Synthesis and Properties of Bis(t-butyl)methoxides of Chromium(III,IV), Manganese(II), Iron(III), Cobalt(II), and Copper(I). The Crystal and Molecular Structures of Lithium Tetrakis[bis(t-butyl)methoxo]chromate-(III)–Tetrahydrofuran (1/1), Tetrakis[bis(t-butyl)methoxo]chromium(IV), and Lithium Tetrakis[bis(t-butyl)methoxo]ferrate(III)–Bis(t-butyl)-methanol (1/1) †

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By the interaction either of transition-metal dialkylamides with bis(t-butyl)methanol or of the halide with the lithium alkoxide, a series of neutral alkoxides or lithium alkoxo-metallate anions have been prepared for chromium(III,IV), manganese(II), iron(III), cobalt(II), and copper(I). Electron paramagnetic resonance and electronic absorption spectra are reported. The crystal and molecular structures of the complexes $LiCr(OCHBu^t_2)_4 \cdot thf$ (1), $Cr(OCHBu^t_2)_4$ (2), and $LiFe(OCHBu^t_2)_4 \cdot Bu^t_2CHOH$ (3) have been determined by an *X*-ray crystallographic study. Compound (1) is triclinic, space group $P\bar{1}$, with a = 19.986(2), b = 11.618(2), c = 11.390(1) Å, α = 117.61(1), β = 76.45(1), γ = 93.11(1)°, and Z = 2. Compound (2) is monoclinic, space group $C2/c$, with a = 20.249(3), b = 10.748(1), c = 20.275(2) Å, β = 116.68(1)°, and Z = 4. Compound (3) is monoclinic, space group $P2_1/n$, with a = 18.308(3), b = 22.505(4), c = 11.979(5) Å, β = 94.20(1)°, and Z = 4. The structures were determined using data measured on an automatic diffractometer and refined by least squares to R values of 0.068 (3 396 observed data), 0.067 (2 057 data), and 0.061 (4 879 data) for (1), (2), and (3) respectively. All structures contain a distorted tetrahedrally co-ordinated Cr or Fe atom; and in (1) and (3), the lithium ion is incorporated into the MO_4 co-ordination sphere, and bridges two of the four alkoxo-oxygen atoms. The transition-metal geometries are discussed in terms of steric and electronic factors.

As part of studies of ligands with large steric requirements, we described the synthesis of various transition-metal adamantoxo-complexes.[1] Here we describe similar complexes of the more sterically demanding alkoxo-ligand from bis(t-butyl)methanol (2,2,4,4-tetramethylpentan-3-ol), together with *X*-ray structural data on three of them.

RESULTS AND DISCUSSION

Although many alkoxo-complexes can be obtained by alcoholysis of the corresponding metal dialkylamide, $M(NR_2)_n$ (R = alkyl or $SiMe_3$),[2,3] bis(t-butyl)methanol does not react, even in boiling toluene, with some first-row transition-metal dialkylamides, notably the tris and tetrakis compounds, $V(NEt_2)_4$, $Cr[N(SiMe_3)_2]_3$, or $Cr(NEt_2)_4$, presumably for steric reasons, although the bis compounds, *e.g.* $Mn[N(SiMe_3)_2]_2$, do react. However, the tris and tetrakis alkoxides can be obtained from the metal halide and lithium bis(t-butyl)methoxide.

The Scheme summarises the reactions studied. Electron paramagnetic resonance and absorption spectra are collected in Table 1.

Chromium.—In light petroleum at room temperature, $LiOCHBu^t_2$ and a small excess of $CrCl_3(thf)_3$ (thf = tetrahydrofuran) gives a blue-green solution from which royal-blue, air-sensitive crystals of $Cr(OCHBu^t_2)_3 \cdot thf$ can be isolated. This compound is very soluble in non-polar solvents, as are the other complexes with this ligand, and is monomeric in benzene. The i.r. spectrum of this complex differs significantly from that of the clearly monomeric compound $Cr(OCHBu^t_2)_4$ (see below), particularly in the region of M–O stretching modes, and a broad band at 555 cm^{-1} is taken as an indication of a dimeric structure in the solid state. Light petroleum solutions of the complex do not give rise to an e.s.r. signal, either at room temperature or at −160 °C. The magnetic moment in the solid state at 23 °C ($\mu_{eff.}$ = 3.2 B.M.) ‡ is somewhat lower than the expected spin-only value for three unpaired electrons per Cr atom.

TABLE 1

Electron paramagnetic resonance and electronic absorption spectra of bis(t-butyl)methoxides

Compound	E.s.r.	Electronic [a] (λ/nm)
$Cr(OCHBu^t_2)_3 \cdot thf$		700
$LiCr(OCHBu^t_2)_4 \cdot thf$	$g_\perp$ *ca.* 3.22 $g_\parallel$ *ca.* 2.0 [b]	690
$Cr(OCHBu^t_2)_4$		716, 567
$Mn(OCHBu^t_2)_2$	g = 1.9585 [a]	Absorption rising to charge-transfer band at 300
$LiFe(OCHBu^t_2)_4 \cdot Bu^t_2CHOH$	g_x = 4.067, 21.3 g_y = 6.93 g_z = 5.54, 1.65(3) [b]	Absorption rising to charge-transfer band at 260
$Co(OCHBu^t_2)_2$		653, 597, 513, 434

[a] In light petroleum, 25 °C. [b] In light petroleum, −160 °C.

At ambient temperature the mass spectrum shows $Cr(OR)_3^+$ (R = $CHBu^t_2$) as highest peak. On heating, the dimeric species $Cr_2(OR)_3^+$, $Cr_2(OR)_4^+$, and $Cr_2(OR)_5^+$ and some fragments thereof are observed in addition.

