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FULL PAPER

Chromium complexes of hydroxyl-functionalised 1,3,5-triazacyclohexanes

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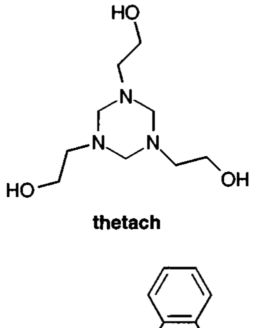
The chromium co-ordination chemistry of three 1,3,5-triazacyclohexanes bearing hydroxyl-functionalised substituents on nitrogen has been explored. The complexes $[CrL_3(C_3H_6N_3R_3)]$ (L = CO, R = CH_2CH_2OH, $CH_2CH_2CH_2OH$ or *o*-hydroxybenzyl; L = Br, R = $CH_2CH_2CH_2OH$) have been prepared. Characterisation of the carbonyl complexes by spectroscopic and structural methods indicated that the triazacyclohexanes co-ordinate to the chromium centre through the three nitrogen atoms only. Crystal structure determinations for 1,3,5-tri(*o*-hydroxybenzyl)-1,3,5-triazacyclohexane and $[Cr(CO)_3(C_3H_6N_3R_3)]$ (R = CH_2CH_2OH or $CH_2CH_2CH_2OH$) have been made.

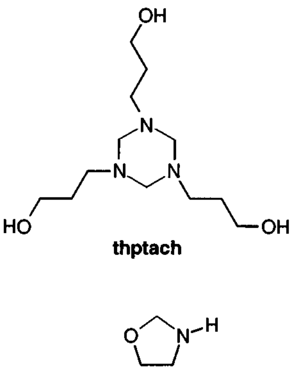
Introduction

Since 1990 there has been much research concerned with the preparation and properties of η^3-1,3,5-triazacyclohexane (tach) metal complexes.[1–17] Although the literature dealing with triazacyclohexanes is extensive and triazacyclohexanes bearing functional groups (*e.g.* hydroxyl, allyl, nitro, nitrile, esters, amides, pyridyl)[18] are well known, studies of the co-ordination chemistry of this family of ligands has been limited to 1,3,5-triazacyclohexanes with simple substituents (*e.g.* Me, *t*-Bu, *i*-Pr, $PhCH_2$).

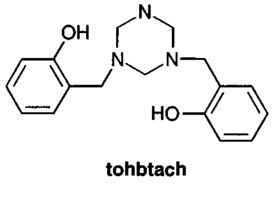
We are interested in the co-ordination chemistry of three hydroxyl-functionalised 1,3,5-triazacyclohexanes, 1,3,5-tri(2-hydroxyethyl)-1,3,5-triazacyclohexane (thetach), 1,3,5-tri(3-hydroxypropyl)-1,3,5-triazacyclohexane (thptach) and 1,3,5-tri(*o*-hydroxybenzyl)-1,3,5-triazacyclohexane (tohbtach). These functionalised triazacyclohexanes are readily synthesized[19–21] yet the presence of hydroxyl groups in these compounds complicates their chemistry.[20–23] For example, at elevated temperatures thetach and thptach can be converted into oxazolidine **1** and tetrahydro-1,3-oxazine **2** respectively.[20,21] In this paper we explore the effect of pendant hydroxyl groups on the chromium co-ordination chemistry of functionalised triazacyclohexanes. Crystal structure determinations for $[Cr(CO)_3(thetach)]$, $[Cr(CO)_3(thptach)]$ and tohbtach are reported.



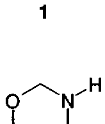
thetach



thptach



tohbtach



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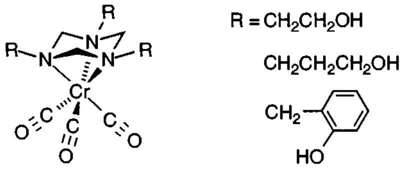
Results and discussion

Synthesis of $[Cr(CO)_3(thetach)]$ and $[Cr(CO)_3(thptach)]$

The simplest method for the synthesis of $[Cr(CO)_3(tach)]$ complexes is by the reaction of the tach with $[Cr(CO)_6]$ in a low polarity-high boiling solvent (*e.g.* mesitylene).[10] The high temperature promotes liberation of carbon monoxide from the chromium hexacarbonyl, and the choice of a low polarity solvent is beneficial because the chromium tricarbonyl complexes precipitate from the reaction mixture. This method is not useful for the synthesis of $[Cr(CO)_3(thetach)]$ and $[Cr(CO)_3(thptach)]$ because thetach and thptach are insoluble in non-polar solvents and can undergo conversion into their respective cyclic monomers, **1** and **2**, at elevated temperatures.[20,21]

The synthesis of $[Cr(CO)_3(thetach)]$ and $[Cr(CO)_3(thptach)]$ was achieved *via* a labile source of the *fac*-$Cr(CO)_3$ unit, $[Cr(CO)_3(CH_3CN)_3]$. Use of this precursor avoids the need for high temperatures which are incompatible with thetach and thptach. When thptach was added to a solution of $[Cr(CO)_3(CH_3CN)_3]$ in tetrahydrofuran (thf) $[Cr(CO)_3(thptach)]$ was formed cleanly and within 1 h had precipitated from the reaction mixture as an orange powder. The complex $[Cr(CO)_3(thetach)]$ was obtained by an analogous procedure, but only precipitated after diethyl ether was added.



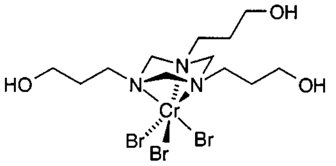
Both in solution and in the solid state, the tach ligand in $[Cr(CO)_3(thetach)]$ and $[Cr(CO)_3(thptach)]$ is bound to the Cr through only the three nitrogen atoms. The IR spectra of the complexes (KBr disks) contain CO stretching modes characteristic of the *fac*-$Cr(CO)_3$ unit, while the solution ^1H NMR spectra show multiplets characteristic of the axial and equatorial triazacyclohexane ring protons, similar to those seen for other $[Cr(CO)_3(tach)]$ complexes.[10]

Both $[Cr(CO)_3(thetach)]$ and $[Cr(CO)_3(thptach)]$ are air sensitive in the solid state as well as in solution. While $[Cr(CO)_3(thetach)]$ is soluble in thf and acetone, $[Cr(CO)_3(thptach)]$, despite having a substituent with a longer chain length which should promote more solvent–solute interactions, is practically insoluble in thf, only sparingly soluble in acetone, but very soluble in dmso. X-Ray diffraction studies (see below) of the two compounds indicate differences in degrees of intermolecular hydrogen bonding that may account for the difference in solubilities. The structure of [Cr(CO)$_3$(thptach)] consists of a strongly hydrogen-bonded network in which the thptach units lie in "infinite sheets", with each thptach unit participating in six hydrogen bonds to adjacent thptach units. In contrast, the structure of [Cr(CO)$_3$(thetach)] is less ordered, with each thetach unit participating in fewer (and apparently weaker) hydrogen bonds (see Structural characterisation). A stronger arrangement of hydrogen bonds in [Cr(CO)$_3$(thptach)] is also indicated by the lower OH infrared stretching frequency[24] for [Cr(CO)$_3$(thptach)] (3290 cm^{-1}) compared with that for [Cr(CO)$_3$(thetach)] (3360 cm^{-1}).

