Probing the effects of ligand structure on activity and selectivity of Cr(III) complexes for ethylene oligomerisation and polymerisation

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A series of distorted octahedral Cr(III) complexes containing tridentate S-, S/O- or N-donor ligands comprised of three distinct architectures: facultative { $S(CH_2CH_2SC_{10}H_{21})_2$ (L¹) and $O(CH_2CH_2SC_{10}H_{21})_2$ (L²)}, tripodal { $MeC(CH_2S^nC_4H_9)_3$ (L³), $MeC(CH_2SC_{10}H_{21})_3$ (L⁴)} and macrocyclic { $(C_{10}H_{21})[9]aneN_3$ (L⁵), (C₁₀H₂₁)_3[9]aneN_3 (L⁶), with [9]aneN₃ = 1,4,7-triazacyclononane} are reported and characterised spectroscopically. Activation of [$CrCl_3(L)$] with MMAO produces very active ethylene trimerisation, oligomerisation and polymerisation catalysts, with significant dependence of the product distribution upon the ligand type present. The properties of the parent [$CrCl_3(L)$] complexes are probed by cyclic voltammetry, UV-visible, EPR, EXAFS and XANES measurements, and the effects upon activation with Me₃Al investigated similarly. Treatment with excess Me₃Al leads to substitution of Cl ligands by Me groups, generation of an EPR silent Cr species (consistent with a change in the oxidation state of the Cr to either Cr(II) or Cr(IV)) and substantial dissociation of the neutral S and S/O-donor ligands.

Introduction

In recent years there has been a substantial acceleration in research activity concerned with homogeneous transition metal catalysts for ethylene oligomerisation and polymerisation.¹⁻³ Chromium catalysts play an important role in both of these processes.^{4,5} The chromium-based heterogeneous Phillips catalyst for ethylene polymerisation⁶ produces polyethylene with broad molecular weight distributions (C_6 – C_{20} range) as a unique property. Presently, α -olefins are produced by the Alfen⁷ or Shell Higher Olefin⁸ Processes. Cr-based catalysts also play a central role in the selective ethylene trimerisation and tetramerisation reactions,⁹⁻¹⁴ and Cr(III) complexes coordinated to a range of tridentate ligands bearing a combination of S, N and P donor atoms have also shown great potential in ethylene polymerization.¹⁵⁻¹⁷

In contrast to the wide range of Cr(III) complexes with hard N and O donor ligands, far fewer examples of complexes with soft donor ligands, such as thioethers, are known,^{18,19} and there are few reported examples of Cr(III) thioether complexes as catalysts for ethylene trimerisation, oligomerisation or polymerisation. On the other hand, Cr(III) complexes coordinated to harder N-based acyclic and cyclic ligands do show good activities for the combined oligomerisation and polymerisation.⁴⁻⁶

The trimerisation of ethylene to 1-hexene is of wide interest due to the importance of this co-monomer in the production of linear low-density polyethylene (LLDPE).²⁰ While some ethylene trimerisation catalysts are based on Ti and Ta, Cr-based systems generally display higher activities, selectivities, and thermal stabilities.¹⁴ The application of soft thioether-containing ligands in homogeneous catalysis has recently been reported by McGuinness and co-workers¹¹ using mixed donor ligands, $HN(CH_2CH_2SR)_2$ (R = Me, Et, "Bu, "decyl) which, when reacted with $[CrCl_3(THF)_3]$ and activated with methylaluminoxane (MAO), give rise to highly active and selective catalysts for the trimerisation of ethylene to 1-hexene. $[CrCl_3(L)]$ ($L = HN(CH_2CH_2SC_{10}H_{21})_2$) is the most effective pre-catalyst. From a mechanistic point of view, it is believed that a change in the oxidation state of the metal centre occurs upon activation with MAO. Used as a cocatalyst, MAO is normally thought to implicate a cationic active metal centre²¹ through the Cr(II)/Cr(IV) couple.²² Even if this route seems more likely than the cycle involving neutral species (Cr(I)/Cr(III)), evidence to support it is still very limited.

Here we describe the synthesis and investigation of a series of Cr(III) complexes of the type [$CrCl_3(L)$], where L is a neutral tridentate ligand, for ethylene trimerisation, oligomerisation and polymerisation reactions. This work focuses on the effect of the ligand donor set and architecture on the activity and selectivity. The ligands, L, were chosen to cover a wide area of catalytic activity; from the geometry-open-chain, tripodal, macrocycleto the type of donor atoms, hard donor amine (N) and ether (O) atoms and soft donor thioether (S) atoms. Using long chain terminal alkyl groups improves the solubility of the Cr complexes in organic solvents for the catalytic studies, and can lead to increased activity.11 The series of Cr(III) complexes has been studied using IR, UV-visible and EPR spectroscopy. Partial structural data were obtained via Cr K-edge X-ray Absorption Fine Structure (XAFS) measurements. The activated catalysts were then employed for ethylene trimerisation, oligomerisations or polymerisation using MMAO (modified methylaluminoxane) as cocatalyst. The structures of the complexes derived from $[CrCl_3(L)]$ (L = L¹-L⁴) in toluene and activated with an excess of the molecular alkylating agent Me₃Al have also been investigated

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using Cr K-edge EXAFS and X-ray Absorption Near-Edge Structure (XANES) measurements, UV-visible and EPR spectroscopy. Me₃Al was specifically employed in preference to MMAO for the spectroscopic studies to permit accurate stoichiometric ratios to be used, avoiding the difficulties associated with the ill-defined MMAO reagent.

Results and discussion

The ligands are comprised of three distinct geometries: facultative {S(CH₂CH₂SC₁₀H₂₁)₂ (L¹), O(CH₂CH₂SC₁₀H₂₁)₂ (L²)}, tripodal (MeC(CH₂SⁿC₄H₉)₃ (L³) MeC(CH₂SC₁₀H₂₁)₃ (L⁴)) and macrocyclic {(C₁₀H₂₁)[9]aneN₃ (L⁵), (C₁₀H₂₁)₃[9]aneN₃ (L⁶)} and their preparations and spectroscopic properties are described in the Experimental section. The methods used were based upon modifications of literature preparations for similar species.²³⁻²⁶

The distorted octahedral complexes $[CrCl_3(L)](L = L^1-L^6)$ were prepared by reaction of $[CrCl_3(THF)_3]$ with one mol. equiv. of L in anhydrous CH_2Cl_2 and isolated in good yields as purple or green coloured solids $(L = L^1-L^5)$ or oily compounds $(L = L^6)$ by removal of the solvent *in vacuo* and washing with hexane. These neutral compounds are readily soluble in both chlorinated solvents and organic solvents such as toluene. The complexes $[CrCl_3(L)](L = L^3-L^6)$ are also relatively sensitive to moisture, hence were stored and handled in a dry N₂-purged glove-box.