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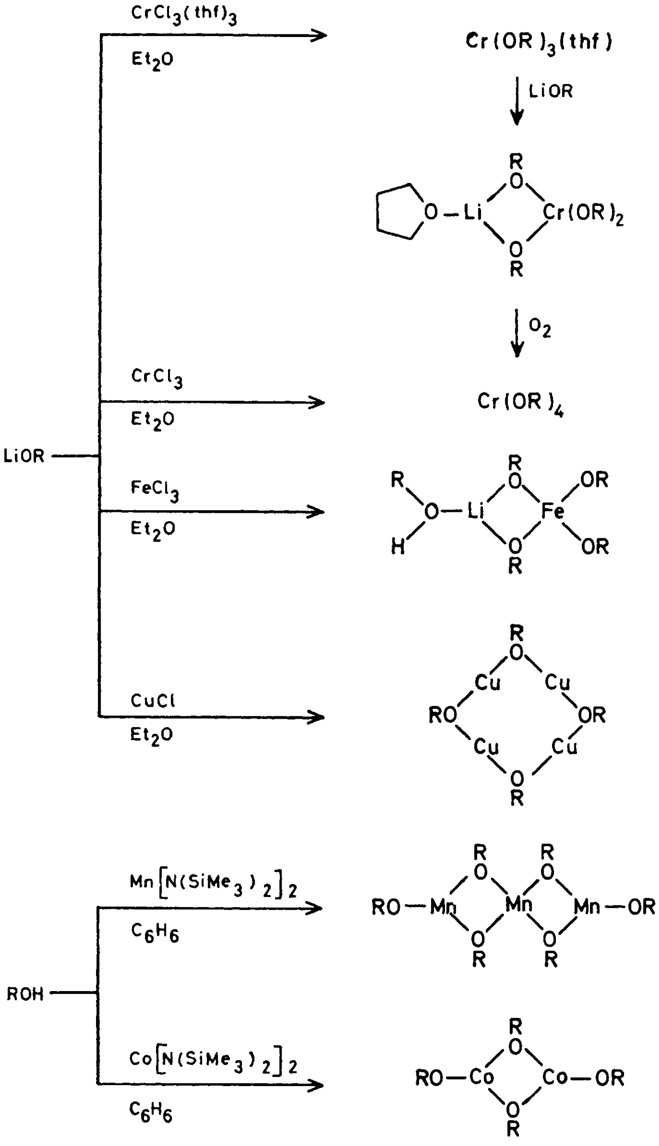
† No reprints available.

‡ Throughout this paper: 1 B.M. = 9.274 × 10^{-24} A m^2.

Using a slight excess of LiOCHBu$^t_2$ over CrCl$_3$(thf)$_3$, air-sensitive dichroic (blue or intense green, depending on orientation) crystals of LiCr(OCHBu$^t_2$)$_4$·thf (1) are obtained. The compound is monomeric in benzene. The i.r. spectrum suggests alkoxide bridges. The mass spectrum is virtually identical to that of Cr(OCHBu$^t_2$)$_3$·thf.



SCHEME R = CHBu$^t_2$

No e.s.r. signal is observed at room temperature, but a frozen petroleum solution (−150 °C) gives a spectrum typical of a d^3 ($S = \frac{3}{2}$) species in a fairly strong axial or near axial ligand field.

The compound LiCr(OCHBu$^t_2$)$_4$·thf does not react with PMe$_3$, but is readily oxidised by traces of O$_2$ or by CuCl to form Cr^{IV}(OCHBu$^t_2$)$_4$ (2). The latter may be obtained directly from anhydrous CrCl$_3$ in diethyl ether or light petroleum, plausibly by disproportionation, whereas the presence of thf evidently stabilises the Cr^{III} species. The chromium(IV) compound forms bottle green crystals which give turquoise-blue solutions in light petroleum or toluene; the solid is unaffected by air, apparently indefinitely, although solutions are air-sensitive.

As for tetrakis(1-adamantoxo)chromium(IV), no e.s.r. signal could be observed either at room temperature or at −160 °C. This behaviour appears not to be uncommon for d^2 ($S = 1$) species. Tetrakis(t-butoxo)-chromium(IV) required cooling to 10 K in order to obtain a spectrum.[4]

The absence of any strong bands between 450 and 700 cm^{-1} in the i.r. spectrum of Cr(OCHBu$^t_2$)$_4$ underlines the monomeric character of the compound in the solid state. The ν(M–O) vibration is found at 718(s) cm^{-1}. The mass spectrum shows Cr(OR)$_3^+$ as highest peak, accompanied by Cr(OR)$_2^+$ and some fragmentation. A parent ion is not observed.

Only one other sec-alkoxo chromium(IV) species, Cr(OCHMeBu^t)$_4$ is known;[5] the steric bulk of the ligands probably prevents internal oxidation–reduction to lower valent species as in other cases.[4] Surprisingly, few well authenticated chromium(III) alkoxides are known,[4,6] there being several poorly characterised ones.[7] All are pale green insoluble polymers probably containing CrO$_6$ octahedra and a polymeric structure has also been suggested for LiCr(OBu^t)$_4$.[8] By contrast, the molecular weights for the three compounds indicate monomeric species and thus, a maximum co-ordination number of 4. This has been confirmed for both (1) and (2) by X-ray crystallography. The structures are illustrated in Figures 1 and 2 respectively, whilst important bond lengths and angles are listed in Tables 2 and 3.

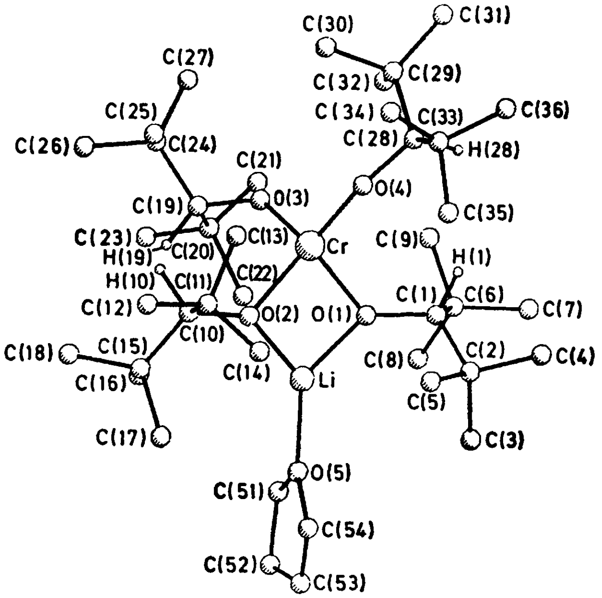


FIGURE 1 Structure of LiCr[OCH(CMe$_3$)$_2$]$_4$·C$_4$H$_8$O, showing the atom-numbering system. Methyl hydrogens are omitted for clarity

The compound Cr(OCHBu$^t_2$)$_4$, (2), exists as discrete molecules which possess C_2 symmetry. The O–Cr–O angles are close to tetrahedral [108.8—112.4(2)°] but show a slight tetragonal flattening in the direction of the two-fold axis. Whilst this might be related to the non-spherical *d* shell for the d^2 Cr^{IV} ion, it could also of course, be due to steric forces. Although there are no exceptionally short intramolecular interligand contacts there are many close to the limiting values for the sums of relevant van der Waals radii. In fact, the only indications of serious steric repulsions are within the ligands themselves where interactions between the CMe$_3$ groups have enlarged angles C(2)–C(1)–C(5) and C(11)–C(10)–C(15) to *ca.* 121°. Thus, although there does not seem to be any interligand compression, the molecule can be considered to be crowded and it is easy to see why co-ordination oligomerisation does not occur, as it does with less bulky alkoxides.