Synthesis of an hydroxyalkyl-tach chromium(III) complex

Köhn and co-workers[4,5] synthesized a number of η^3-1,3,5-triazacyclohexane chromium(III) complexes by reaction of the tach ligand with [CrCl$_3$(thf)$_3$] in thf under anhydrous conditions. Generally the complexes are purple, air-stable solids that can be washed with water, and have very low solubilities when the substituents on the 1,3,5-triazacyclohexane unit are small. We have found that when thptach is added to [CrCl$_3$(thf)$_3$] in thf under anhydrous conditions a purple solid forms, but it is extremely moisture sensitive and rapidly dissolves to form green solutions when added to water. These observations suggest that, even though the hydroxyl groups were spectators in reactions of thptach with the "soft" chromium centre in Cr(CO)$_3$, they do participate in co-ordination reactions at the "harder" Cr in CrCl$_3$. The resulting purple solid was presumably a monomeric or polymeric complex in which one or more of the pendant hydroxyl groups of thptach are involved in co-ordination to chromium; facile displacement of co-ordinated hydroxyl groups by water would account for the water-sensitivity of this material.

Complications arising from reactions of the hydroxyl groups of thptach were avoided by preparing the chromium(III) complex *via* [Cr(CO)$_3$(thptach)]. In a procedure analogous to one used by Wieghardt and co-workers[25] in chromium–triazacyclononane systems, [CrBr$_3$(thptach)] was synthesized by oxidation of [Cr(CO)$_3$(thptach)] with bromine in carbon tetrachloride. It was obtained as a purple, air stable, but hygroscopic solid. Although the solid was easily suspended in water, the aqueous phase slowly became green and the purple solid decomposed after prolonged standing (4–5 d). The complex was extremely insoluble in all solvents except dmso, in which it also slowly decomposed by ligand displacement and metal solvation. A purple dmso solution of [CrBr$_3$(thptach)] slowly turned green over 6 d.

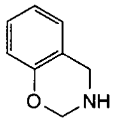


[CrBr$_3$(thptach)]

Synthesis of [Cr(CO)$_3$(tohbtach)]

Tohbtach was prepared from an excess of *o*-hydroxybenzylamine and formalin (38% w/w formaldehyde solution) in ethanol.[19] For the free tohbtach molecule in the solid state X-ray crystallography reveals intramolecular hydrogen bonding between each phenolic hydrogen and the corresponding tach ring nitrogen (see Structural characterisation). The ^{1}H NMR spectra of tohbtach in various solvents suggest that this intramolecular hydrogen bonding persists in solution; the phenolic proton appears in the region typical of hydrogen-bonded phenols (*e.g.* δ 9.6 in d_6-acetone). Related triazacyclononanes also exhibit this pattern of intramolecular hydrogen bonding.[26]

The tohbtach ligand was stable in chloroform, acetone and dmso solutions at room temperature, but underwent decomposition when dissolved in methanol or when heated gently in dmso. Products arising from the decomposition of tohbtach include *o*-hydroxybenzylamine, 3,4-dihydro-2*H*-1,3-benzoxazine **3**, and 3,3′-methylenebis(3,4-dihydro-2*H*-1,3-benzoxazine) **4**. Compound **4** occurs as a by-product of the synthesis of tohbtach under certain conditions.[19,23] Perhaps disruption of the intramolecular hydrogen bonding by the more polar solvents such as methanol and dmso destabilises the ligand, leading to the decomposition reactions.



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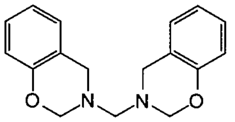

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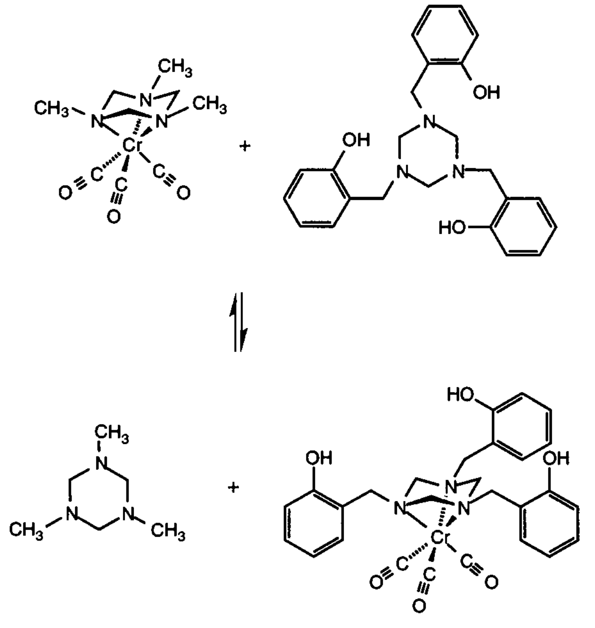
Attempts to synthesize [Cr(CO)$_3$(tohbtach)] by reaction of tohbtach with chromium hexacarbonyl in aromatic solvents were unsuccessful; the ligand decomposed at the temperatures required for carbonyl substitution. When [Cr(CO)$_3$(CH$_3$CH$_2$CN)$_3$] [a reactive source of the Cr(CO)$_3$ unit] was treated with tohbtach in acetone solution [Cr(CO)$_3$(tohbtach)] was formed within minutes. Studies by NMR spectroscopy indicated that the reaction was essentially quantitative, but the yield of [Cr(CO)$_3$(tohbtach)] after isolation was only 50%. Poor stability of [Cr(CO)$_3$(tohbtach)] was the main reason for the mediocre yield; this compound was extremely sensitive to air in both the solid state and in solution, and even in the absence of air it decomposed in solution to give free tohbtach, **4** and various unidentified products.