The IR spectroscopic data for the complexes $[CrCl_3(L)](L = L^{1} L^{6}$) (Table 1) provide evidence for coordinated L. Peaks observed in the region 200–400 cm⁻¹ may be tentatively assigned to v(Cr-Cl), hence give some structural information on the complexes (mer vs. fac isomers). The steric constraints of the tripodal ligands L^3 and L^4 are such that monomeric complexes must be *fac* isomers. This is borne out by the two bands observed in the 200-400 cm⁻¹ region assigned to the v(Cr-Cl) stretching modes. Similarly the macrocyclic geometry of the tridentate ligands L^5 and L^6 is such that they coordinate *facially* in octahedral complexes. The IR spectrum for $[CrCl_3(L^5)]$ also exhibits a peak at 3189 cm⁻¹, characteristic of the N-H stretching mode. The IR spectrum of $[CrCl_3(L^1)]$ shows a broad peak at 342 cm⁻¹ and earlier work on crown thioether chemistry and the implications of the ligand design suggest the complex adopts a facial geometry. On the other hand, spectroscopic studies indicate the mer isomer is formed for [CrCl₃(L²)], which reveals three ν (Cr–Cl) as expected ($C_{2\nu}$ or C_8).

The octahedral Cr(III) d³ system is expected to exhibit three quartet excited states and hence show three spin-allowed d–d transitions in the UV-visible spectrum: ${}^{4}T_{2g} \leftarrow {}^{4}A_{2g}$ (v_{1}); ${}^{4}T_{1g}$

(F) $\leftarrow {}^{4}A_{2g}$ (v_{2}); ${}^{4}T_{1g}$ (P) $\leftarrow {}^{4}A_{2g}$ (v_{3})²⁷ (the latter is usually obscured due to more intense LMCT transitions). Although the complexes reported here have symmetry lower than $O_{\rm h}$, the absence of clear splitting of the d-d transitions means that analysis of the electronic spectra based on approximate $O_{\rm h}$ symmetry is reasonable. Two low energy d-d transitions are observed for each of the Cr(III) complexes. The complexes $[CrCl_3(L^1)]$, $[CrCl_3(L^3)]$ and $[CrCl_3(L^4)]$ exhibit $Dq \sim 1440 \text{ cm}^{-1}$ (Table 1), similar to those reported in the literature for related species,²⁸⁻³⁰ e.g. Dq = 1433 cm^{-1} for [CrCl₃{[9]aneS₃}], 1420 cm^{-1} for [CrCl₃{[18]aneS₆}] and 1 470 cm⁻¹ for [CrCl₃{MeC(CH₂SCH₃)₃}]. The geometry of the ligand (open-chain vs. tripodal) does not affect the ligandfield splitting. The aza-macrocycle complexes $[CrCl_3(L^5)]$ and [CrCl₃(L⁶)] give a higher value with $Dq \sim 1680$ cm⁻¹, relatively low compared to species such as $[Cr{H_2NCH_2CH_2NH_2}_3]^{3+}$ (Dq = 2180 cm^{-1} , $[Cr{[9]aneN_3}_2]^{3+}$ (2 270 cm⁻¹) and $[Cr{[18]aneN_6}]^{3+}$ (2146 cm^{-1}) ,³¹ reflecting the presence of N₆ donor sets in these species compared to N₃Cl₃ donor sets in the new complexes.

We also probed the redox properties of $[CrCl_3(L)]$ ($L = L^{1}-L^{6}$) by cyclic voltammetry. Electrochemical data were recorded at room temperature under an N₂ atmosphere and with a scan rate of 100 mV s⁻¹ over a range of 1.5 to -1.5 V. A 0.2 M solution of $[Bu^{n}_{4}N]BF_{4}$ in anhydrous $CH_{2}Cl_{2}$ was employed as base electrolyte with a double platinum working and counter electrode and a standard calomel reference electrode (Table 2).

The Cr(III) thioether complexes show irreversible reductions (Table 2), possibly due to a structural rearrangement which is slow in comparison to the electron transfer process, and/or irreversible ligand loss upon reduction. No reductive activity was observed for the N-donor ligand complexes.

Table 2 Electrochemical data and Dq values for [CrCl₃(L)] (L = L¹–L⁶) in 0.2 M [Bu^a₄N]BF₄ in CH₂Cl₂, scan rate = 100 mV s⁻¹, E_{PC} = reduction potential

Complex	$E_{\rm PC}/{\rm V}^a$	Dq/cm^{-1}
$\begin{array}{l} [CrCl_3(L^1)] \\ [CrCl_3(L^2)] \\ [CrCl_3(L^3)] \\ [CrCl_3(L^4)] \\ [CrCl_3(L^5)] \\ [CrCl_3(L^6)] \end{array}$	-1.28 -1.25 -1.35 -1.27 $_^{b}$	1 430 1 396 1 440 1 439 1 684 1 680

" Voltages are quoted vs. $[Fe(\eta^5-C_5H_5)_2]/[Fe(\eta^5-C_5H_5)_2]^+$." No reduction observed.

Table 1 Selected electronic and IR spectroscopic^{*a*} data for $[CrCl_3(L)]$ (L = L¹-L⁶)

Complex	v_1/cm^{-1}	v_2/cm^{-1}	Dq/cm^{-1}	$\epsilon_1, \\ \epsilon_2/\mathrm{dm}^3 \mathrm{mol}^{-1}\mathrm{cm}^{-1}$	v(Cr–Cl)/cm ⁻¹
$[CrCl_{3}(L^{1})] \\ [CrCl_{3}(L^{2})] \\ [CrCl_{3}(L^{3})] \\ [CrCl_{3}(L^{4})] \\ [CrCl_{3}(L^{4})] \\ [CrCl_{3}(L^{5})] \\ [CrC$	14 300 13 960 14 400 14 390 16 840	19 330 21 050 20 320 20 280 20 620 21 790	1 430 1 396 1 440 1 439 1 684	200, 280 250, 400 185, 220 	342 (br) 389, 364, 347 357, 334 360, 333 327, 307 315, 208

^a UV-visible spectra recorded in toluene solution. IR spectra recorded as Nujol mulls.