The question as to whether the d^2 configuration of the Cr^{IV} ion may have a distortive influence on the CrO$_4$ geometry is an interesting one. Spectroscopic results on ML$_4$ species with L = alkylamide or alkoxide were interpreted in terms of a distorted tetrahedral structure,[9] but a recent determination of the structure of Mo(NMe$_2$)$_4$ showed it to have an almost perfectly tetrahedral structure.[10] The relative complexity of the present structure (in terms of asymmetry of the alkoxy group and the degree of rotational freedom provided by the Cr–O and O–C bonds) unfortunately does not allow us to throw any more light on this question.

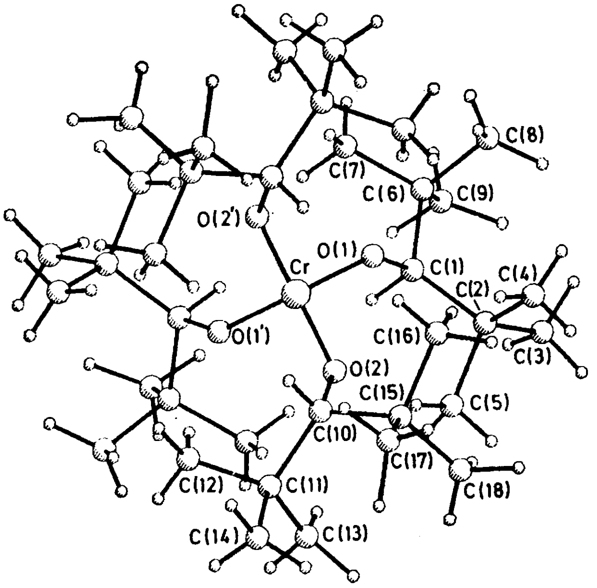


FIGURE 2 Structure of Cr[OCH(CMe$_3$)$_2$]$_4$, showing the atom-numbering scheme in the asymmetric unit. The smallest circles represent the hydrogen atoms and are not numbered

Indeed, the situation may be further complicated by the fact that the metal–oxygen links may be reinforced by multiple bonding (which may be a further stabilising feature). Thus, the Cr–O bond lengths [1.771 and 1.774(3) Å] are very short and may indicate a considerable degree of O→Cr $p\pi$–$d\pi$ bonding. The most effective arrangement for such interactions is likely to occur if the alkoxide oxygen is sp^2 or sp hydridised, leaving one or two filled, essentially pure *p*, orbitals available for π donation. The rather large Cr–O–C angles [140.5, 141.1(2)°] are consistent with this idea although, of course, these angles are also likely to be affected by the ligand packing. However, it is worth noting that a total of four ligand→metal π bonds would give an 18-electron system.

TABLE 2

Selected interatomic distances and interbond angles for (1) *

(*a*) Distances (Å)

Cr · · · Li	2.733(9)	Li–O(1)	1.861(12)
Cr–O(1)	1.905(3)	Li–O(2)	1.832(9)
Cr–O(2)	1.972(4)	Li–O(5)	1.943(10)
Cr–O(3)	1.823(4)		
Cr–O(4)	1.828(4)		

O–C distances in alkoxide 1.405(6)—1.420(8)
C–C distances in alkoxide 1.52(1)—1.60(1)

(*b*) Angles (°)

O(1)–Cr–O(2)	84.6(1)	O(1)–Cr–O(3)	119.8(2)
O(2)–Cr–O(3)	102.4(2)	O(1)–Cr–O(4)	108.2(1)
O(2)–Cr–O(4)	136.3(2)	O(3)–Cr–O(4)	106.1(2)
O(5)–Li–O(1)	130.9(6)	O(5)–Li–O(2)	138.8(7)
O(1)–Li–O(2)	89.9(4)		
Cr–O(1)–Li	93.0(3)	Cr–O(1)–O(1)	127.3(3)
Li–O(1)–C(1)	135.7(4)	Cr–O(2)–Li	91.8(4)
Cr–O(2)–C(10)	129.6(3)	Li–O(2)–C(10)	138.6(5)
Cr–O(3)–C(19)	137.4(4)	Cr–O(4)–C(28)	158.2(5)
Li–O(5)–C(51)	121.4(7)	Li–O(5)–C(54)	125.8(7)

* Estimated standard deviations are given in parentheses in this and other Tables throughout this paper. A full listing is given in SUP 22835.

The structure of LiCr(OCHBu$^t_2$)$_4$·thf, (1), is quite different and can be considered as a strongly associated ion pair. The Cr^{III} ion is bonded to four alkoxide ligands as in the neutral Cr^{IV} species, but the lithium ion forms a bridge between the oxygen atoms of two of the alkoxides, with short, and presumably strong, Li–O bonds of 1.832 and 1.861 Å and is further co-ordinated by a thf molecule with an Li–O bond length of 1.943 Å. The formation of this CrO$_2$Li ring has, not unnaturally, severely distorted the four-fold co-ordination of the chromium ion. The Cr–O bonds to the two terminal alkoxides are quite short, 1.823 and 1.828(4) Å, and compare with the values found in Cr(OCHBu$^t_2$)$_4$ when

TABLE 3

Selected interatomic distances and interbond angles for (2) [a]

(*a*) Distances (Å)

Cr–O(1)	1.771(3)	Cr–O(2)	1.774(3)
O(1)–C(1)	1.433(6)	O(2)–C(10)	1.431(5)

C–C distances in alkoxides 1.496(13)—1.566(6)

(*b*) Angles (°)

O(1)–Cr–O(1') [b]	110.3(2)	O(2)–Cr–O(1)	108.8(2)
O(2)–Cr–O(2')	112.4(2)		
Cr–O(1)–C(1)	141.1(2)	Cr–O(2)–C(10)	140.5(2)

[a] A full listing is given in SUP 22835. [b] The primed atoms in Tables 3 and 4 and Figure 2 are related to the unprimed ones by a two-fold axis at $\frac{1}{4}$, y, $\frac{1}{4}$.

the different oxidation states are taken into account. The bonds to the oxygen atoms bridged by the Li^+ ion are much longer and have probably been weakened. However, the three-co-ordinate oxygen atoms are planar (as in the lithium ion) and if this is considered to imply sp^2 hybridisation then $O \rightarrow Cr$ $p\pi$–$d\pi$ bonding is still feasible. The O–Cr–O angles also vary far more than in $Cr(OCHBu^t_2)_4$ with values of 84.6° (between the oxygens bridged by the Li ion) to 136.3° and as can be seen from Table 2, the remaining values are spread out between these extremes. Thus, in spite of the potential C_2 symmetry (along the $Li \cdots Cr$ vector), the geometry is quite distorted. This point will be discussed later with the structure of the related iron(III) complex.

