1 mmol) was reacted with 1-adamantylmethanol (660 mg, 4 mmol) in OEt$_2$ (20 cm^3) within 3 h at room temperature. The mixture was concentrated to give brown microcrystalline (6) on cooling (350 mg, 0.49 mmol; 49%).

Niobium Compounds.—*Tetrakis*(1-*adamantoxo*)*niobium*(IV), (7). The complex Nb(NEt$_2$)$_4$ (1 mmol) was added to a solution of 1-adamantylmethanol (610 mg, 4 mmol) in OEt$_2$ (20 cm^3) and stirred for 2 h. The olive green solution was taken to dryness and the residue recrystallised from diethyl ether (5 cm^3). Yield 480 mg (69%).

Pentakis(1-*adamantoxo*)*niobium*(V), (8). The complex Nb(NEt$_2$)$_4$ (1 mmol) was added to a solution of 1-adamantylmethanol (610 mg, 4 mmol) in benzene (30 cm^3). The mixture was refluxed for 30 min, the solvent removed *in vacuo*, the mixture redissolved in diethyl ether, filtered, and concentrated to give an off-white solid, which was washed with diethyl ether (2 × 5 cm^3). Yield 320 mg (40%).

Pentakis(2-*adamantoxo*)*niobium*(V), (9). The complex Nb(NEt$_2$)$_4$ (0.8 mmol) was added to a solution of 2-adamantanol (530 mg, 3.48 mmol) in diethyl ether (15 cm^3). The mixture was stirred overnight. The white precipitate was filtered off and dried. Yield 500 mg (76%).

Tetrakis(1-*adamantylmethoxo*)*niobium*(IV)·0.5*diethylamine*,

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* During the course of this work, complex (19) has been independently described by B. Horvath, R. Moseler, and E. G. Horvath, *Z. anorg. Chem.*, 1979, **449**, 41.

(10). The complex $Nb(NEt_2)_4$ (1 mmol) was added to a solution of 1-adamantylmethanol (4 mmol) in diethyl ether (10 cm^3). The deep blue solution was concentrated and left to crystallise. To improve crystallisation, light petroleum (3 cm^3) was added. On cooling, a microcrystalline blue solid formed (250 mg, 32%).

Chromium Compounds.—Tris(1-*adamantoxo*)*chromium*(III), (11). A light petroleum solution of $Cr[N(Pr^i)_2]_3$ (1 mmol) was added to 1-adamantanol (460 mg, 3 mmol) in benzene (20 cm^3). The mixture was refluxed for 2 h. Diethyl ether (20 cm^3) was added and the grey-green precipitate collected. Yield *ca.* 350 mg (70%).

Reaction of 1-*adamantanol with* $Cr(NEt_2)_3$ *at low temperature.* The complex $Cr(NEt_2)_3$ was prepared *in situ* at −60 °C by adding $CrCl_3(thf)_3$ (3.36 g, 9 mmol) to a solution of $LiNEt_2$ (30 mmol) in OEt_2 (30 cm^3). To the deep green solution was then added 1-adamantanol (4.1 g, 27 mmol) in thf (30 cm^3) and the mixture allowed to warm to room temperature. After stirring overnight, the deep purple solution was filtered, concentrated to 15 cm^3, and diethyl ether (30 cm^3) added. Some precipitated LiCl was removed and the solution concentrated to give a purple solid (pink when dry). Yield of (12), 1.1 g.