XAFS spectra of parent Cr(III) complexes

We have carried out Cr K-edge XAFS measurements on the parent Cr(III) complexes to probe d(Cr-S), d(Cr-N), d(Cr-O) and d(Cr-Cl) in the first coordination sphere and to allow comparisons with the EXAFS data on the activated complexes (below).

Spectra were recorded from solid pellets of the complex diluted with BN and also for 5.0 mM solutions in toluene. Cr K-edge XAFS measurements on the solution formed after the *in situ* reaction between the complex and Me₃Al were also undertaken.

The EXAFS data for $[CrCl_3(L^1)]$ (Fig. 1) show a good fit for 2.7 Cl and 2.8 S atoms, with the bond lengths consistent with crystal structures involving other Cr(III) thioether complexes, *e.g.* $[CrCl_3(L^1)] d(Cr-Cl) = 2.32(6) \text{ Å}$, d(Cr-S) = 2.45(5) Å, fac- $[CrCl_3\{[18]aneS_6\}] d(Cr-S) = 2.459(3)$, 2.442(5), 2.440(5) Å, d(Cr-Cl) = 2.305(5), 2.279(5), 2.291(5) Å.²⁸ The Debye–Waller terms are relatively low, which suggests that both shells are integral to the fit. The model proposed gives the best results when multiple scattering is included, supporting the *facial* configuration deduced from the IR spectra (*vide supra*). For *mer*-MX₃L₃, where L is a tridentate ligand containing donor atoms of the same type (in our case, L = S or N; M = Cr; X = Cl), there are three environments: X–M–X, L–M–L and X–M–L, and the multiple scattering effects in the EXAFS measurements are negligible as they tend to 'cancel' one another. However, in *fac*-MX₃L₃ there is only one type of X–M–L multiple scattering unit and in this case the multiple scattering provides a large contribution to the EXAFS (L¹, L³⁻⁶) (Fig. 1). The partial structural data for the complexes [CrCl₃(L)] (L = L¹–L⁶) obtained *via* Cr K-edge EXAFS are summarised in Table 3.

Catalysis

The complexes $[CrCl_3(L)]$ (L = L¹–L⁶) (10 µmol for L¹, L⁵ and L⁶ in 100 mL toluene and 30 µmol for L², L³ and L⁴ in 80 mL of methylcyclohexane) were studied for their catalytic activities towards ethylene oligomerisation and polymerisation using MMAO as activator. The results at 40 bar of ethylene and with a MMAO/Cr ratio of 300:1 are summarised in Table 4.



Fig. 1 The Cr K-edge k^3 -weighted EXAFS, Fourier transform and sine transform for a solid pellet of [CrCl₃(L¹)]/BN.

Table 3 Cr K-edge k^3 -weighted EXAFS data for [CrCl₃(L)] (L = L¹–L⁶) measured as powders diluted with BN

Complex	C.N. ^{<i>a</i>,<i>b</i>} Cr–Cl	d(Cr–Cl)/Å	$2\sigma^2/\text{\AA}^{2c}$	C.N. $Cr-E^d$	d(Cr–E)/Å	$2\sigma^2/\text{\AA}^2$	R ^e (%)	Ef ^f /eV
$\begin{matrix} [CrCl_3\{L^1\}]\\ [CrCl_3\{L^2\}] \end{matrix}$	2.7(4)	2.32(6)	0.011(1)	S: 2.8(5)	S: 2.45(5)	0.010(2)	23.2	-6.3(3)
	2.7(4)	2.25(3)	0.015(5)	S: 2.0(2)	S: 2.37(7)	S: 0.008(0)	27.0	-2.8(8)
$[CrCl_3{L^3}]$ $[CrCl_3{L^4}]$	2.5(3) 2.5(5)	2.26(2) 2.25(3)	0.011(8) 0.003(8)	S: 2.5(4) S: 2.5(2)	0: 2.10(3) S: 2.43(3) S: 2.38(4)	0:0.007(7) 0.010(2) 0.001(7)	25.2 25.9	-5.7(9) -1.1(7)
$[CrCl_3\{L^5\}]$ $[CrCl_3\{L^6\}]$	2.7(2)	2.33(9)	0.007(6)	N: 2.5(5)	N: 2.01(8)	0.007(6)	26.0	-3.4(8)
	2.5(4)	2.32(6)	0.011(8)	N: 3.0(1)	N: 2.00(6)	0.004(9)	25.2	4.8(1)

^{*a*} C.N. = coordination number. ^{*b*} Standard deviations in parentheses. ^{*c*} Debye–Waller factor. ^{*d*} E = S, O or N. ^{*e*} Defined as $\left[\int (\chi^T - \chi^E)k^3 dk / \int (\chi^E k^3 dk)\right] \times 100$ (where T is theoretical and E is experimental). ^{*f*} Ef, the difference calculated between the calculated Fermi level energy and the theoretically known values for the element.

Table 4Summary of the results of ethylene trimerisation, oligomerisation and polymerisation using $[CrCl_3(L)]$ ($L = L^1 - L^6$) activated with MMAO

Complex	T∕°C	C ₆ (wt%)	$1-C_{6}^{a}$ (wt%)	C ₈ -C ₂₂ (wt%)	Productivity ^c /g g(Cr) ⁻¹	PE/G	PE (wt%)
$[CrCl_3(L^1)]$	80	71.8	99.4	27.1	3165	0.05	1.0
$[CrCl_3(L^2)]$	80	b	b	b	2295	3.58	
$[CrCl_3(L^3)]$	80	b	b	b	31089	48.5	
$[CrCl_3(L^4)]$	80	b	b	b	8827	13.77	_
$[CrCl_3(L^5)]$	90	15.7	92.8	63.8	5804	0.76	8.4
$[CrCl_3(L^6)]$	90	14.9	89.6	63.2	3168	0.53	10.6

^{*a*} Selectivity for 1-hexene as a percentage of total C_6 fraction. ^{*b*} Any liquid phase was absorbed by the polymer and not analyzed further. ^{*c*} Note that the productivity reported is not necessarily a true reflection of the stability of the catalyst as they were stopped after 30 minutes, calculation of the productivity based on a wt/wt basis (polymer/chromium).