We may finally note that the reaction sequence leading from $Cr(OR)_3$ *via* $LiCr(OR)_4$ to $Cr(OR)_4$ may provide a model for the alkylation of $CrCl_3(thf)_3$ by bulky alkylating agents such as $LiCH_2SiMe_3$.[11] A blue-purple intermediate was observed which was stable only in thf or diethyl ether, but could not be isolated and was readily oxidised to the chromium(IV) alkyl. It seems plausible to assume that this intermediate has a structure similar to that of $LiCr(OCHBu^t_2)_4(thf)$ with alkyl bridges and some Li–Cr interaction.

Manganese.—The dialkylamide $Mn[N(SiMe_3)_2]_2$ reacts with Bu^t_2CHOH at room temperature, but refluxing in benzene is desirable to obtain a pure product, $Mn(OCHBu^t_2)_2$, as pale pink crystals. This very air-sensitive compound is readily soluble in non-polar solvents, in striking contrast to other manganese(II) alkoxides described as insoluble polymers,[1,12] and is trimeric in benzene. It seems reasonable to assume a chain structure with two terminal three-co-ordinate Mn atoms each with one terminal ligand, similar to those confirmed for manganese dialkyls.[13] The degree of association appears to depend on the availability of electron density from the ligands as well as ligand size since $[Mn(CH_2CMe_2Ph)_2]_2$ [13] and $\{Mn[N(SiMe_3)_2]\}$ [14] are dimeric, whereas $[Mn(CH_2SiMe_3)_2]_n$ [13] is polymeric and $[Mn(CH_2CMe_3)_2]_4$ [13] tetrameric.

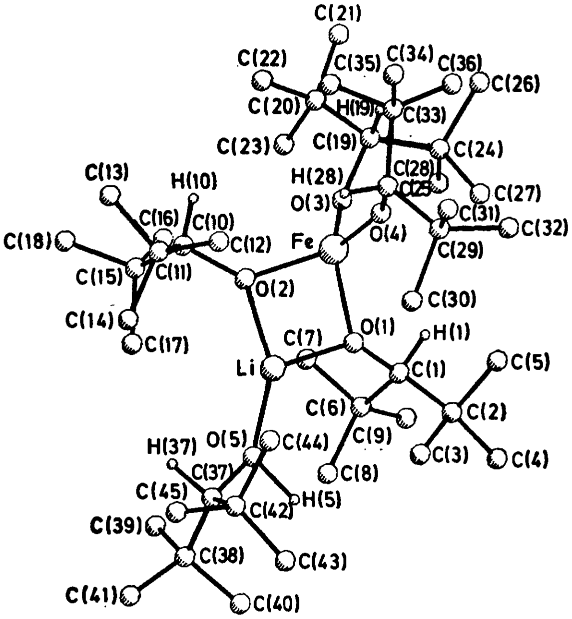


FIGURE 3 Structure of $LiFe(OCHBu^t_2)_4 \cdot Bu^t_2CHOH$, showing the atom-numbering system. Methyl hydrogens are omitted for clarity

Iron.—The interaction in diethyl ether of $FeCl_3$ and $LiOCHBu^t_2$ leads to air-sensitive yellow crystals of $LiFe(OCHBu^t_2)_4 \cdot Bu^t_2CHOH$ (3) whose molecular structure (Figure 3) is similar to that of $LiCr(OCHBu^t_2)_4 \cdot thf$ except for the different solvent molecule co-ordinated to lithium. This alcohol gives rise to a sharp ν(O–H) band in the i.r. spectrum at 3 585 cm^{-1}.

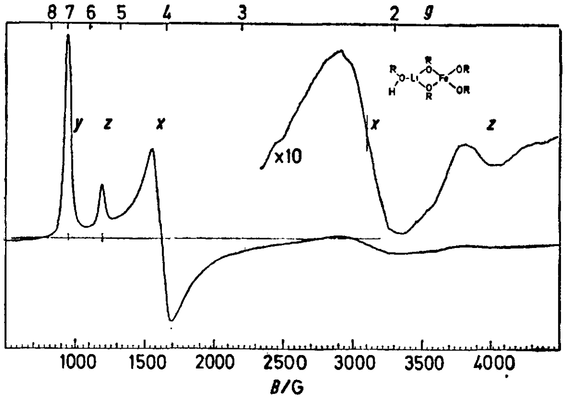


FIGURE 4 E.s.r. spectrum of $LiFe(OCHBu^t_2)_4 \cdot Bu^t_2CHOH$ in light petroleum at −160 °C

A co-ordination number of four is common for neutral iron(III) alkoxides which are dimers[15,16] $[Fe_2(OR)_6$, R = Pr^i, Bu^t, or $SiMe_3]$ and probably trimers[17] $[Fe_3(OR)_9$, R = Me, Et, Pr^i, or $Bu^t]$. Discrete, four-co-ordinate ions are also present in $Na[Fe(OSiMe_3)_4]$ [16] and $[SbMe_4][Fe(OSiMe_3)_4]$ [18] which was shown to be isostructural to $[SbMe_4][Al(OSiMe_3)_4]$.[19] A higher co-ordination number is only reached in octahedral $K_3[Fe(OMe)_6]$.[20]

Frozen solutions of $LiFe(OCHBu^t_2)_4 \cdot Bu^t_2CHOH$ give an interesting e.s.r. spectrum (Figure 4), which disappears on warming to room temperature. It confirms the presence of high-spin Fe^{III} ($S = \frac{5}{2}$) in a nearly axial, but distorted, ligand field ($\lambda = E/D$ *ca.* 0.07) with fairly large zero-field splitting (D *ca.* 0.45 cm^{-1}; interpretation using a D/B graph).

The highest peak observed in the mass spectrum of the iron complex is due to $Fe(OR)_3^+$.

Attempts to isolate the neutral $Fe(OCHBu^t_2)_3$ were unsuccessful.

As mentioned above, the structure of compound (3) is essentially equivalent to that of compound (1). Important bond lengths and angles are given in Table 4. Many details of the molecular geometries of the two compounds are remarkably similar. Of particular interest are the angles at the alkoxide oxygen atoms, especially those of the two terminal ligands [O(3), O(4)]. The closeness of the respective values suggests that since the two molecules are accommodated in two different crystal structures, their part of the molecular geometry may well be controlled by *intra*molecular forces. On the other hand, the angles at the metal atoms are rather different [*cf.* O–Cr–O (max.) *ca.* 136°, O–Fe–O (max.) = 118°]. A close examination of the interligand contacts reveals that the large M–O–C angles at the oxygens O(3), O(4) may well be determined by the ligand packing. The incorporation of the extra (LiOR) units in these structures has increased the ligand congestion. For example, the C–C–C angles at the secondary carbons in the alkyl groups have been reduced by *ca.* 2—3° compared with complex (1), and the thf and alcohol molecules on the Li atom are very much involved in the interligand contacts. However, it is very difficult to decide on the cause of the greater variation in O–Cr–O angles in $LiCr(OCHBu^{t}_{2})_{4}\cdot thf$ which correlates with an unsymmetrical flattening of the CrO_4 tetrahedron. There seem to be no steric reasons why, for example, angle O(2)–Cr–O(4) should be disparately large and so it is very tempting to consider that the origin of this flattening may be electronic. This idea is not unacceptable since of the two species, the chromium(III) derivative, with an unsymmetrical *d* shell would be the most likely to show a distortion. It may then also be true that the small distortion found in compound (2), a d^2 Cr^{IV} species, might after all, be due to electronic factors.