The 1,3,5-trimethyl-1,3,5-triazacyclohexane (tmtach) group in [Cr(CO)$_3$(tmtach)] is labile and can be displaced by other ligands, including bulkier trialkyltriazacyclohexanes.[10] When tohbtach was added to a solution of [Cr(CO)$_3$(tmtach)] in dmso an equilibrium mixture containing both [Cr(CO)$_3$(tohbtach)] and [Cr(CO)$_3$(tmtach)] was formed (Scheme 1), but when the experiment was repeated in acetone no reaction was detected. Indeed, when one equivalent of tmtach was added to a solution of [Cr(CO)$_3$(tohbtach)] in acetone the tohbtach ligand was



Scheme 1

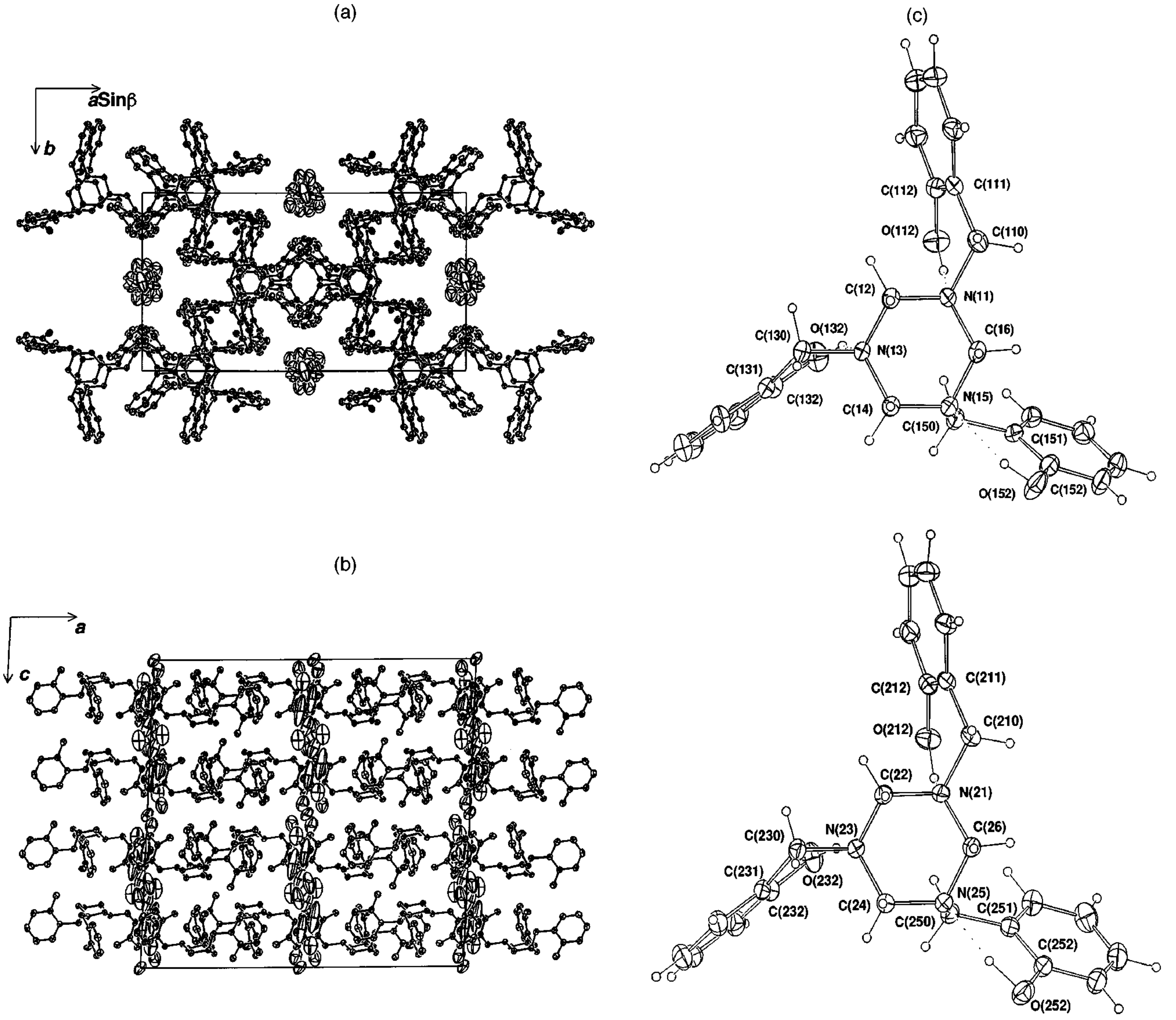


Fig. 1 (a), (b) Projections of the unit cell contents of tohbtach down *c* and *b* respectively, showing the overlap of the components of the parent molecules and the solvating tunnels through the structure. Here and in other figures, 'thermal ellipsoids' are depicted at the 20% probability amplitude level, hydrogen atoms having arbitrary radii of 0.1 Å. (c) The two independent molecules of tohbtach, projected normal to their central ring planes, showing the intramolecular hydrogen bonds.

displaced within an hour, leaving a sample that contained [Cr(CO)$_3$(tmtach)] and free tohbtach. The difference in hydrogen-bond acceptor abilities of acetone and dmso may be responsible for the different outcomes of these experiments. In acetone, strong intramolecular hydrogen bonding within tohbtach would stabilise free tohbtach, and at the same time inhibit the triazacyclohexane unit from forming a complex with chromium. Dimethyl sulfoxide, a stronger hydrogen-bond acceptor than acetone, would disrupt the intramolecular hydrogen bonding in tohbtach and so promote formation of [Cr(CO)$_3$(tohbtach)].

Structural characterisation

The results of the room temperature single crystal structure determination of the tohbtach ligand are consistent in terms of stoichiometry and connectivity with its description as such; two molecules comprise the asymmetric unit of the structure, together with a quantity of poorly defined solvent. The crystal packing is of interest, the central C_3N_3 ring 'planes' of the two molecules of the asymmetric unit lying quasi-parallel and normal to the *c* axis of the almost orthogonal cell. Together with pairs of symmetry equivalents, the central rings pack superimposed up the *c* dimension, so well aligned that a tunnel remains exposed through their centres in that projection [Fig. 1(a)], while the associated phenyl groups form a second hollow column. The consequence of this aggregation is that a further set of tunnels, largest of all, remains which accommodates the solvent molecules in a columnar array parallel to *c* [Fig. 1(a), (b)]. About the central C_3N_3 rings the ease of inversion at the nitrogens is reflected in the substituents being diversely axial or equatorial, the proportion being 1 : 2 in each molecule, with the substituent at N(5) being axial. Regardless of whether the substituent is axial or equatorial, an intramolecular hydrogen bond is formed between the phenolic hydrogen and the parent nitrogen, as in a number of the previously studied 2-hydroxybenzyl substituted triazacyclononanes,[26] the approach of the hydrogen being equatorial or axial, *i.e.* the converse of the mode of substitution; $N\cdots O$ range between 2.637(4) to 2.687(4) Å for the equatorial substituents, being slightly longer [2.728(4), 2.732(4)] for the axial (Table 1). Inspection of Table 1 shows that, although molecular geometries in general are unremarkable, in detail the ambience of N(5) as different from N(1,3) is consistently reflected in small but subtle variations in almost all parameters involving it.