The [CrCl₃(L)] complexes exhibit moderate to high activities for ethylene oligomerisation and polymerisation. The products obtained using [CrCl₃(L⁵)] and [CrCl₃(L⁶)] are comprised of oligomers with a distribution that closely resembles Schulz–Flory rules.³²⁻³⁴ The weight of C₈–C₂₂ fractions was used to calculate the Schulz–Flory distribution coefficient β by fitting the following simplified Schulz–Flory equation:

$$\chi_{\rho} = \beta/(1+\beta)^{\rho}$$
 where $\chi_{\rho} =$ mole fraction of $C_{2\rho+2}$ olefin.

Calculation of the β factor for [CrCl₃(L⁵)] and [CrCl₃(L⁶)] gave values of 0.68 and 0.70 respectively, which are comparable with literature values for related compounds.³⁵

Complexes containing N–H groups generally show relatively high catalytic activity compared with other analogues. However, this does not apply for $[CrCl_3(L^5)]$, leading to the suggestion that the stereochemistry of the complex might also significantly influence the catalytic activity and selectivity.

Surprisingly, the thioether complex $[CrCl_3(L^1)]$ gave an active and selective catalyst for the trimerisation of ethylene to 1-hexene, although the catalyst was active only for a few minutes (probably due to the loss of the thioether ligand, *vide infra*). This is the first example of a *fac*-CrCl₃ complex bearing a simple trithioether ligand showing such activity. The catalyst based upon $[CrCl_3(L^2)]$, containing the mixed S/O-donor ligand gave no evidence for C₆ formation. Complexes $[CrCl_3(L^3)]$ and $[CrCl_3(L^4)]$ showed significant polymerisation activity, with the butyl derivative giving higher productivity under the same catalytic conditions.

To investigate the first stage of activation of these complexes, we have followed the reaction with Me₃Al by UV-visible spectroscopy. To a freshly prepared 5 mM toluene solution of $[CrCl_3(L)]$ was added five mol. equivs. of Me₃Al and UV-visible spectra were recorded after ~one minute. Excess Me₃Al was used to allow for possible multiple substitution of the Cl atoms by Me groups. Fig. 2 shows typical UV-visible spectra for a complex in solution under these conditions.

Addition of Me₃Al causes an immediate change in the colour of the solution from purple to yellow/green. The UV-visible spectrum shows a change from two bands to one, the latter at different energy (Table 5). Either a blue shift is occurring as the chlorine ligands are substituted by methyl groups in Cr(III) species and the peak corresponding to v_2 is obscured by the charge transfer bands, and/or substitution of the chlorine atoms by methyl groups is accompanied by a change in oxidation state at the chromium. The latter would lend support to a Cr(II)/(IV) redox cycle. **Table 5** Selected UV-visible spectroscopic data for a 5 mM toluene solution of $[CrCl_3(L)]$ ($L = L^1 - L^6$) before and after treatment with 5 mol. equivs. of Me₃Al (ν_1 corresponds to the lowest energy transition in each case)

Complex	v_1^a/cm^{-1}	v_1^{b}/cm^{-1}
$[CrCl_3(L^1)]$	14 300	16015
$[CrCl_3(L^2)]$	13960	16795
$[CrCl_3(L^3)]$	14 400	16990
$[CrCl_3(L^4)]$	14 390	16865
$[CrCl_3(L^5)]$	16840	17450
$[CrCl_3(L^6)]$	16800	17 375

" Before treatment.	^b After treatment	with 5 mol.	equivs.	of Me ₃ Al.
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Fig. 2 UV-visible spectra of a 5 mM toluene solution of [CrCl₃(L³)] before (red) and after (black) treatment with five mol. equivs. of Me₃Al.

EPR studies

The reactions between $[CrCl_3(L)] (L = L^1 - L^6)$ and Me₃Al have also been studied by EPR spectroscopy. Q- and K-band EPR spectra were recorded for the complexes in a frozen toluene–CH₂Cl₂ glass at 115 K. A broad isotropic signal characteristic for paramagnetic d³ systems was observed for all the chromium(III) complexes, with g values of ~1.99, as expected for Cr(III).

Addition of three mol. equivs. of Me_3Al to a CH_2Cl_2 -toluene solution of the parent Cr(III) complex and quenching to 77 K leads to significant diminution of the strong isotropic d³ signal, giving an EPR silent species in each case (Fig. 3), consistent with a change in the oxidation state from Cr(III) to either Cr(II) or Cr(IV). Addition of excess (30 mol. equivs.) Me_3Al led to complete loss of the EPR resonance in all cases.



Fig. 3 EPR spectra (Q-band) of $[CrCl_3(L^6)]$ in toluene–CH₂Cl₂ before (blue) and after (red) treatment with three mol. equivs. of Me₃Al (115 K), g = 1.98.

XAFS studies on Cr complexes with added Me₃Al

The Cr K-edge EXAFS data for $[CrCl_3(L)]$ (L = L¹–L⁴) after treatment with 30 mol. equivs. of Me₃Al (excess) in toluene are presented in Fig. 4 and Table 6. The analysis for the activated systems shows a first coordination shell of on average three C atoms at ~2.1 Å. A second shell was modelled satisfactorily by ~0.3 S atoms, giving d(Cr-C) = 2.07 Å and d(Cr-S) = 2.44 Å. These results are consistent with substitution of all of the Cl atoms by Me groups upon addition of Me₃Al. It is also clear that the neutral S- and S/O-donor ligands substantially dissociate after addition of Me₃Al, leaving on average one S atom coordinated to Cr in \sim one third of the molecules.

We have also used XANES spectroscopy to investigate the absorption edge features for $[CrCl_3(L)]$ ($L = L^1-L^4$) before and after addition of excess (30 equiv.) Me₃Al (Fig. 5 displays the XANES for $[CrCl_3(L^1)]$ and $[CrCl_3(L^3)]$). It is clear from the spectra that significant changes in edge position and shape occur. Moreover, the energy shift of the absorption edge upon addition of AlMe₃ is negative for compounds containing L¹ and L², whereas the energy shift is positive for compounds containing L³ and L⁴. In our previous work we have demonstrated that significant changes within the XANES region can result from changes in oxidation state, coordination number, ligand donor type and geometry.³⁶ Hence, it is not possible at this stage to make definitive assignments on the basis of these spectra alone. Further experimental work and theoretical modelling are required to determine how the individual factors influence the XANES in these types of compounds.