TABLE 4

Selected interatomic distances and interbond angles for (3) *

(*a*) Distances (Å)

Fe · · · Li	2.713(3)		
Fe–O(1)	1.935(2)	Li–O(1)	1.871(7)
Fe–O(2)	1.908(2)	Li–O(2)	1.873(7)
Fe–O(3)	1.829(2)	Li–O(5)	1.950(7)
Fe–O(4)	1.806(2)		

O–C distances in alkoxides 1.368—1.421(5)
C–C distances in alkoxides 1.499—1.572(6)

(*b*) Angles (°)

O(1)–Fe–O(2)	96.3(1)	O(1)–Fe–O(3)	111.4(1)
O(2)–Fe–O(3)	117.5(1)	O(1)–Fe–O(4)	114.5(1)
O(2)–Fe–O(4)	114.2(1)	O(3)–Fe–O(4)	110.9(1)
O(5)–Li–O(1)	125.5(4)	O(5)–Li–O(2)	114.1
O(1)–Li–O(2)	89.2(3)		
Fe–O(1)–Li	90.9(2)	Fe–O(1)–C(1)	131.2(2)
Li–O(1)–C(1)	134.1(3)	Fe–O(2)–Li	91.7(2)
Fe–O(2)–C(10)	133.5(2)	Li–O(2)–C(10)	134.6(3)
Fe–O(3)–C(19)	139.5(2)	Fe–O(4)–C(28)	153.5(2)
Li–O(5)–C(37)	149.3(2)		

* A full listing is given in SUP 22835.

Cobalt.—The deep blue $Co(OCHBu^{t}_{2})_{2}$ was prepared by interaction of $Co[N(SiMe_3)_2]_2$ and the alcohol in diethyl ether. The air-sensitive compound is very soluble in non-polar solvents and is a dimer in benzene (cryoscopy), presumably with three-co-ordinate Co^{II} atoms. Solvent molecules may co-ordinate in solution, since the presence of tetrahedral Co^{II} is suggested by the electronic spectrum in diethyl ether or light petroleum. The compound does not give an e.s.r. signal.

Interaction of $CoCl_2$ with $LiOCHBu^{t}_{2}$ gives a purple-blue, highly light petroleum-soluble product, probably $LiCo(OCHBu^{t}_{2})_{3}$. It could not be purified.

Copper.—Pale yellow crystals of $CuOCHBu^{t}_{2}$ were obtained from $LiOCHBu^{t}_{2}$ and an excess of CuCl in diethyl ether. The compound is very air-sensitive and decomposes at room temperature, particularly in light, over a period of several weeks. It is considerably more stable, though, than other copper(I) alkoxides of primary and secondary alcohols, which have to be prepared at 0 °C;[21] $[CuOMe]_n$ may even decompose explosively.[22] The structure of $CuOCHBu^{t}_{2}$, which is a tetramer in benzene, is probably a planar eight-membered ring with two-co-ordinate, *sp*-hybridised Cu^{I}, in accord with the known structure of $[CuOBu^{t}]_{4}$.[23]

Other Reactions.—The compound $Mo(NMe_2)_4$ reacts with $Bu^{t}_{2}CHOH$ in light petroleum at room temperature. The colour of the reaction mixture changes from purple *via* green to brown, but no product could be isolated. The compound VCl_4 reacts with $LiOCHBu^{t}_{2}$ in light petroleum to give an air-sensitive, purple solution, from which black-purple crystals were obtained in small yield, but they could not be purified satisfactorily. The reaction with $NiBr_2$ yielded a red-purple lithium-containing product, but similar purification problems were encountered. Anhydrous $NiCl_2$ does not react.

EXPERIMENTAL

Microanalyses were by Pascher Microanalytical Laboratory. The instruments Perkin-Elmer 597 (i.r.), Perkin-Elmer 551 (u.v.–vis.), and Varian E 12 *X*-band (e.s.r.) were used. All manipulations were carried out in an argon atmosphere. Solvents were dried over sodium–benzophenone and distilled immediately prior to use. The light petroleum had b.p. 40—60 °C. Anhydrous $CrCl_3$ was prepared by action of $SOCl_2$ on the hydrate and pumping at 100 °C for 48 h *in vacuo*; $CrCl_3(thf)_3$ was prepared from $CrCl_3$ by thf extraction. The compounds $Mn[N(SiMe_3)_2]_2$ [24] and $Co[N(SiMe_3)_2]$ [25] were prepared according to the literature methods. Pivalaldehyde was used as supplied by Aldrich Chemicals. Bis(t-butyl)methanol was prepared by treating pivalaldehyde with t-butyl-lithium in light petroleum, followed by hydrolysis. It was purified by sublimation at 40 °C and 10^{-2} Torr. The lithium alkoxide was obtained by addition of n-butyl-lithium to the alcohol in light petroleum.

Melting points were determined in sealed tubes under argon and molecular weights cryoscopically in benzene. Analytical data are collected in Table 5. Infrared spectra were recorded as Nujol mulls between CsI plates. Bands obscured by Nujol are not listed. The magnetic moment of $Cr(OCHBu^{t}_{2})_{3}\cdot thf$ was measured using an apparatus constructed by Dr. D. F. Evans.

Tris[bis(t-butyl)methoxo]chromium(III)*–Tetrahydrofuran-*(1/1).—To a solution of $LiOCHBu^{t}_{2}$ (6 mmol) in diethyl ether (20 cm³) was added $CrCl_3(thf)_3$ (760 mg, 2.03 mmol) in small portions. The mixture was stirred at room temperature overnight, to give a green solution. The solvent was evaporated *in vacuo* and the purple residue extracted with 2 × 15 cm³ light petroleum. The filtrate was concentrated and left to crystallise at −30 °C. Yield: *ca.* 300 mg (27%).

I.r.: 1 460s, 1 390m, 1 364m, 1 355w, 1 310w, 1 298w, 1 261w, 1 240w, 1 208w, 1 164w, 1 073w, 1 050s, 1 037m, 995vs, 965m, 918w, 890w, 860w, 773m, 767m, 718w, 696m, 665m, 640m, 555s, br, 520, and 465w.