TABLE 5

Analytical data for alkoxides

Compound	M.p. (θ_c/°C)	Found (%) C	H	N	Other	M [a]	Calculated (%) C	H	N	Other	M
(1)	>350	72.7	9.3			580	73.6	9.3			653
(2)	>350	73.7	9.2			570	73.6	9.3			653
(3)	105—106	73.6	9.7			640	74.6	9.7			709
(4)	>250 (decomp.)	72.4	9.4	<0.4		*b*	73.2	9.2	0.0		
(5)	>250 (decomp.)	72.2	9.1	<0.3		*b*	73.2	9.2	0.0		
(6)	145 (decomp.)	74.0	9.6	<0.3		680	74.2	9.6	0.0		712
(7)	>140 (decomp.)	68.7	8.5	<0.2	O: 9.3	670	68.8	8.7	0.0	O: 9.2	698
(8)	>350	70.6	8.7	<0.2		800	70.7	8.9	0.0		849
(9)	>350	70.3	9.7	<0.2		*b*	70.7	8.9	0.0		
(10)		69.9	9.7	1.0		803	69.9	9.4	0.90		*c*
(11)	>350	69.3	8.6		O: 10.5	*b*	71.3	9.0		O: 10.7	
(12)	>350	62.2	8.2		Cl: 6.7	*b*	65.7	8.3		Cl: 6.5	
(13)	>350	66.1	8.8		Cl: 4.9	*b*	67.0	8.4		Cl: 5.0	
(14)	>350	73.0	9.3			*b*	73.1	9.2			
(15)	184—185 (decomp.)	67.6	9.1	1.9		*b*	67.6	9.0	1.9		
(16)	>250 (decomp.)	67.2	9.3	1.8		*b*	67.6	9.1	1.9		
(17)	235 (decomp.)	70.7	8.9		O: 7.9	*b*	69.0	9.1		O: 8.4	
(18)	229—230 (decomp.)	64.5	9.0		P: 3.8		66.5	9.0		P: 4.0	
(19)	>350	67.2	8.8	0.2		*b*	67.2	8.5	0.0		
(20)	>350	68.6	8.9	<0.2		*b*	68.6	8.9	0.0		
(21)	>350	70.6	9.0			*b*	70.7	8.9			
(22)	216—220 (decomp.)	70.9	9.3		O: 9.1	1 040	71.8	9.3		O: 8.70	1 004
(23)	>310 (decomp.)	65.2	8.1			*b*	66.5	8.4			
(24)	225 (decomp.)	67.6	9.0	<0.1		*b*	67.8	8.8	0.0		

[a] Cryoscopically in benzene. [b] Compound is insufficiently soluble. [c] See text.

The purple precipitate obtained in this reaction (2.24 g) was only sparingly soluble in thf. Small quantities were recrystallised from thf–OEt_2 to give (13) which analysed for $[Cr(1\text{-}ado)_3]_4(LiCl)_3$.

On washing (13) with toluene, a very small amount of a blue solid was obtained and identified as $Cr(1\text{-}ado)_4$, (14) (see below).

Tetrakis(1-*adamantoxo*)*chromium*(IV), (14). (a) *From* $Cr(NEt_2)_4$. The complex $Cr(NEt_2)_4$ (2 mmol) was added to a solution of 1-adamantanol (1.2 g, 8 mmol) in diethyl ether (50 cm^3) and stirred for 2 h at room temperature. On cooling, peacock blue crystals separated (0.90 g, 69%).

(b) *By oxidation of* Cr^{III} *with* CuCl. The compound $CrCl_3(thf)_3$ (1 g, 2.7 mmol) was treated with 1-adamantoxosodium (11.4 mmol) at gentle reflux in thf (50 cm^3) for 1.5 h until formation of a blue-purple solid was complete. The mixture was cooled to ambient temperature, and anhydrous CuCl (0.26 g, 2.6 mmol) was introduced. The mixture was refluxed for 4 h, the solvent removed, and the grey-purple residue extracted with hot (80 °C) toluene (40 cm^3). Filtration and cooling afforded blue crystals (0.75 g, 43%).

Reaction of $Cr(1\text{-}ado)_4$ *with* $LiCH_2SiMe_3$. To a suspension of $Cr(1\text{-}ado)_4$ (310 mg, 0.47 mmol) was added $LiCH_2SiMe_3$ (2.3 mmol) in light petroleum at −70 °C. The mixture was allowed to reach room temperature, stirred for 1.5 h, and filtered. The solvent was removed and the purple oily residue cooled to −30 °C to afford purple needles of $Cr(CH_2SiMe_3)_4$ [21] (160 mg, 87%). These were rinsed with cold light petroleum and dried *in vacuo*.

Molybdenum Compounds.—Tetrakis(1-*adamantoxo*)*dimethylaminemolybdenum*(IV), (15). The compound $Mo(NMe_2)_4$ (1 mmol), in light petroleum solution, was added to a carefully degassed solution of 1-adamantanol (610 mg, 4 mmol) in OEt_2 (30 cm^3). A deep green solution formed which was stirred briefly. Crystallisation at room temperature gave green crystals which were collected and dried (350 mg, 47%).