Conclusions

A range of new Cr(III) complexes with various neutral tridentate N-, S- and O-donor ligands has been investigated using IR,

Table 6 Cr K-edge k^3 -weighted EXAFS structural data for 5 mM toluene solutions of [CrCl₃(L)] (L = L¹-L⁴) treated with an excess of Me₃Al

Complex	C.N. C	d(Cr–C)/Å	$2\sigma^2/\text{\AA}^2$	C.N. S	d(Cr–S)/Å	$2\sigma^2/\text{\AA}^2$	R (%)	FI	<i>E</i> f/eV
$\begin{array}{l} [CrCl_{3}(L^{1})] \\ [CrCl_{3}(L^{2})] \\ [CrCl_{3}(L^{3})] \\ [CrCl_{3}(L^{4})] \end{array}$	3.0(2)	2.07(7)	0.011(4)	0.3(3)	2.44(5)	0.007(1)	37.6	11.0	-3.1(8)
	2.6(4)	2.11(6)	0.015(1)	0.5(1)	2.47(2)	0.009(4)	39.8	10.4	-2.0(9)
	2.8(5)	2.09(3)	0.011(9)	0.3(7)	2.44(3)	0.003(4)	36.2	11.2	-8.2(1)
	2.9(7)	2.06(4)	0.013(1)	0.2(3)	2.40(7)	0.006(1)	36.7	12.4	-4.6(5)



Fig. 4 The Cr K-edge k^3 -weighted EXAFS, Fourier transform and sine transform for a 5 mM toluene solution of $[CrCl_3(L^1)]$ treated with an excess (30 mol. equivs.) of Me₃Al at room temperature.



Fig. 5 Normalized X-ray absorption data for [CrCl₃(L)]; 5 mM in toluene solution (solid black line) and with excess Me₃Al (30 mol. equivs.) (dashed line). (a) $L = L^1$; (b) $L = L^3$.

UV-visible and EPR spectroscopy along with cyclic voltammetry and XAFS studies. Treatment of these compounds with MMAO led to catalytically active species; the catalytic activity towards ethylene trimerisation, oligomerisation and polymerisation shows significant dependence upon the ligand donor set. Of the trithioether ligand complexes only $[CrCl_3(L^1)]$ with the facultative S–S– S donor set is active towards selective trimerisation of ethylene. Substitution of the central S-donor by oxygen suppresses this activity whilst allowing some polymerisation. The activated solutions of the complexes containing the tripod S_3 donor ligands (L³ and L⁴) produced polymer with MMAO co-catalyst. In contrast, the complexes containing the hard N₃-donor ligands ($L = L^5$ or L6) produced a Schulz-Flory distribution of oligomers and each exhibited an electronic transition at ~ 17400 cm⁻¹ after treatment with Me₃Al (*cf.* \sim 16 600 cm⁻¹ for the S-based ligand complexes), suggesting a subtly different ligand environment is present in these systems with retention of some N-donor ligand coordination. Further experiments to investigate this are underway.

The UV-visible and EPR measurements suggest that a change in the oxidation state of the Cr centre occurs in all cases upon addition of excess Me₃Al, plausibly to EPR silent Cr(II). Investigation of the partial structure of the active species has been achieved using XAFS spectroscopy. Treatment of the Cr(III) complexes with excess Me₃Al leads to substitution of the Cl ligands by Me groups and substantial dissociation of the ligands L^1-L^4 from the metal centre. However, the nature of structural changes responsible for the difference in catalytic activity between L^1 and L^2-L^4 remains unclear at present. One limitation of the EXAFS experiments described here is the relatively long time-scale for data acquisition (presently ~1–3 h) due to the need to use dilute solutions and the low energy of the Cr edge being investigated. Experiments to elucidate these structural differences and to trap the early intermediates in the catalysis are being developed in our laboratories.

Experimental

All procedures involving air sensitive materials were performed under an inert atmosphere of N_2 and using standard Schlenk techniques. Solvents were dried using standard techniques and distilled under nitrogen prior to use or stored in Young's ampoules over dry molecular sieves under nitrogen. Unless stated, commercial reagents were used as received from Aldrich. ¹H and ${}^{13}C{}^{1}H$ NMR spectra were recorded on a Bruker AV300 spectrometer and were referenced internally from the residual protio solvent (1H) or the signals of the solvent (13C). Mass spectra were on electrospray mode (positive or negative) using a VG Biotech Platform. Microanalyses were obtained from the University of Strathclyde microanalytical service and from the London Metropolitan University elemental analysis service. Infrared spectra were recorded as Nujol mull between CsI plates, using a Perkin Elmer 983 IR spectrometer over the range 4000-180 cm⁻¹. UV-visible spectra were recorded on a Perkin Elmer Lambda 19 spectrometer in toluene or CH₂Cl₂ solutions or by diffuse reflectance. EPR spectra were obtained from the EPSRC National EPR Service, University of Manchester. K-band (~24.0 GHz) and Q-band (~34.00 GHz) spectra were recorded using an ESP 300 spectrometer. Cyclic voltammetry measurements were performed using an Eco Chemie PGSTAT20. Platinum beads were used as both working and auxiliary electrodes and a calomel reference electrode was used with 0.2 M tetrabutylammonium tetrafluoroborate [Buⁿ₄N]BF₄ as base electrolyte. All experiments were performed in degassed CH₂Cl₂ and standardised against the ferrocene/ferrocenium couple. The Cr K-edge XAFS measurements were performed at station BM26A (DUBBLE) at the European Synchrotron Radiation Facility in Grenoble, France.³⁷ Data were collected in transmission mode from samples diluted with boron nitride and in fluorescence mode (using a 9 element germanium detector from Ortec, with XPRESS signal processing³⁸) from 5 mM toluene solutions. For the Me₃Alactivated species the solutions were prepared in a Schlenk tube under rigorously anhydrous conditions. The reaction mixture was stirred for ~ 30 s after addition of Me₃Al and then transferred to the dry, N₂-purged XAFS cell for data collection. The spectra were calibrated using a Cr foil, using the 1st maximum of the 1st derivative at 5989.0 eV. Background subtraction utilized the program PAXAS³⁹ and EXAFS analysis employed the spherical wave code EXCURV98.40 The ligands L1-L6 were prepared using modified literature procedures.23-26