Lithium Tetrakis[bis(t-butyl)methoxo]chromate(III)*–Tetrahydrofuran*(1/1), (1).—A mixture of $CrCl_3(thf)_3$ (950 mg, 2.5 mmol) and $LiOCHBu^t_2$ (9 mmol) was stirred in diethyl ether at room temperature for 2 h and taken to dryness. The residue was extracted into light petroleum (2 × 15 cm^3), the filtrate concentrated to 5 cm^3 and left to crystallise. Yield: 500 mg (28%).

I.r.: 1 480s, 1 392m, 1 365m, 1 310w, 1 262vw, 1 240w, 1 213m, 1 163m, 1 085m(sh), 1 055vs, 1 040s, 1 000vs, br, 950m, 920m, 890m, 860w, 769s, 700s, 676s, 658m, 633m, 560s, 520w, 450w, 435s, and 382m.

TABLE 5

Analytical data for bis(t-butyl)methoxides

Compound	M.p. (θ_c/°C)	Found (%) C	H	N	O	M[a]	Required (%) C	H	N	O	M
$Cr(OCHBu^t_2)_3$·thf	130—132	67.0	11.9		11.9	490	67.2	11.8		11.6	554
$LiCr(OCHBu^t_2)_4$·thf	124—126	68.1	12.1				68.2	12.0			
$Cr(OCHBu^t_2)_4$	206	68.9	12.3		9.7		69.2	12.3		10.2	
$Mn(OCHBu^t_2)_2$	244—245	61.5	11.2	<0.2	8.8	1 060	63.6	11.2	0.0	9.4	341[b]
$LiFe(OCHBu^t_2)_4$·Bu^t_2CHOH	144	69.2	12.0		9.8		69.3	12.4		10.3	
$Co(OCHBu^t_2)_2$	decomp. >130	62.4	11.1	<0.1		720	62.6	11.1	0.0		345[b]
$CuOCHBu^t_2$	decomp. >150	51.5	9.1		7.9	780	52.3	9.3		7.7	207[b]

[a] Cryoscopically in benzene. [b] Calculated for monomer.

Tetrakis[bis(t-butyl)methoxo]chromium(IV), (2).—(*a*) *By oxidation with* CuCl. A mixture of $LiCr(OCHBu^t_2)_4$·thf (250 mg, 0.36 mmol) and CuCl (100 mg, 1 mmol) in light petroleum–diethyl ether 2 : 1 (30 cm^3) was stirred for 2 h at room temperature and worked up as before.

(*b*) *From* $CrCl_3$. A mixture of $CrCl_3$ (480 mg, 3 mmol) and $LiOCHBu^t_2$ (9 mmol) in diethyl ether (20 cm^3) was stirred for 2 days. Recrystallisation from light petroleum gave green crystals (520 mg, 37%).

I.r.: 1 484s, 1 470s, 1 391m, 1 366m, 1 302m, 1 242w, 1 230w, 1 210m, 1 164w, 1 035m, 965vs, 860w, 767m, 718s, 645w, 566w, 520w, 438m, and 382m.

Bis[bis(t-butyl)methoxo]manganese(II).—A mixture of $Mn[N(SiMe_3)_2]_2$ (2 mmol) and Bu^t_2CHOH (600 mg, 4.17 mmol) was refluxed in benzene (10 cm^3) for 2 h. The solvent was removed and the residue extracted into light petroleum. Yield: 140 mg (20%).

I.r.: 1 470vs, 1 390s, 1 386s, 1 325w, 1 260w, 1 241w, 1 216w, 1 167w, 1 100vs, 1 055vs, 1 032m, 1 021m, 1 000vs,

TABLE 6

Crystal data and details of data collection and structure refinement

	Compound (1)	Compound (2)	Compound (3)
Formula	$LiCr[OCH(CMe_3)_2]_4 \cdot C_4H_8O$	$Cr[OCH(CMe_3)_2]_4$	$LiFe[OCH(CMe_3)_2]_4 \cdot HOCH(CMe_3)_2$
(*a*) Crystal data			
M	704.04	625.00	780.05
Crystal system	Triclinic	Monoclinic	Monoclinic
a/Å	19.986(2)	20.249(3)	18.308(3)
b/Å	11.618(2)	10.748(1)	22.505(4)
c/Å	11.390(1)	20.275(2)	11.979(5)
α/°	117.61(1)	90	90
β/°	76.45(1)	116.68(1)	94.20(1)
γ/°	93.11(1)	90	90
U/Å^3	2 273.9	3 942.4	4 922.4
Space group	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)
Z	2	4	4
D_c/g cm^{-3}	1.03	1.05	1.05
F(000)	784	1 392	1 742
X-Ray wavelength/Å	1.541 78	1.541 78	0.710 69
Linear absorption coefficient, μ/cm^{-1}	22.6	25.5	3.1
Crystal size/mm	0.24 × 0.20 × 0.15	0.24 × 0.20 × 0.16	0.30 × 0.25 × 0.22
(*b*) Data collection			
$\theta_{min.},\theta_{max.}$/°	3, 65	3, 65	1.5, 24
ω Scan width parameters, A, B in width = $A + B \tan\theta$	0.85, 0.15	0.85, 0.15	0.85, 0.35
Horizontal aperture parameters, A,B in aperture = $A + B \tan\theta$	4.0, 0.0	4.0, 0.0	4.0, 0.0
Total data collected	7 894	3 760	8 663
Total unique data	7 148	3 359	7 848
Observed data	3 396	2 057	4 879
Significance level	$F_o > 4\sigma(F_o)$	$F_o > 3\sigma(F_o)$	$F_o > 4\sigma(F_o)$
(*c*) Refinement			
No. of parameters	497	338	575
Weighting scheme coefficient, g in $w = 1/[\sigma^2|F_o| + gF_o^2]$	0.0014	0.0020	0.0008
Final $R = \Sigma\Delta F/\Sigma|F_o|$	0.068	0.067	0.061
$R' = (\Sigma\Delta F^2/\Sigma wF_o^2)^{\frac{1}{2}}$	0.072	0.079	0.064

980s, 958m, 920w, 856w, 770m, 684s, 622s, 550m, 523m, 486s, 458s, and 390m.

Lithium Tetrakis[bis(t-butyl)methoxo]ferrate(III)*-Bis(t-butyl)methanol*(1/1), (3).—The compound was prepared as described above from $FeCl_3$ (460 mg, 2.85 mmol) and LiOCHBu$^t_2$ (8.6 mmol) in diethyl ether (20 cm^3). Yield: *ca.* 1.5 g (68%).