With the co-ordination of the Cr(CO)$_3$ moiety by such ligands as N_3 donors, the capacity for intramolecular hydrogen-

Table 1 Selected geometries of tohbtach

(a) Distances (Å) and angles (°): the two values in each entry are for molecules $n = 1$ or 2

N(n1)–C(n2)	1.464(4), 1.465(4)	N(n1)–C(n6)	1.470(4), 1.464(4)
N(n3)–C(n4)	1.469(4), 1.471(4)	N(n3)–C(n2)	1.457(4), 1.464(4)
N(n5)–C(n6)	1.449(4), 1.451(4)	N(n5)–C(n4)	1.458(4), 1.458(4)
N(n11)–C(n10)	1.477(4), 1.478(4)	N(n31)–C(n30)	1.476(4), 1.477(4)
N(n51)–C(n50)	1.456(4), 1.469(4)		
C(n2)–N(n1)–C(n6)	109.2(2), 109.5(2)	C(n2)–N(n3)–C(n4)	109.3(2), 108.8(2)
C(n4)–N(n5)–C(n6)	110.3(2), 109.8(2)		
N(n3)–C(n4)–N(n5)	111.1(2), 111.4(2)	N(n1)–C(n6)–N(n5)	111.5(2), 110.9(2)
N(n1)–C(n2)–N(n3)	108.1(2), 107.8(2)		
C(n10)–N(n1)–C(n2)	111.7(2), 111.4(2)	C(n30)–N(n3)–C(n2)	110.7(2), 110.7(2)
C(n10)–N(n1)–C(n6)	111.7(2), 111.8(2)	C(n30)–C(n3)–C(n4)	111.6(2), 111.4(2)
C(n50)–N(n5)–C(n4)	113.1(2), 113.4(2)	C(n50)–N(n5)–C(n6)	113.8(2), 113.3(2)
Torsion angles			
C(n6)–N(n1)–C(n2)–N(n3)	61.9(3), −62.4(8)	C(n10)–N(n1)–C(n2)–N(n3)	−174.1(2), 173.3(2)
N(n1)–C(n2)–N(n3)–C(n4)	−62.2(3), 61.8(3)	C(n10)–N(n1)–C(n6)–N(n5)	177.1(2), −175.9(2)
C(n2)–N(n3)–C(n4)–N(n5)	59.3(3), −59.7(3)	C(n30)–N(n3)–C(n4)–N(n5)	−177.9(2), 178.0(2)
N(n3)–C(n4)–N(n5)–C(n6)	−55.0(3), 56.2(3)	C(n30)–N(n3)–C(n2)–N(n1)	174.4(2), −175.4(2)
C(n4)–N(n5)–C(n6)–N(n1)	54.9(3), −56.0(3)	C(n50)–N(n5)–C(n6)–N(n1)	−73.6(3), 71.9(3)
N(n5)–C(n6)–N(n1)–C(n2)	−58.9(3), 60.1(3)	C(n50)–N(n5)–C(n4)–N(n3)	73.8(3), −71.7(3)

(*b*) (Intramolecular) hydrogen bonds: a/e denote whether the benzylic substituent at N(*lm*) is axial or equatorial

lmn	a/e	H(*lmn*)–O(*lmn*)	H(*lmn*) · · · N(*lm*)	N(*lm*) · · · O(*lmn*)	O(*lmn*)–H(*lmn*) · · · N(*lm*)
112	e	0.93(3)	1.77(3)	2.637(4)	154(3)
132	e	1.09(3)	1.67(3)	2.687(4)	154(3)
152	a	0.92(4)	1.88(4)	2.728(4)	152(4)
212	e	1.27(4)	1.47(4)	2.649(4)	150(3)
232	e	1.02(4)	1.69(4)	2.658(4)	158(4)
252	a	1.10(5)	1.70(5)	2.732(3)	154(4)

bond formation of the above type is eliminated, so that such interactions are now found to predominate between the terminal OH groups of the pendant substituents. In [Cr(CO)$_3$(thptach)] one molecule comprises the asymmetric unit of the structure; the molecules are packed in layers parallel to *b* and the *ac* diagonal, Fig. 2(a), and within each layer are organised in alternate rows of carbonyls 'up' or 'down'. Hydrogen bonds, characterised by their O, H · · · O distances and O–H · · · O angle are found between successive layers O,H(113) · · · O(133) $(1 - x, -y, 1 - z)$ 2.683(3), 1.99(4) Å, 173(4)°; O,H(133) · · · O(153) $(1 - x, 1 - y, 1 - z)$ 2.635(3), 1.93(4) Å, 167(4)°; O,H(153) · · · O(113) $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$ 2.713(3), 1.97(3) Å, 171(4)° [Fig. 2(b)]. The structure of [Cr(CO)$_3$(thetach)] is more complex, four molecules comprising the asymmetric unit of the structure, disposed pseudosymmetrically in monoclinic space group $P2_1$. Short hydroxyl O · · · O intermolecular distances indicative of hydrogen-bonding interactions are listed in Table 2. Again, the molecules are disposed in layers within the lattice, the arrangement within a given layer being polar (Fig. 3). For the molecule of the more precisely determined [Cr(CO)$_3$(thptach)], geometries within the molecular core are given in Table 3. Within the limits of larger errors, the geometries of [Cr(CO)$_3$(thetach)] do not differ non-trivially, apart from the varied conformations of the ligand substituents, some of which do not appear to be involved in hydrogen bonding.