Procedure for catalysis

The reactor was prepared by filling/venting with ethylene (5 \times 10 bar). Toluene (100 mL) or methylcyclohexane (80 mL) was added and the reactor heated to 80 °C or 90 °C. To activate the

complexes [CrCl₃(L)], MMAO (1.9 M in heptane) was added to the complexes previously dissolved in toluene. The solution was mixed and immediately added to the reactor. Ethylene (40 bar) was added and fed as required to maintain a constant pressure. The reactor was allowed to run until ethylene uptake ceased. The reactor was then cooled with ice to ~10 °C and the ethylene slowly vented. Nonane (1000 μ L) was added followed by MeOH and HCl (10%) to destroy the MMAO. The reactor was opened and the polymer collected, dried, weighed and when possible a liquid fraction was collected for GC analysis.

Preparations

 $S(CH_2CH_2SC_{10}H_{21})_2$ (L¹). Bis(2-mercaptoethyl)sulfide (7.16 g, 46.0 mmol) was dissolved in EtOH (200 mL) under N₂, and sodium (2.14 g, 93.0 mmol) was added in small pieces. When the sodium had dissolved the mixture was heated to reflux and 1-iododecane (25.0 g, 93.0 mmol) added dropwise. The EtOH was removed in vacuo and water (35 mL) was added. The mixture was extracted with Et₂O (3 \times 35 mL) and the organic extracts were dried (MgSO₄), filtered, and the solvent was removed in vacuo to afford the ligand as a white solid. Yield: 16.28 g, 80%. Mp: 54.5–55.5 °C. ¹H NMR (CDCl₃): δ 0.88 (t, 6H, $CH_{3}C_{9}H_{18}S_{-}$, 1.26 (s, 28H, $CH_{3}C_{7}H_{14}C_{2}H_{4}S_{-}$), 1.58–2.54 (m, 8H, $C_8H_{17}CH_2CH_2S$ -), 2.74 (m, 8H, $C_{10}H_{21}SC_2H_4S$ -). ¹³C{¹H} NMR (CDCl₃): δ 14.25 (CH₃C₉H₁₈S-), 22.81 (CH₃CH₂C₈H₁₆S-), 28.88, 29.04, 29.38, 29.45, 29.67, 29.70, 29.88 (C₂H₅C₇H₁₄CH₂S-), 32.0, 32.48 ($C_9H_{19}CH_2SCH_2CH_2S$). Calculated for $C_{24}H_{50}S_3$: C, 66.36; H, 11.52; S, 22.12; found C, 66.25; H 11.60; S, 22.19%.

 $O(CH_2CH_2SC_{10}H_{21})_2$ (L²). To a solution of bis(2-chloroethyl)ether (3.42 g, 24.0 mmol) in EtOH (250 mL) was added NaOH (2.868 g, 1.25 mol). 1-Decanethiol (8.35 g, 48.0 mmol) was added dropwise and the mixture refluxed for 4 h under N_2 . The solvent was then removed in vacuo and water (35 mL) was added to the remaining oil. The mixture was extracted with diethyl ether (3 \times 35 mL). The organic extracts were dried (MgSO₄), filtered and the solvent was removed in vacuo to afford a colourless oil that crystallised upon standing at room temperature. Yield: 8.1 g, 81%. ¹H NMR (CDCl₃): δ 0.80 (t, 6H, CH₃C₉H₁₈S-), 1.17 (m, 28H, CH₃C₇H₁₄C₂H₄S), 1.56-2.46 $(m, 8H, C_8H_9CH_2CH_2S-), 2.63 (t, 4H, C_{10}H_{21}SCH_2CH_2O-), 3.55$ (t, 4H, $C_{10}H_{21}SCH_2CH_2O_{-}$). ¹³C{¹H} NMR (CDCl₃): δ 14.48 $(CH_{3}C_{9}H_{18}S-)$, 23.06 $(CH_{3}CH_{2}C_{8}H_{16}S-)$, 29.28, 29.65, 29.70, 29.95, 30.22, 31.93, 32.29, 33.10 (C₂H₅C₈H₁₆SCH₂CH₂O–), 71.16 (C10H21SCH2CH2O-). Calculated for C24H50OS2: C, 68.83; H, 12.03; found C, 68.78; H, 12.00%.

MeC(CH₂SⁿC₄H₉)₃ (L³). Ammonia (100 mL) was condensed onto dry, degassed THF (100 mL) in a 1 L flask equipped with a condenser and using a Me₂CO/CO₂ slush bath (-78 °C). A small piece of solid Na was added to the mixture, leading to a dark blue solution. (ⁿC₄H₉)₂S₂ (12.82 g, 72.0 mmol) was added slowly to produce a creamy white mixture. The remaining Na (3.31 g, 0.144 mol) was added slowly in small pieces and the NH₃ was then allowed to evaporate. The mixture was concentrated *in vacuo* to remove the THF. A mixture of ethanol and MeC(CH₂Br)₃ (7.34 g, 24.0 mmol) was added dropwise to the Na⁺S(ⁿC₄H₉)⁻ first diluted with 150 mL of ethanol. The resulting mixture was refluxed for 70 h under nitrogen. The grey reaction mixture was cooled, filtered and the filtrate concentrated *in vacuo* and was washed with a saturated NaHCO₃ solution. Diethyl ether (50 mL) was added and the aqueous layer was extracted. The organic layer was dried (MgSO₄), filtered and the solvent was removed *in vacuo* to afford a clear orange oil which was distilled (80 °C; 0.5 mm Hg). Yield: 4.1 g, 51%. ¹H NMR (CDCl₃): δ 0.89 (t, 9H, CH₃C₃H₆S–), 1.06 (s, 3H, CH₃C), 1.35 (m, 6H, CH₃CH₂C₂H₄S), 1.55 (m, 6H, C₂H₅CH₂CH₂S–), 2.51 (t, 6H, C₃H₇CH₂S), 2.63 (s, 6H, C₄H₉SCH₂). ¹³C{¹H} NMR (CDCl₃): δ 13.66 (CH₃C₃H₆S–), 21.95 (CH₃CH₂C₂H₄S–), 23.80 (CH₃C), 32.03 (C₂H₅CH₂CH₂S–), 33.82 (C₃H₇CH₂S), 38.88 (CH₃C), 41.84 (C₄H₉SCH₂). Calculated for C₁₇H₃G₃: C, 60.65; H, 10.78; found C, 60.56; H, 10.81%. HRMS analysis (ESI): *m/z* calculated [M + H]⁺: 336.1981; found: 336.1979.