I.r.: 3 590m, 1 475vs, 1 390s, 1 363m, 1 318w, 1 310w, 1 263m, 1 240m, 1 210w, 1 187w, 1 164m, 1 079m, 1 035vs, 1 000vs, 970m, 957w, 950w, 920m, 860w, 768s, 745w, 682s, 635s, 553s, 510s, 420m, and 388m.

TABLE 7

Fractional co-ordinates (Cr × 10^5; others × 10^4) of the non-hydrogen atoms for (1)

Atom	*x*	*y*	*z*
Cr	25 593(5)	27 033(8)	11 023(9)
Li	2 435(6)	78(9)	−224(10)
O(1)	2 995(2)	1 267(3)	−580(3)
O(2)	2 058(2)	1 365(3)	1 497(4)
O(3)	1 862(2)	3 692(3)	1 160(4)
O(4)	3 218(2)	3 822(4)	1 745(4)
O(5)	2 298(3)	−1 726(4)	−1 404(5)
C(1)	3 655(3)	1 202(5)	−1 422(6)
C(2)	4 121(3)	12(6)	−1 720(6)
C(3)	4 002(4)	−1 307(6)	−2 900(7)
C(4)	4 886(3)	257(7)	−2 024(7)
C(5)	3 969(4)	−160(6)	−415(7)
C(6)	3 557(3)	1 367(5)	−2 670(6)
C(7)	4 239(3)	1 236(8)	−3 708(7)
C(8)	3 048(3)	395(6)	−3 435(6)
C(9)	3 250(3)	2 765(7)	−2 082(7)
C(10)	1 606(3)	1 493(6)	2 721(6)
C(11)	2 063(4)	1 595(6)	3 741(6)
C(12)	1 637(5)	1 647(9)	5 080(8)
C(13)	2 370(5)	2 912(8)	4 173(8)
C(14)	2 652(4)	588(9)	3 110(9)
C(15)	1 061(4)	451(7)	2 430(7)
C(16)	778(4)	352(7)	1 248(8)
C(17)	1 363(5)	−928(7)	2 000(10)
C(18)	436(5)	813(10)	3 635(10)
C(19)	1 147(3)	3 649(5)	1 287(5)
C(20)	999(3)	3 233(6)	−134(6)
C(21)	1 331(4)	4 095(7)	−796(7)
C(22)	1 331(3)	1 848(6)	−1 078(6)
C(23)	234(3)	3 147(8)	−141(8)
C(24)	792(3)	4 973(6)	2 550(6)
C(25)	1 043(4)	5 091(6)	3 783(6)
C(26)	7(3)	4 960(8)	2 932(8)
C(27)	997(4)	6 172(6)	2 362(7)
C(28)	3 753(3)	4 663(6)	1 754(7)
C(29)	3 440(3)	6 037(6)	2 148(7)
C(30)	2 874(4)	6 585(7)	3 460(8)
C(31)	3 961(4)	7 086(8)	2 260(10)
C(32)	3 089(4)	5 891(7)	1 027(8)
C(33)	4 260(3)	4 542(7)	2 564(8)
C(34)	3 967(5)	5 168(9)	4 102(9)
C(35)	4 411(4)	3 112(7)	2 046(10)
C(36)	4 947(4)	5 121(10)	2 307(12)
C(51)	1 875(6)	−2 074(10)	−2 400(10)
C(52)	1 818(7)	−3 516(13)	−2 888(14)
C(53)	2 340(9)	−3 948(10)	−2 433(13)
C(54)	2 566(7)	−2 882(8)	−1 377(11)

Bis[bis(t-butyl)methoxo]cobalt(II).—To a solution of Bu$^t_2$CHOH (580 mg, 4 mmol) in diethyl ether (10 cm^3) was added a solution of Co[N(SiMe$_3$)$_2$]$_2$ in light petroleum. The mixture was stirred at room temperature for 45 min, concentrated to *ca.* 5 cm^3, and left to crystallise at −30 °C. Yield: 190 mg (28%).

I.r.: 1 475vs, 1 390s, 1 365s, 1 320w, 1 263m, 1 215w, 1 170m, 1 094vs, 1 053s, 1 037m, 1 024m, 995m, 993s, 935w, 920w, 840m, br, 773w, 766w, 707m, 630m, 555m, 525m, br, and 390m.

Bis(t-butyl)methoxocopper(I).—To a suspension of CuCl (740 mg, 7.5 mmol) in diethyl ether (20 cm^3) was added LiOCHBu$^t_2$ (4.2 mmol) in light petroleum (7 cm^3). The mixture was stirred for 2 days. The yellow solution was taken to dryness, extracted with light petroleum (2 × 20 cm^3), concentrated to 10 cm^3, and left to crystallise. Yield: 620 mg (71% based on lithium alkoxide).

I.r.: 1 483m, 1 470s, 1 391s, 1 360s, 1 262w, 1 239w, 1 215w, 1 164w, 1 057vs, 1 035m, 1 005vs, 953m, 920w, 860w, 772m, 670s, 570m, 548w, and 513w.

X-*Ray Crystallographic Data*.—Crystals of all three compounds were sealed under an argon atmosphere in Lindemann capillaries. The crystal quality of compound (1) was, in general, poor and the specimen finally chosen for the study was still of lower quality than would have been preferred. For each compound, the unit-cell parameters were determined by least-squares refinement of the setting angles for 25 reflections automatically centred on a Nonius CAD4 diffractometer and the crystal system confirmed by comparison of symmetry related intensities. The centrosymmetric space group $P\bar{1}$ (no. 2) was indicated for (1) by intensity statistics and confirmed by successful structure analysis. For (2), the systematic absences, *hkl*, with the space groups *Cc* (no. 9) or *C*2/*c* (no. 15), confirmed the latter to be correct by subsequent calculations. In the case of (3), the space group $P2_1/n$ (no. 14) was uniquely determined by the systematic absences, *h*0*l* for $h + l \neq 2n$ and 0*k*0 for $k \neq 2n$. The crystal data and details of data collection and structure refinement are summarised in Table 6.