Table 2 Putative hydrogen-bonding interactions (Å) of [Cr(CO)$_3$(thetach)]

O(112) · · · O(152) $(-x, \frac{1}{2} + y, 1 - z)$	2.71(1)
O(132) · · · O(212) $(1 - x, \frac{1}{2} + y, 1 - z)$	2.61(2)
O(152) · · · O(252)	2.78(1)
O(212) · · · O(232) $(1 - x, y - \frac{1}{2}, 1 - z)$	2.72(2)
O(232) · · · O(432) $(1 - x, \frac{1}{2} + y, 1 - z)$	2.76(1)
O(312) · · · O(452) $(1 - x, y - \frac{1}{2}, -z)$	2.91(1)
O(332) · · · O(352) $(2 - x, y - \frac{1}{2}, -z)$	2.92(1)
O(352) · · · O(452)	2.77(1)

The present rather precise data for the core geometry of [Cr(CO)$_3$(thptach)] present the opportunity for comparison with those of its trimethyl and tri-*tert*-butyl congeners, and this is done in Table 4. Significant and non-trivial differences are found between the three adducts with different substituents; *cf.* the methyl substituted analogue, the N–C substituent distance may be marginally larger in the present complex, as is also C–N within the ring, while Cr–N is very appreciably larger and Cr–N–C may be slightly larger. Overall, the similarity to the *t*-Bu substituted adduct is much closer than to the methyl, perhaps rather surprisingly, with the differences between them more or less trivial.

Experimental

General procedures were as described previously.[10] The complex [Cr(CO)$_3$(CH$_3$CH$_2$CN)$_3$][27] and 1,3,5-tri(*o*-hydroxybenzyl)-1,3,5-triazacyclohexane (tohbtach)[19] were prepared according to literature methods.

Synthesis of the hydroxyalkyl ligands

thetach. Paraformaldehyde (5.54 g, 0.18 mol) was added portionwise to a stirred solution of ethanolamine (11.3 g, 0.18 mol) in ethanol (100 cm^3). Stirring was continued overnight. The mixture was then filtered and the filtrate concentrated *in vacuo* to afford thetach as a colourless, viscous oil, in quantitative yield. δ_H [(CD$_3$)$_2$CO] 2.57 (6 H, apparent t, splitting 5.6 Hz, 6 × H1′), 3.4 (6 H, br s, 3 × NCH$_2$N), 3.59 (6 H, apparent t, splitting 5.6 Hz, 6 × H2′) and 4.4 (3 H, br s, 3 × OH); δ_C [(CD$_3$)$_2$CO] 56.1 (C1′), 60.3 (C2′) and 74.9 (NCH$_2$N). The ^{1}H NMR and IR spectra were consistent with the literature.[20,28]

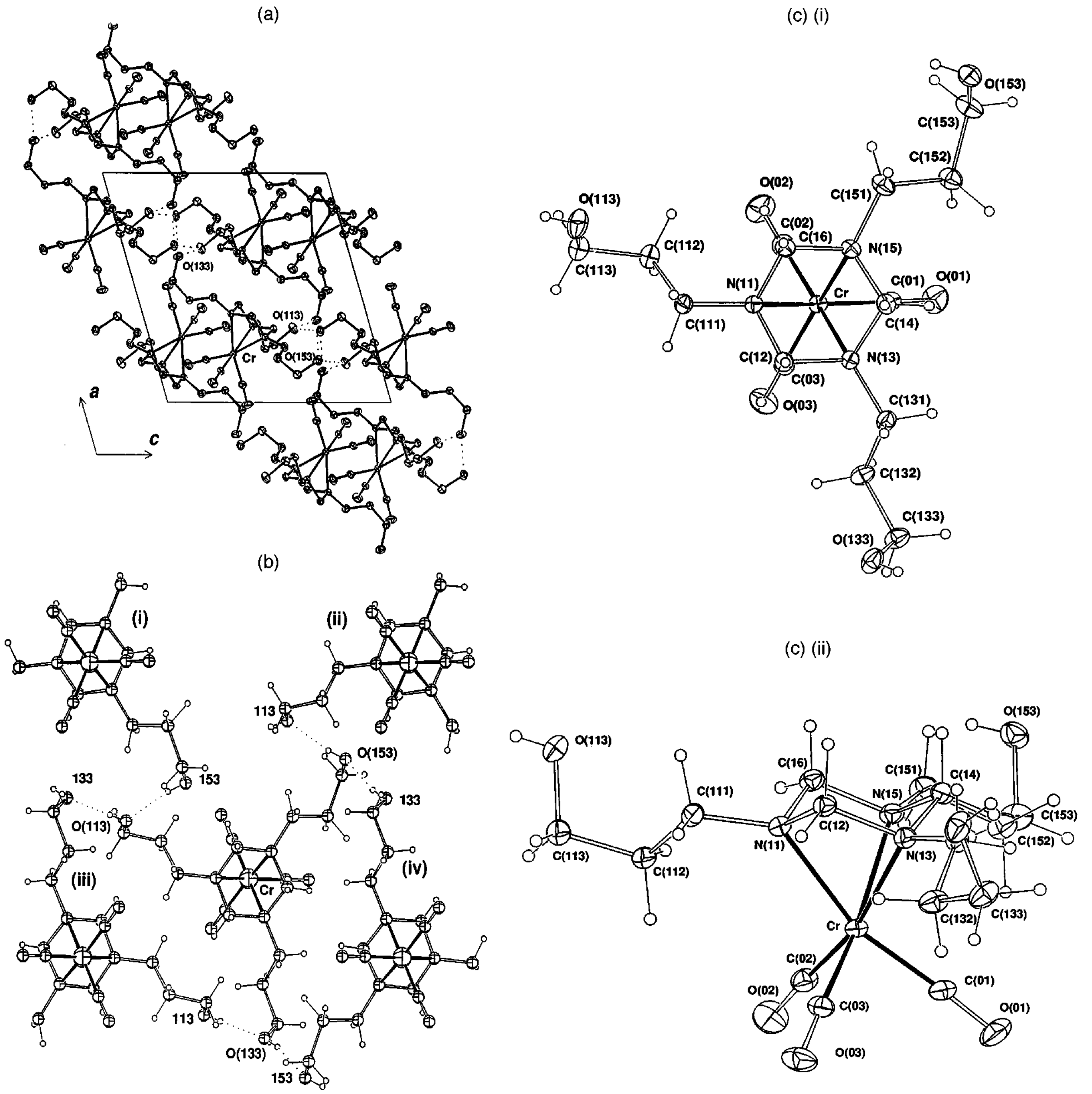


Fig. 2 (a) Projection of the unit cell contents of [Cr(CO)$_3$(thptach)] down *b* showing the layering of the molecules in the plane of *b* and the *ac* diagonal, and the interlayer hydrogen bonds. (b) A single molecule (the asymmetric unit) of one layer, showing its hydrogen bonding ambience between two rows of opposite polarity of the next layer (molecules i at $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$, ii at $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$, iii at $1 - x, -y, 1 - z$ and iv at $1 - x, 1 - y, 1 - z$). (c) A single molecule, projected (i) down and (ii) quasi-normal to, the potential 3 axis.