The complex $Mo(2\text{-}ado)_4(NHMe_2)$, (16), was obtained similarly. To obtain crystals, the solution must be concentrated to *ca.* 5 cm^3. Yield *ca.* 300 mg (40%).

Tetrakis(1-*adamantylmethoxo*)*molybdenum*(IV) (17). The compound $Mo(NMe_2)_4$ (1 mmol) was added to a solution of 1-adamantylmethanol (640 mg, 3.85 mmol) in OEt_2 (10 cm^3). A dark blue solution formed which was taken to dryness and pumped *in vacuo* for 1 h. Diethyl ether (5 cm^3) was added, and the solution left at room temperature overnight. After addition of light petroleum (10 cm^3), the dark blue-green solid which formed was collected. Yield *ca.* 400 mg (53%).

Tetrakis(1-*adamantoxo*)*trimethylphosphinemolybdenum*(IV), (17). To $Mo(1\text{-}ado)_4(NHMe_2)$ (100 mg, 0.13 mmol) was added OEt_2 (4 cm^3) and PMe_3 (0.4 cm^3, *ca.* 4 mmol) by trap-to-trap distillation *in vacuo*. Removal of traces of oxygen by freeze-pumping the solvent is essential. The mixture was warmed and refluxed gently for *ca.* 0.5 h. The dark blue crystals which separated from the blue solution were collected, quickly washed with cold light petroleum, and dried. Yield 50 mg (49%).

More crystals were obtained from the filtrate, but they were contaminated with small amounts of red-brown crystals which analysed for $MoO_2(1\text{-ado})_2(PMe_3)$.

Manganese Compounds.—The complex $Mn[N(SiMe_3)_2]_2$ (1 mmol) was added to 2 equivalents of 1-adamantanol or 1-adamantylmethanol, respectively, in OEt_2 (20 cm^3). The mixture was refluxed for 30 min and the precipitate collected. Yield: (19), 350 mg (98%); (20), 360 mg (93%).

Table 6

Fractional co-ordinates ($\times$ 10^5 for Mo; $\times$ 10^4 for others) of the non-hydrogen atoms for $Mo(1\text{-ado})_4(NHMe_2)$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Mo	19 114(2)	12 185(2)	25 930(2)
O(1)	384(2)	1 744(2)	2 344(2)
O(2)	2 593(2)	−305(2)	2 567(2)
O(3)	1 943(2)	1 701(2)	1 021(2)
O(4)	2 667(2)	2 095(2)	3 422(2)
N(1)	2 086(2)	641(2)	4 525(2)
C(1)	−465(2)	2 578(2)	2 663(3)
C(2)	−158(3)	2 897(3)	3 938(3)
C(3)	−1 128(3)	3 781(3)	4 229(3)
C(4)	−1 408(4)	4 746(3)	3 415(4)
C(5)	−1 760(4)	4 494(3)	2 127(4)
C(6)	−797(4)	3 600(4)	1 840(4)
C(7)	−2 056(4)	3 356(4)	4 057(4)
C(8)	−2 401(3)	3 105(4)	2 795(4)
C(9)	−1 429(3)	2 194(3)	2 498(4)
C(10)	−2 705(4)	4 075(4)	1 983(5)
C(11)	3 420(2)	−1 006(2)	2 069(3)
C(12)	3 952(3)	−2 041(3)	2 870(3)
C(13)	4 862(3)	−2 862(3)	2 392(3)
C(14)	5 710(3)	−2 310(3)	2 436(4)
C(15)	5 177(3)	−1 275(3)	1 546(3)
C(16)	4 271(3)	−493(3)	2 019(3)
C(17)	2 959(3)	−1 299(3)	835(3)
C(18)	3 862(3)	−2 073(3)	349(3)
C(19)	4 709(3)	−1 545(3)	301(3)
C(20)	4 391(4)	−3 099(3)	1 152(4)
C(21)	1 341(2)	1 831(2)	−179(3)
C(22)	727(3)	3 019(3)	−563(3)
C(23)	134(3)	3 161(3)	−1 873(3)
C(24)	964(4)	2 730(3)	−2 606(3)
C(25)	1 575(3)	1 549(3)	−2 251(3)
C(26)	2 146(3)	1 426(3)	945(3)
C(27)	532(3)	1 218(3)	−409(3)
C(28)	−52(3)	1 347(3)	−1 735(3)
C(29)	797(4)	915(3)	−2 459(4)
C(30)	−656(3)	2 533(3)	−2 091(4)
C(31)	3 110(2)	2 887(2)	3 147(3)
C(32)	4 047(3)	2 372(3)	2 579(4)
C(33)	4 552(3)	3 210(3)	2 367(4)
C(34)	3 705(4)	4 117(3)	1 535(4)
C(35)	2 767(3)	4 652(3)	2 095(4)
C(36)	2 262(3)	3 816(3)	2 337(3)
C(37)	3 520(3)	3 333(3)	4 320(3)
C(38)	4 016(3)	4 174(3)	4 102(4)
C(39)	3 174(4)	5 086(3)	3 273(4)
C(40)	4 965(3)	3 641(4)	3 542(5)
C(41)	3 229(3)	226(3)	5 226(3)
C(42)	1 517(4)	−139(3)	4 594(4)