 $MeC(CH_2SC_{10}H_{21})_3$ (L⁴). $MeC(CH_2Br)_3$ (4.0 g, 13.0 mmol) was dissolved in EtOH (200 mL) and NaOH (2.1 g, 52.0 mmol) was added to the mixture. Decanethiol (7.5 g, 43.0 mmol) was added dropwise over a period of 30 min and the resulting mixture was refluxed under N₂ for 24 h. The resulting mixture was cooled, filtered and the filtrate was washed with saturated NaHCO₃ solution (30 mL). The aqueous layer was then extracted with diethyl ether $(3 \times 50 \text{ mL})$. The organic layer was dried (MgSO₄), filtered and the solvent was removed in vacuo to afford an orange oil. Yield: 2.75 g, 36%. ¹H NMR (CDCl₃): δ 0.90 (t, 9H, CH₃C₉H₁₈S–), 1.08 (s, 3H, CH₃C), 1.29 (m, 42H, CH₃C₇ H_{14} C₂H₄S–), 1.62 (m, 6H, C₈H₁₇CH₂CH₂S-), 2.52 (t, 6H, C₉H₁₉CH₂S-), 2.60 (s, 6H, $C_{10}H_{21}SCH_2$). ¹³C{¹H} NMR (CDCl₃): δ 14.07 (CH₃C₉H₁₈S–), 22.66 (CH₃CH₂C₈H₁₆S-), 23.80 (CH₃C), 29.00, 29.26, 29.30, 29.54, 29.96 (C₃H₇C₅H₁₀C₂H₄S-), 30.83 (C₈H₁₇CH₂CH₂S-), 31.89 (C₂H₅CH₂C₇H₁₄S-), 34.06 (C₉H₁₉CH₂S-), 40.75 (CH₃C), 41.84 $(C_{10}H_{21}SCH_2)$. HRMS analysis (ESI): m/z calculated $[M + H]^+$: 588.4796; found: 588.4789.

1-Decyl-1,4,7-triazacyclononane $(C_{10}H_{21})$ [9]aneN₃ (L⁵). Decanoyl chloride (2.01 g, 10 mmol) was added dropwise at room temperature to a stirred solution containing 1,4,7triazacyclononane-1,4-dicarboxylic acid di-tert-butyl ester (3.15 g, 9.60 mmol) and triethylamine (2.7 mL) in distilled CH₂Cl₂ (100 mL). The solution was left to stir overnight under N_2 and then washed with water $(3 \times 30 \text{ mL})$; the organic layer was dried (MgSO₄), filtered and the CH₂Cl₂ was removed. The intermediate 1,4,7-tri(nonylcarbonyl)-1,4,7-triazacyclononane was obtained as a pale yellow oil. Yield: 1.96 g, 69%. ¹H NMR (CDCl₃): δ 0.94 (t, 3H, CH₃C₈H₁₆CON-), 1.25-1.30 (m, 12H, CH₃C₆H₁₂CH₂CON-), 1.32–1.65 (m, 20H, C(CH₃)₃ and C₇H₁₅CH₂CON–), 2.22–2.39 (m, 4H, [9]aneN₃ ring), 3.10–3.35 (m, 4H, [9]aneN₃ ring), 3.43– 3.6 (m, 4H, [9]aneN₃ ring). ${}^{13}C{}^{1}H$ NMR (CDCl₃): δ 14.07 (CH₃C₈H₁₆CON-), 22.63, 24.22, 25.35, 28.85, 29.25, 29.47, 31.85, 33.40, 35.28, 48.18, 49.67, 52.94 ([9]aneN3 ring and CH₃C₈H₁₆CON-), 155.36 (C=O BOC), 173.13 (C₉H₁₉CON-). Electrospray MS (CH₂Cl₂): m/z = 484 ((C₉H₁₉CO)-diBOC- $[9]aneN_3 + H)^+$.

The amide ($C_9H_{19}CO$)-diBOC-[9]aneN₃ (3.30 g, 6.83 mmol) was dissolved in dry THF (50 mL); a solution of BH₃THF (48 mL) was added, and the mixture was refluxed overnight under N₂. After cooling to room temperature, the excess BH₃THF was quenched by slow addition of methanol, and the colourless solution was evaporated to leave a colourless oil. This was dissolved in 1-butanol (50 mL), water (50 mL), and concentrated HCl (80 mL)

and refluxed overnight. After the mixture was cooled, sodium hydroxide was added until pH > 12, and the product was extracted with CH₂Cl₂ (6 × 50 mL). The combined organic extracts were dried (MgSO₄), filtered and evaporated *in vacuo* to give the desired product as an orange oil. Yield: 0.9 g, 49%. ¹H NMR (CDCl₃): δ 0.95 (t, 3H, CH₃C₉H₁₈N–), 1.12–1.65 (m, 16H, CH₃C₈H₁₆CH₂N–), 2.38–2.55 (m, 2H, C₉H₁₉CH₂N–), 2.56–2.75 (m, 4H, [9]aneN₃ ring), 2.78–3.04 (m, 8H, [9]aneN₃ ring). ¹³C{¹H} NMR (CDCl₃): δ 14.08 (CH₃C₉H₁₈N), 22.66, 27.23, 27.31, 29.28–29.56 (C₃H₇C₄H₈C₃H₆N–), 31.87 (CH₃C₈H₁₆CH₂N–), 43.15, 44.72 ([9]aneN₃ ring), 49.78 (C₉H₁₉CH₂N–), 56.55 ([9]aneN₃ ring). Electrospray MS (CH₂Cl₂): *m/z* = 270 ((C₁₀H₂₁)[9]aneN₃ + H)⁺. Calculated for C₁₆H₃₅N₃: C, 71.31; H, 13.09; N, 15.59; found C, 71.24; H, 12.90; N, 15.50%.