thptach. Paraformaldehyde (2.5 g, 83 mmol) was added portionwise to a stirred solution of 3-amino-1-propanol (5.6 g, 75 mmol) in ethanol (30 cm^3). Stirring was continued overnight. The mixture was then filtered and the filtrate concentrated *in vacuo* to afford thptach, as a colourless, viscous oil, in quantitative yield. δ_H [(CD$_3$)$_2$CO] 1.64 (6 H, apparent tt, splitting 6.3 Hz, 6 × H2′), 2.55 (6 H, apparent t, splitting 6.7 Hz, 6 × H1′), 3.4 (6 H, br s, 3 × NCH$_2$N), 3.68 (6 H, apparent t, splitting 6.0 Hz, 6 × H3′) and 4.2 (3 H, br s, 3 × OH); δ_C [(CD$_3$)$_2$CO] 30.5 (C2′), 50.8 (C1′), 61.6 (C3′) and 74.9 (NCH$_2$N). The ^{1}H NMR and IR spectra were consistent with the literature.[21]

Synthesis of chromium complexes

[Cr(CO)$_3$(thetach)]. A solution of [Cr(CO)$_6$] (0.88 g, 4.0 mmol) in acetonitrile (40 cm^3) was heated at reflux for 18 h. The solution was filtered through alumina–Celite and the filtrate concentrated *in vacuo* to afford a yellow solid. A solution of thetach (0.88 g, 4.0 mmol) in thf (10 cm^3) was added to the yellow solid, the resulting orange solution was diluted with diethyl ether (45 cm^3) and the mixture refluxed for 16 h during which time an orange precipitate formed. The solid was collected, washed with ether (15 cm^3) and dried *in vacuo* to yield [Cr(CO)$_3$(thetach)] as an orange powder (0.77 g, 54%), mp 130 °C (decomp.) (Found: C, 40.31; H, 5.87; N, 12.02. $C_{12}H_{21}CrN_3O_6$ requires C, 40.56; H, 5.96; N, 11.83%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1912 and 1765br (CO); δ_H [(CD$_3$)$_2$CO] 2.79 (6 H, apparent t, splitting 5.2 Hz, 6 × H1′), 3.85 (6 H, apparent t, splitting 5.2 Hz, 6 × H2′), 4.33 (3 H, apparent d, splitting 8.6 Hz, 3 × NC*H*HN) and 4.84 (3 H, apparent d, splitting 8.6 Hz, 3 × NCH*H*N); δ_C [(CD$_3$)$_2$CO] 57.3 (C1′), 60.2 (C2′), 82.1 (NCH$_2$N) and 237.0 (CO); *m*/*z* 355.0845 (M) (requires 355.0835).

[Cr(CO)$_3$(thptach)]. A solution of [Cr(CO)$_6$] (2.36 g, 10.7 mmol) in acetonitrile (70 cm^3) was heated at reflux for 15 h. The acetonitrile was removed *in vacuo* and the residual yellow solid dissolved in thf (120 cm^3). The compound thptach (3.17 g, 12.1

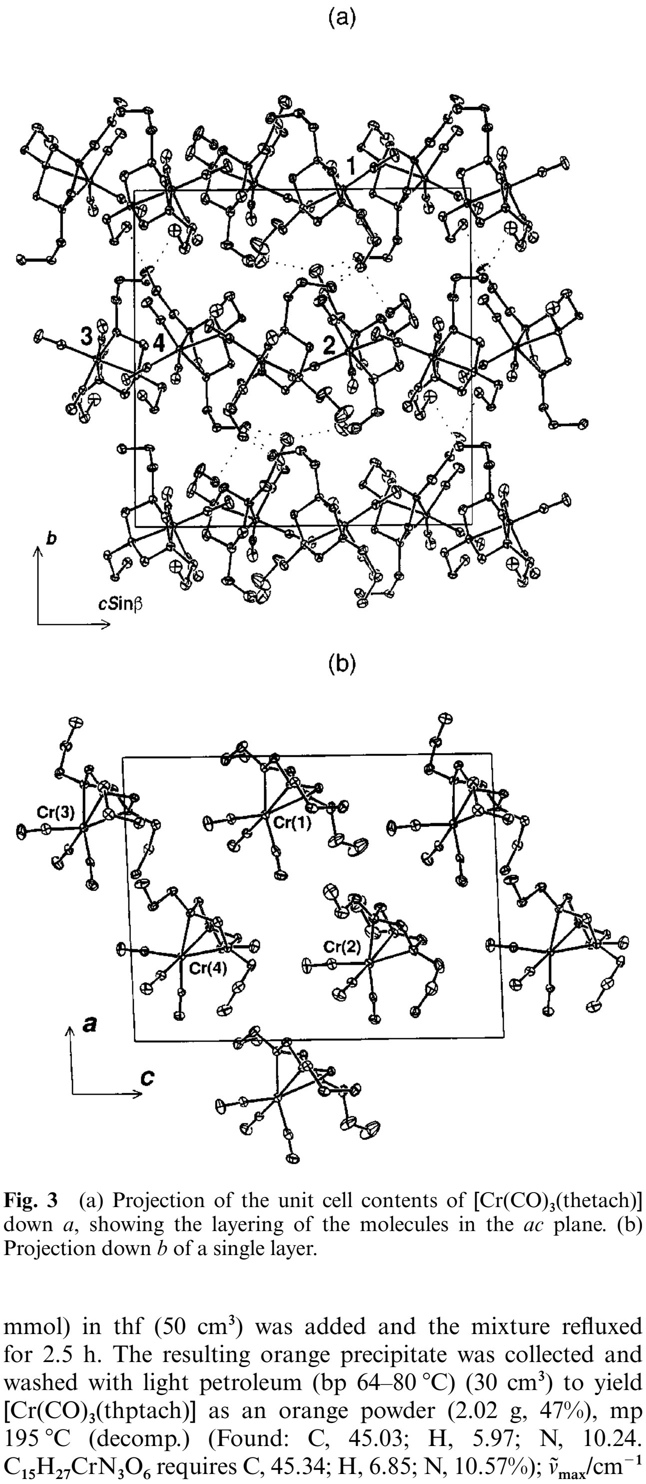


Fig. 3 (a) Projection of the unit cell contents of [Cr(CO)$_3$(thetach)] down *a*, showing the layering of the molecules in the *ac* plane. (b) Projection down *b* of a single layer.