Iron Compounds.—*Tris*(1-*adamantoxo*)*iron*(III), (21). The complex $Fe[N(SiMe_3)_2]_3$ (0.8 mmol) was added to a solution of 1-adamantanol (400 mg, 2.7 mmol) in benzene (20 cm^3). The mixture was refluxed for 4 h and the pale yellow precipitate collected. Yield *ca.* 200 mg (0.39 mmol, 49%).

Tris(1-*adamantylmethoxo*)*iron*(III), (22), was obtained in a similar way. As it is more soluble, the solution was concentrated, and light petroleum (20 cm^3) added. Yield 150 mg (0.27 mmol, 34%).

Cobalt Compounds.—*Bis*(1-*adamantoxo*)*cobalt*(II), (23). The complex $Co[N(SiMe_3)_2]_2$ (0.9 mmol) was added to a solution of 1-adamantanol (300 mg, 2 mmol) in benzene (10 cm^3). The mixture was refluxed briefly, the purple

Table 7

Fractional co-ordinates ($\times$ 10^3) of the hydrogen atoms in $Mo(1\text{-ado})_4(NHMe_2)$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
H(1)	178(3)	122(3)	474(3)
H(2a)	50(4)	313(4)	408(4)
H(2b)	−7(3)	217(3)	449(4)
H(3)	−95(3)	395(3)	501(3)
H(4a)	−75(5)	489(4)	351(5)
H(4b)	−205(4)	536(4)	357(4)
H(5)	−195(3)	516(4)	161(4)
H(6a)	−108(4)	322(4)	108(4)
H(6b)	3(4)	371(4)	215(4)
H(7a)	−265(4)	384(4)	423(4)
H(7b)	−184(4)	276(4)	465(4)
H(8)	−301(4)	283(3)	267(4)
H(9a)	−109(4)	151(4)	316(4)
H(9b)	−160(3)	210(3)	159(4)
H(10a)	−269(4)	386(4)	138(4)
H(10b)	−332(5)	464(5)	224(5)
H(12a)	428(3)	−186(3)	362(3)
H(12b)	336(3)	−235(3)	293(3)
H(13)	520(3)	−344(3)	285(3)
H(14a)	601(3)	−218(3)	303(4)
H(14b)	632(3)	−277(3)	204(3)
H(15)	572(3)	−90(3)	158(3)
H(16a)	457(3)	−36(3)	287(3)
H(16b)	393(3)	14(3)	163(3)
H(17a)	263(3)	−67(3)	38(3)
H(17b)	245(3)	−162(3)	92(3)
H(18)	358(3)	−220(3)	−40(3)
H(19a)	441(3)	−94(3)	−21(3)
H(19b)	532(3)	−201(3)	−2(3)
H(20a)	383(3)	−342(3)	113(3)
H(20b)	295(3)	−352(3)	90(3)
H(22a)	21(3)	331(3)	−13(3)
H(22b)	128(3)	338(3)	−44(3)
H(23)	−31(3)	390(3)	−211(3)
H(24a)	64(3)	281(3)	−344(4)
H(24b)	138(3)	311(3)	−250(3)
H(25)	207(3)	127(3)	−266(3)
H(26a)	251(3)	59(3)	−78(3)
H(26b)	265(3)	181(3)	−79(3)
H(27a)	1(3)	145(2)	2(3)
H(27b)	85(3)	44(3)	−22(3)
H(28)	−62(3)	100(3)	−189(3)
H(29a)	41(3)	103(3)	−330(4)
H(29b)	108(3)	5(3)	−226(4)
H(30a)	−106(3)	264(3)	−294(4)
H(30b)	−122(3)	278(3)	−162(3)
H(32a)	495(3)	176(3)	309(3)
H(32b)	380(3)	230(3)	186(3)
H(33)	514(3)	285(3)	204(3)
H(34a)	402(3)	467(4)	138(4)
H(34b)	348(3)	384(3)	83(4)
H(35)	220(3)	526(3)	157(4)
H(36a)	120(3)	355(3)	171(3)
H(36b)	161(3)	416(3)	273(3)
H(37a)	297(3)	361(3)	469(3)
H(37b)	404(3)	275(3)	482(3)
H(38)	428(3)	436(3)	481(4)
H(39a)	343(3)	560(3)	318(4)
H(39b)	357(3)	547(3)	363(3)
H(40a)	538(3)	412(3)	356(4)
H(40b)	549(4)	309(4)	408(4)
H(41a)	331(3)	−2(3)	609(4)
H(41b)	357(3)	−46(3)	494(4)
H(41c)	365(4)	74(4)	509(4)
H(42a)	184(3)	−73(3)	427(3)
H(42b)	161(4)	−38(3)	545(4)
H(42c)	67(4)	26(4)	410(5)