TABLE 8

Fractional co-ordinates (× 10^4) of the non-hydrogen atoms for (2)

Atom	*x*	*y*	*z*
Cr	0 *	4 389(1)	2 500 *
O(1)	333(2)	3 448(3)	3 302(1)
O(2)	−744(2)	5 307(3)	2 464(2)
C(1)	187(3)	2 292(4)	3 564(2)
C(2)	−345(3)	2 557(5)	3 910(3)
C(3)	−449(4)	1 452(7)	4 331(4)
C(4)	−98(5)	3 701(7)	4 428(4)
C(5)	−1 108(3)	2 818(8)	3 267(4)
C(6)	946(3)	1 621(4)	4 012(2)
C(7)	1 376(4)	1 692(7)	3 572(4)
C(8)	1 406(5)	2 212(9)	4 776(4)
C(9)	827(5)	234(6)	4 106(5)
C(10)	−1 113(3)	6 459(4)	2 168(2)
C(11)	−1 806(3)	6 165(5)	1 413(2)
C(12)	−1 519(4)	5 776(9)	870(3)
C(13)	−2 290(5)	5 153(9)	1 491(5)
C(14)	−2 284(4)	7 323(7)	1 080(4)
C(15)	−1 190(3)	7 160(5)	2 802(3)
C(16)	−422(3)	7 174(6)	3 471(3)
C(17)	−1 409(6)	8 538(7)	2 593(5)
C(18)	−1 716(5)	6 574(10)	3 043(5)

* Parameters fixed by symmetry.

Intensity data were collected on the CAD4 diffractometer using Cu-K_α (Ni filter) or Mo-K_α (graphite monochromator) radiation and an ω—2θ scan technique, in a manner described previously.[26] During data collection, the standard reflections suffered 5% loss in intensities for (1) due to crystal deterioration, but compounds (2) and (3) remained quite stable. All data sets were corrected for Lorentz and polarisation effects and that for (1) for the small amount of crystal decay. No corrections were applied for absorption or extinction.

The structures of all three compounds were solved first by locating the metal atoms from Patterson syntheses and the remaining atoms from successive difference electron-density syntheses interspersed with cycles of least-squares refinement. In the final stages of refinement, all non-hydrogen atoms were treated anisotropically. For (2), all the hydrogen atoms were located from difference maps and refined with individual isotropic temperature factors [$U_{iso.}$ = 0.027—0.141(30) Å^2; C–H = 0.79—1.11(9) Å]. For (1) the quality of the data did not allow us to locate the hydrogen atoms from difference maps, so those on the CHBu$^t_2$ groups were placed in calculated positions and their contribution included in the structure factor calculations; one common $U_{iso.}$ for these atoms refined to 0.152(3) Å^2. The hydrogens on the thf molecule were ignored. For (3), the hydrogens on C(1), C(10), C(19), C(28), C(37), and O(5) were obtained from difference maps and isotropiclly refined [C–H = 0.96—1.05(5) Å] and those on the methyl groups treated as in (1). For these hydrogens, a common $U_{iso.}$ refined to 0.110(4) Å^2.

TABLE 9

Fractional co-ordinates (Fe × 10^5, others × 10^4) of the non-hydrogen atoms for (3)

Atom	*x*	*y*	*z*
Fe	11 430(5)	31 358(4)	−533(5)
Li	619(4)	2 206(3)	1 089(5)
O(1)	1 398(1)	2 309(1)	181(2)
O(2)	265(1)	2 957(1)	644(2)
O(3)	1 059(1)	3 322(1)	−1 543(2)
O(4)	1 741(1)	3 653(1)	720(2)
O(5)	535(2)	1 571(1)	2 178(2)
C(1)	1 823(2)	1 916(2)	−438(3)
C(2)	2 491(2)	1 712(2)	343(3)
C(3)	2 282(2)	1 527(2)	1 510(4)
C(4)	2 936(3)	1 204(2)	−122(5)
C(5)	2 995(2)	2 247(2)	477(4)
C(6)	1 329(2)	1 453(2)	−1 091(3)
C(7)	671(3)	1 778(2)	−1 631(4)
C(8)	1 064(3)	948(2)	−364(4)
C(9)	1 719(3)	1 171(3)	−2 069(4)
C(10)	−410(2)	3 258(2)	702(3)
C(11)	−530(2)	3 432(2)	1 946(4)
C(12)	187(2)	3 664(2)	2 499(4)
C(13)	−1 066(3)	3 954(2)	2 003(4)
C(14)	−771(3)	2 920(2)	2 675(4)
C(15)	−1 002(2)	2 894(2)	14(4)
C(16)	−845(2)	2 939(2)	−1 231(4)
C(17)	−1 000(2)	2 232(2)	318(4)
C(18)	1 772(2)	3 138(2)	98(5)
C(19)	1 273(2)	3 776(2)	−2 275(3)
C(20)	584(2)	3 958(2)	−3 031(3)
C(21)	726(3)	4 405(2)	−3 962(4)
C(22)	91(2)	4 272(2)	−2 249(4)
C(23)	187(2)	3 421(2)	−3 573(4)
C(24)	1 972(2)	3 586(2)	−2 825(3)
C(25)	1 862(3)	3 096(3)	−3 689(4)
C(26)	2 336(3)	4 131(3)	−3 349(5)
C(27)	2 516(2)	3 361(2)	−1 898(4)
C(28)	1 907(2)	4 073(2)	1 572(3)
C(29)	2 566(2)	3 834(2)	2 324(4)
C(30)	2 326(3)	3 228(2)	2 770(4)
C(31)	2 770(3)	4 222(3)	3 344(4)
C(32)	3 241(2)	3 749(2)	1 675(5)
C(33)	1 901(2)	4 703(2)	1 053(4)
C(34)	2 005(4)	5 199(2)	1 942(5)
C(35)	1 142(3)	4 795(2)	483(4)
C(36)	2 440(3)	4 789(2)	172(5)
C(37)	191(2)	1 336(2)	3 053(4)
C(38)	−124(2)	713(2)	2 762(4)
C(39)	−580(3)	773(2)	1 640(5)
C(40)	462(3)	251(2)	2 581(6)
C(41)	−621(3)	486(3)	3 625(5)
C(42)	578(3)	1 493(2)	4 197(4)
C(43)	1 173(3)	1 066(3)	4 577(5)
C(44)	937(4)	2 103(3)	4 098(5)
C(45)	34(5)	1 576(4)	5 059(6)

In the final stages of refinement, the weighting scheme $w = 1/[\sigma^2(F_0 + gF_0^2)]$ was used, with the parameter *g* chosen to give approximately flat analyses of variance.

Final atomic fractional co-ordinates for non-hydrogen atoms are given in Tables 7—9. Anisotropic thermal parameters of these atoms and parameters for hydrogen atoms, together with non-bonded contacts and lists of observed and calculated structure factors have been deposited in Supplementary Publication No. SUP 22835 (73 pp.).*

Neutral-atom scattering factors were taken from refs. 27 (for H) and 28 (for the others), with those of the heavier elements being modified for anomalous dispersion taking the $\Delta f'$ and $\Delta f''$ values from ref. 29. The final cycles of least-squares refinement for compounds (1) and (3) were performed on the University of Cambridge IBM 370/373 computers; all other calculations were done on the Queen Mary College ICL 1904 S and 2980 computers. The SHELX [30] program was used for structure determination and refinement. The diagrams were drawn using PLUTO.[31]

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

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