mmol) in thf (50 cm^3) was added and the mixture refluxed for 2.5 h. The resulting orange precipitate was collected and washed with light petroleum (bp 64–80 °C) (30 cm^3) to yield [Cr(CO)$_3$(thptach)] as an orange powder (2.02 g, 47%), mp 195 °C (decomp.) (Found: C, 45.03; H, 5.97; N, 10.24. $C_{15}H_{27}CrN_3O_6$ requires C, 45.34; H, 6.85; N, 10.57%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1906, 1767 and 1740 (CO); δ_H [(CD$_3$)$_2$CO] 1.91 (6, m, 6 × H2′), 2.70 (6 H, m, 6 × H1′), 3.66 (6 H, m, 6 × H3′), 3.68 (3 H, m, 3 × OH), 4.08 (3 H, apparent d, splitting 8.6 Hz, 3 × NC*H*HN) and 4.65 (3 H, apparent d, splitting 8.6 Hz, 3 × NCH*H*N); δ_C [(CD$_3$)$_2$CO] 30.3 (C2′), 52.3 (C1′), 60.2 (C3′), 80.9 (NCH$_2$N) and 237.7 (CO).

[CrBr$_3$(thptach)]. Bromine (0.20 cm^3, 3.8 mmol) was added to a stirred suspension of [Cr(CO)$_3$(thptach)] (0.34 g, 0.86 mmol) in carbon tetrachloride (50 cm^3). The mixture was refluxed for 14 h during which time a purple precipitate formed. The solid was collected, washed with carbon tetrachloride (20 cm^3) and dried in air, to afford [CrBr$_3$(thptach)] as a purple powder, in quantitative yield, mp 260 °C (decomp.) (Found: C, 25.5; H, 4.54; N, 7.01. $C_{12}H_{27}CrBr_3N_3O_3$ requires C, 26.1; H, 4.92; N, 7.60%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3385vs, 2940s, 2883, 1457s, 1328, 1102vs, 1058vs, 946s and 532.

[Cr(CO)$_3$(tohbtach)]. A solution of [Cr(CO)$_3$(CH$_3$CH$_2$CN)$_3$] (0.50 g, 1.7 mmol) in acetone (2.5 cm^3) was added to a solution of tohbtach (0.73 g, 1.8 mmol) in acetone (15 cm^3). The solution was stirred for 1 h then concentrated *in vacuo*. The residue was triturated with ether (15 cm^3) until a precipitate formed. The solid was collected, washed with ether (30 cm^3) and dried *in vacuo* to yield [Cr(CO)$_3$(tohbtach)] as a pale yellow-orange powder (0.46 g, 50%), mp 150 °C (decomp.) (Found: C, 60.71; H, 5.61; N, 7.98. $C_{27}H_{27}CrN_3O_6$ requires C, 59.89; H, 5.03; N, 7.76%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1912, 1772 and 1725 (CO); δ_H [(CD$_3$)$_2$CO] 3.72 (3 H, apparent d, splitting 8.6 Hz, 3 × NC*H*HN), 3.90 (6 H, s, C*H*$_2$C$_6$H$_4$), 4.81 (3 H, apparent d, splitting 8.6 Hz, 3 × NCH*H*N), 6.84 (6 H, m, aryl H), 7.15 (3 H, m, aryl H) and 7.38 (3 H, m, aryl H); δ_C [(CD$_3$)$_2$CO] 54.4 (*C*H$_2$C$_6$H$_4$), 79.8 (NCH$_2$N), 116.2 (aryl), 120.5 (aryl), 120.6 (aryl), 130.6 (aryl), 133.4 (aryl), 156.5 (COH) and 237.4 (CO).

X-Ray crystallography

Crystals of tohbtach, [Cr(CO)$_3$(thptach)] and [Cr(CO)$_3$(thetach)] suitable for X-ray diffraction studies were grown from ethyl acetate–hexane, acetone–dmso (10 : 1)–benzene and acetone–hexane solutions respectively, *via* solvent vapour diffusion.

Structure determinations. Unique room temperature four-circle diffractometer data sets were measured (2θ–θ scan mode, $2\theta_{max}$ as specified; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; *T ca.* 20 °C) yielding *N* independent reflections, N_o being considered 'observed' and used in the full matrix least squares refinement after absorption correction in the case of the chromium complexes. With a large cell, small specimens and a non-centrosymmetric space group the processing of [Cr(CO)$_3$(thetach)] proved intractable, and the determination was only brought to an acceptable outcome with the acquisition of data using a Bruker AXS CCD area-detector instrument, 27676 total reflections reducing to a unique set ($R_{int} = 0.023$) following processing incorporating an 'empirical' absorption correction using proprietary software SAINT/SADABS/XPREP, 'Friedel pairs' being kept distinct. Anisotropic thermal parameters were refined for all structures. Conventional residuals R, R' (statistical weights) on $|F|$ are quoted at convergence. Neutral atom complex scattering factors were employed, computation using the XTAL 3.4/5 program system.[29] Individual variations, abnormalities, idiosyncrasies, *etc.* are noted.

Crystal/refinement data. 'tohbtach' ≡ $C_{24}H_{27}N_3O_3 \cdot 0.25CH_3CH_2O_2CCH_3 \cdot \frac{5}{8}H_2O$, $M = 438.8$, monoclinic, space group $C2/c$ (C^6_{2h}, no. 16), $a = 26.31(1)$, $b = 14.650(7)$, $c = 25.42(2)$ Å, $\beta = 92.71(5)°$, $V = 9788$ Å^3, D_c ($Z = 16$) = 1.19_1 g cm^{-3}, $F(000) = 3748$, $\mu_{Mo} = 0.8$ cm^{-1}, specimen 0.90 × 0.30 × 0.22 mm (no correction), $2\theta_{max} = 50°$, $N = 8607$, $N_o[I > 3\sigma(I)] = 4068$, $R = 0.049$, $R' = 0.058$, $n_v = 837$, $|\Delta\rho_{max}| = 0.21$ e Å^{-3}.

(x, y, z, U_{iso}) were refined for hydrogen atoms associated with the parent molecule. An inauspicious agglomeration of difference map residues was modelled in terms of the above unseemly aggregate of solvent moieties following enquiry concerning the history of the sample.