1,4,7-Tris(decyl)-1,4,7-triazacyclononane $(C_{10}H_{21})_{3}[9]aneN_{3}$ (L6). Decanoyl chloride (4.87 g, 25.0 mmol) was added dropwise at room temperature to a stirred solution containing 1,4,7-triazacyclononane (1.0 g, 7.75 mmol) and NEt₃ (6.5 mL, 46.6 mmol) in distilled CH₂Cl₂ (100 mL). The solution was left to stir overnight under N₂ and then washed with water $(3 \times 30 \text{ mL})$; the organic layer was dried (MgSO₄), filtered and the CH₂Cl₂ was removed. The intermediate 1,4,7-tris(nonylcarbonyl)-1,4,7triazacyclononane was obtained as a pale yellow solid. Yield: 3.47 g, 76%. ¹H NMR (CDCl₃): δ 0.8 (t, 9H, CH₃C₈H₁₆CON–), 1.19 (m, 36H, $CH_3C_6H_{12}C_2H_4CON_{-}$), 1.53 (m, 6H, C₇H₁₅CH₂CH₂CON-), 2.19 (m, 6H, C₇H₁₅CH₂CH₂CON-), 3.32 (s, 6H, $[9]aneN_3$ ring), 3.61 (s, 6H, $[9]aneN_3$ ring). ¹³C{¹H} NMR (CDCl₃): δ 14.01 (CH₃C₈H₁₆CON–), 22.58 (CH₃CH₂C₇H₁₄CON-), 25.20 (C₇H₁₅CH₂CH₂CON-), 29.44-29.46 ($C_3H_7C_4H_8C_2H_4CON_-$), 31.79 ($C_2H_5CH_2C_6H_{12}CON_-$), 33.16 ($C_8H_{17}CH_2CON_{-}$), 49.16, 51.05 ([9]aneN₃ ring), 174.35 (C=O). Electrospray MS (CH₂Cl₂): m/z = 592.5 $((C_9H_{19}CO)_3[9]aneN_3 + H)^+$. IR: $v(C=O) = 1637 \text{ cm}^{-1}$.

The triamide $((C_9H_{19}CO)_3[9]aneN_3)$ (3.30 g, 5.58 mmol) was dissolved in dry THF (50 mL); a solution of BH₃THF (39 mL) was added, and the mixture was refluxed overnight under a dinitrogen atmosphere. After being allowed to cool at room temperature, the excess BH₃THF was quenched by slow addition of methanol, and the colourless solution was evaporated to leave a colourless oil. This was dissolved in 1-butanol (50 mL), water (50 mL), and concentrated HCl (80 mL) and refluxed overnight. After the mixture was cooled, NaOH was added until pH > 12, and the product was extracted with CH_2Cl_2 (6 × 50 mL). The combined organic extracts were dried (MgSO₄), filtered and the solvent evaporated in vacuo to give the desired product as a pale yellow oil. Yield: 2.30 g, 75%. ¹H NMR (CDCl₃): δ 0.88 (t, 12H, $CH_3C_9H_{18}N_{-}$), 1.26–1.43 (m, 48H, $CH_3C_8H_{16}CH_2N_{-}$), 2.45 (t, 6H, $C_9H_{19}CH_2N_{-}$), 2.73 (s, 12H, [9]aneN₃ ring). ¹³C{¹H} NMR (CDCl₃): δ 14.08 (CH₃C₉H₁₈N–), 22.67, 27.60, 28.05, 29.33, 29.61–29.68, 31.91 ($CH_3C_8H_{16}CH_2N_{-}$), 59.00 ($C_9H_{19}CH_2N_{-}$), 55.88 ([9]aneN₃ ring). Electrospray MS (CH₂Cl₂): m/z = 550.7 $((C_{10}H_{21})_{3}[9]aneN_{3} + H)^{+}$. Calculated for $C_{36}H_{75}N_{3}$: C, 78.62; H, 13.74; N, 7.64; found C, 78.53; H, 13.69; N, 7.50%.

[CrCl₃(L¹)]. L¹ (0.50 g, 1.15 mmol) previously dissolved in a minimum volume of CH_2Cl_2 was added to a solution of [CrCl₃(THF)₃] (0.43 g, 1.15 mmol) in dried and degassed CH_2Cl_2 (15 mL). The resulting mixture was stirred at room temperature under nitrogen for 1 h. The solvent was then removed *in vacuo* to

afford a purple solid which was washed with a minimum amount of hexane and dried *in vacuo*. Yield: 1.02 g, 67%. UV-visible (DR): 517, 699 nm. Calculated for $C_{24}H_{50}Cl_3CrS_3$: C, 48.59; H, 8.50; S, 16.22; found C, 48.55; H, 8.52; S, 16.22%.

[CrCl₃(L²)]. Method as above to give a green solid. Yield: 71%. UV-visible (DR): 716, 475 nm. Calculated for $C_{24}H_{50}Cl_3CrOS_2$: C, 49.95; H, 8.73; found: C, 49.87; H, 8.77%.

[CrCl₃(L³)]. Method as above to give a purple solid. Yield: 75%. UV-visible (DR): 694, 492 nm. Calculated for $C_{17}H_{36}Cl_3CrS_3$: C, 41.25; H, 7.33; found: C, 41.17; H, 7.35%.

[CrCl₃(L⁴)]. Method as above to give a dark purple solid. Yield: 76%. UV-visible (DR): 695, 493 nm. Calculated for $C_{35}H_{72}Cl_3CrS_3$: C, 56.24; H, 9.71; found: C, 56.36; H, 9.76%.

[CrCl₃(L⁵)]. Method as above to give a dark purple solid. Yield: 70%. UV-visible (DR): 594, 485 nm. Calculated for $C_{16}H_{35}Cl_3CrN_3$: C, 44.92; H, 8.25; N, 9.82; found: C, 44.82; H, 8.27; N, 9.76%.

[CrCl₃(L⁶)]. Method as above to give a brown oil. Yield: 48%. UV-visible (DR): 595, 459 nm. Calculated for $C_{36}H_{75}Cl_3CrN_3$: C, 61.04; H, 10.67; N, 5.93; found: C, 61.13; H, 10.75; N, 5.88%.

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