residue filtered off, and washed with OEt_2 ($5\ cm^3$). Yield *ca.* 320 mg (0.9 mmol, 100%).

Bis(1-*adamantylmethoxo*)*cobalt*(II), (24), was obtained similarly. Yield *ca.* 360 mg (0.9 mmol, 100%).

X-*Ray Structure Analysis*.—The crystal ($0.30 \times 0.25 \times 0.18$ mm) obtained at room temperature from the reaction mixture in diethyl ether, was mounted and sealed under argon in a Lindemann capillary using silicon grease as adhesive.

The unit-cell parameters were determined from least-squares refinement of the setting angles for 25 reflections [$16 < \theta(\text{Mo-}K_\alpha) < 17°$] automatically centred on a Nonius CAD4 diffractometer.

Crystal Data.—$C_{42}H_{67}MoNO_4$, $M = 745.94$, $a = 13.500(1)$, $b = 13.168(2)$, $c = 11.646(1)$ Å, $\alpha = 91.034(10)$, $\beta = 103.835(8)$, $\gamma = 70.842(10)°$, $U = 1\,894.8$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.31$ g cm^{-3}, $F(000) = 800$, $\mu(\text{Mo-}K_\alpha) = 3.3$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å.

The intensities of 6 382 reflections ($\pm h, \pm k, l$; $1.5 < \theta < 26°$) were measured using monochromated Mo-K_α radiation and an ω—2θ scan method as described earlier.[36] Periodic check of two standard reflections did not show any decay of the crystal during data collection. All intensities were corrected for Lorentz and polarisation effects but not for absorption or extinction. Averaging equivalent reflections and omitting those with $F_o < 3\sigma(F_o)$ yielded 5 267 unique data (internal consistency, $R = 0.009$).

The position of the molybdenum atoms was obtained from a Patterson map and all other atoms were located from successive electron-density synthesis. Full-matrix least-squares refinement of the non-hydrogen atoms, first with isotropic and then anisotropic thermal parameters, reduced the R value to 0.112 and 0.059 respectively. All the hydrogen atoms were then located from difference maps and included in the refinement with isotropic temperature factors. The structure finally refined to $R = 0.041$ and $R'[= (\Sigma w\Delta F^2/\Sigma wF_o^2)^{\frac{1}{2}}] = 0.043$. The weighting scheme $w = 1/[\sigma^2F_o + 0.000\,4\ F_o^2]$ was applied and gave satisfactory analysis of variance.

The positional parameters of the non-hydrogen atoms are given in Table 6 and the hydrogen-atom parameters in Table 7. The anisotropic temperature factors of the non-hydrogen atoms, the isotropic temperature factors of the hydrogen atoms, dimensions of the adamantoxo-ligands and lists of observed and calculated structure factors are deposited as Supplementary Publication No. SUP 22735 (32 pp.).* Neutral-atom scattering factors were taken from refs. 37 (for H) and 38 (for others). All calculations were performed on the Queen Mary College ICL1904S and University of London CDC7600 computers with programs SHELX 76 [39] (structure determination and refinement) and PLUTO [40] (diagram).

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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