[Cr(CO)$_3$(thptach)] ≡ $C_{15}H_{27}CrN_3O_6$, $M = 397.4$, monoclinic, space group $P2_1/n$ (C^5_{2h}, no. 14), $a = 12.582(4)$, $b = 12.186(3)$, $c = 12.849(2)$ Å, $\beta = 107.56(2)°$, $V = 1878$ Å^3, D_c ($Z = 4$) = 1.40_5 g cm^{-3}, $F(000) = 840$, $\mu_{Mo} = 6.4$ cm^{-1}, specimen 0.25 × 0.85 × 1.30 mm, $A^*_{min,max}$ (gaussian correction) = 1.29, 1.62, $2\theta_{max} = 55°$, $N = 4307$, $N_o[I > 2\sigma(I)] = 3703$, $R = 0.049$, $R' = 0.064$, $n_v = 335$, $|\Delta\rho_{max}| = 0.67$ e Å^{-3}.

$(x, y, z, U_{iso})_H$ were refined throughout.

[Cr(CO)$_3$(thetach)] ≡ $C_{12}H_{21}CrN_3O_6$, $M = 355.3$, monoclinic, space group $P2_1$ (C^2_2, no. 4), $a = 12.8160(9)$, $b = 15.026(1)$, $c = 16.478(1)$ Å, $\beta = 92.087(1)°$, $V = 3171$ Å^3, D_c ($Z = 8$) = 1.48_8 g cm^{-3}, $F(000) = 1488$, $\mu_{Mo} = 7.5$ cm^{-1}, specimen 0.18 × 0.17 × 0.07 mm, $T_{min,max} = 0.71$, 0.89, $2\theta_{max} = 58°$, $N = 8034$, N_o

Table 3 Selected geometries of [Cr(CO)$_3$(thptach)]

(a) The chromium environment: *r*/Å is the chromium–ligand atom distance (Å); other entries are the angles (°) subtended at the chromium by the relevant atoms at the head of the row and column

	r	N(13)	N(15)	C(01)	C(02)	C(03)
N(11)	2.201(5)	63.13(7)	63.08(7)	163.34(9)	104.0(1)	105.00(9)
N(13)	2.205(2)		63.17(8)	103.94(9)	164.8(1)	104.1(1)
N(15)	2.200(2)			102.34(9)	104.6(1)	165.09(9)
C(01)	1.817(2)				87.0(1)	87.9(1)
C(02)	1.811(3)					86.5(1)
C(03)	1.811(3)					

(*b*) Selected ligand geometries

N(11)–C(12)	1.467(3)	N(11)–C(16)	1.467(3)
C(12)–N(13)	1.473(3)	C(16)–N(15)	1.462(3)
N(13)–C(14)	1.475(3)	N(15)–C(14)	1.465(4)
N(11)–C(111)	1.480(3)	C(01)–O(01)	1.162(3)
N(13)–C(131)	1.476(4)	C(02)–O(02)	1.171(4)
N(15)–C(151)	1.480(4)	C(03)–O(03)	1.170(3)
Cr–N(11)–C(12)	92.5(1)	Cr–N(11)–C(16)	92.4(1)
Cr–N(13)–C(14)	91.9(1)	Cr–N(13)–C(12)	92.2(1)
Cr–N(15)–C(16)	92.6(1)	Cr–N(15)–C(14)	92.3(1)
Cr–C(01)–O(01)	177.4(2)	Cr–N(11)–C(111)	134.7(1)
Cr–C(02)–O(02)	176.6(3)	Cr–N(13)–C(131)	135.0(1)
Cr–C(03)–O(03)	176.4(2)	Cr–N(15)–C(151)	134.5(2)
C(12)–N(11)–C(16)	108.7(2)	N(11)–C(12)–N(13)	103.3(2)
C(14)–N(13)–C(12)	109.5(2)	N(13)–C(14)–N(15)	103.4(2)
C(16)–N(15)–C(14)	109.2(2)	N(15)–C(16)–N(11)	103.6(2)
C(111)–N(11)–C(12)	112.2(2)	C(111)–N(11)–C(16)	112.8(2)
C(131)–N(13)–C(14)	112.0(2)	C(131)–N(13)–C(12)	112.9(2)
C(151)–N(15)–C(16)	109.6(2)	C(151)–N(15)–C(14)	115.2(2)
Torsion angles			
C(16)–N(11)–C(12)–N(13)	−67.2(2)	C(12)–N(11)–C(16)–N(15)	68.1(2)
C(14)–N(13)–C(12)–N(11)	66.6(2)	C(14)–N(15)–C(16)–N(11)	−67.9(2)
C(12)–N(13)–C(14)–N(15)	−66.2(2)	C(16)–N(15)–C(14)–N(13)	66.7(2)
C(111)–N(11)–C(12)–N(13)	167.4(2)	C(111)–N(11)–C(16)–C(15)	−166.8(2)
C(131)–N(13)–C(12)–N(11)	−167.9(2)	C(131)–N(15)–C(16)–N(11)	165.0(2)
C(131)–N(13)–C(14)–N(15)	167.7(2)	C(151)–N(15)–C(14)–N(13)	−169.5(2)

Table 4 Comparative mean geometries (distances in Å, angles in °) of [Cr(CO)$_3$(txtach)]

	Methyl[a]	(CH$_2$)$_3$OH[b]	^{t}Bu[c]
Cr–C	1.800(7)	1.813(3)	1.80(1)
Cr–N	2.17(2)	2.202(3)	2.210(7)
N–C	1.458(2)	1.468(5)	1.468(6)
N–C(x)	1.471(5)	1.479(2)	1.507(6)
Cr–C–O	176(2)	176.8(5)	176.1(3)
N–Cr–N	63.3(3)	63.13(5)	63.3(2)
C–Cr–C	87(2)	87.1(7)	85.6(9)
N–Cr–C(*trans*)	164.13(6)	164.4(9)	165(1)
N–Cr–C	104(1)	104.0(9)	104.8(9)
Cr–N–C(x)	132(2)	134.7(3)	131.4(6)
Cr–N–C	92.8(5)	92.3(2)	92.1(4)
C–N–C	109.7(2)	109.1(4)	108.0(1)
C–N–C(x)	113.3(7)	112(2)	114.5(8)
Torsion angles			
|C–N–C–N|	67.2(3)	67.1(8)	67.5(3)

[a] Ref. 10. [b] This work. [c] Ref. 10.

$(|F| > 4\sigma|F|) = 4459$, $R = 0.048$, $R' = 0.050$, $n_v = 794$, $|\Delta\rho_{max}| = 0.74$ e Å^{-3}.

Hydrogen atoms were included constrained in (x, y, z, U_{iso}), being located for all but two of the hydroxy moieties. Refinement of the absolute structure parameter (‘x_{abs}’) yielded a value of 0.21(4).

CCDC reference number 186/1378.

See http://www.rsc.org/suppdata/dt/1999/1483/ for crystallographic files in .cif format.

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