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Hard–soft interactions in early transition-metal thioether macrocyclic chemistry: spectroscopic and extended X-ray absorption fine structure studies on chromium(III) thioether complexes

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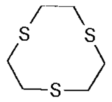
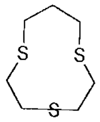
A series of chromium(III) thioether macrocyclic complexes of the form [CrX$_3$([9]aneS$_3$)], [CrX$_3$([10]aneS$_3$)], [(CrX$_3$)$_2$(μ-[18]aneS$_6$)] (X = Cl or Br), [CrX$_2$(14]aneS$_4$)]PF$_6$ and [CrX$_2$([16]aneS$_4$)]PF$_6$ (X = Cl, Br or I) ([9]aneS$_3$ = 1,4,7-trithiacyclononane, [10]aneS$_3$ = 1,4,7-trithiacyclodecane, [18]aneS$_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane, [14]aneS$_4$ = 1,4,8,11-tetrathiacyclotetradecane, [16]aneS$_4$ = 1,5,9,13-tetrathiacyclohexadecane) has been prepared and characterised by IR and UV/VIS spectroscopy, microanalyses, and in some cases electrospray mass spectrometry. Chromium K-edge extended X-ray absorption fine structure studies have provided information on the Cr–X and Cr–S bond-length distributions in a selection of these compounds, and these, together with the relatively low *Dq* values derived from UV/VIS spectroscopy, confirm rather weak chromium(III)–thioether interactions in these unusual species involving hard metal and soft ligand combinations.

In contrast to the vast number of chromium(III) complexes with hard nitrogen- and oxygen-donor ligands,[1] there are very few examples of complexes with soft donor ligands such as phosphines[2–5] or thioethers.[6–9] This is principally due to the severe incompatibility of the hard chromium(III) centre with the soft phosphine or thioether functions.

Thioether macrocycles have been intensively studied in recent years since the ability of these ligands to stabilise unusual oxidation states and co-ordination geometries was noted. Notably, however, to date thioether macrocyclic chemistry has been dominated by middle and late d- and p-block ions.[10] Most significantly, it has been noted that while acyclic thioethers act as relatively poor ligands to metal ions, when the thioether functions are included within a macrocyclic framework they tend to co-ordinate much more readily often to yield quite stable complexes. We have become interested in the possibility of utilising the additional stability characteristic of macrocyclic complexes to stabilise metal/ligand combinations which are usually considered incompatible. In this context we have been investigating the reactions of Cr^{III} with various thioether macrocycles to determine whether the incorporation of macrocyclic environments would render such hard–soft interactions more accessible and to establish the nature of the S (thioether) to Cr^{III} interaction. A few examples of macrocyclic thioether complexes of early transition-metal ions have been reported. These include carbonyl derivatives of Mo^0 and W^0,[11,12] [MoCl$_3$([9]aneS$_3$)] ([9]aneS$_3$ = 1,4,7-trithiacyclononane),[12] the metal(II) species [MI(CO)$_3$([9]aneS$_3$)]$^+$ (M = Mo or W),[13] [CrCl$_3$([9]aneS$_3$)], [Cr(SO$_3$CF$_3$)$_3$([9]aneS$_3$)][7] and some examples with the formula [CrCl$_3$L] (L = S$_4$, S$_5$ or S$_6$ donor macrocycle) which are thought to involve tridentate co-ordination.[8] The crystal structure of the vanadium(IV) species [VOCl$_2$([9]aneS$_3$)] has also been reported, and shows *fac* tridentate [9]aneS$_3$ ligation, giving V–S (*trans* to O) 2.634(5), (*trans* to Cl) 2.470(5) (mean), V–Cl 2.295(5) (mean) and V–O 1.579(4) Å.[14] Very recently we have also reported the synthesis and crystal structure of the corresponding vanadium(III) species [VCl$_3$([9]aneS$_3$)] which also involves *fac* tridentate [9]aneS$_3$ co-ordination, giving V–S 2.486(3), 2.515(2), 2.500(2), V–Cl 2.279(3), 2.310(3), 2.281(3) Å.[15] The only structurally characterised examples of chromium(III) thioether macrocyclic species are [CrCl$_3$([18]aneS$_6$)] ([18]aneS$_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane) which involves *fac* tridentate co-ordination of the hexathia crown to Cr^{III}, leaving three free thioether donors (see text below)[8] and *cis*-[CrCl$_2$([14]aneS$_4$)]PF$_6$ ([14]aneS$_4$ = 1,4,8,11-tetrathiacyclotetradecane), the structure of which we have reported, involving S$_4$Cl$_2$ co-ordination at Cr^{III} with Cr–S 2.393(1), 2.407(2), Cr–Cl 2.295(1) Å.[9] We now report the preparation and spectroscopic characterisation of a series of chromium(III) thioether macrocyclic complexes incorporating [9]aneS$_3$, [10]aneS$_3$ (1,4,7-trithiacyclodecane), [14]aneS$_4$, [16]aneS$_4$ (1,5,9,13-tetrathiacyclohexadecane) and [18]aneS$_6$, together with chromium K-edge extended X-ray absorption fine structure (EXAFS) studies on selected examples.



[9]aneS$_3$



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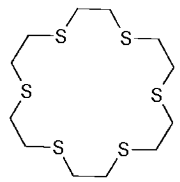

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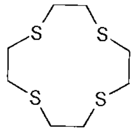

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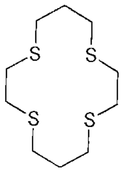
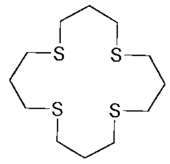


[14]aneS$_4$



[16]aneS$_4$

Results and Discussion

Reaction of [CrX$_3$(thf)$_3$] (X = Cl or Br, thf = tetrahydrofuran) with [9]aneS$_3$ or [10]aneS$_3$ in a 1:1 molar ratio in CH$_2$Cl$_2$ solution gives the products [CrX$_3$([9]aneS$_3$)] or [CrX$_3$([10]aneS$_3$)] as powdered solids in high yield. Similarly, using [CrX$_3$(thf)$_3$] and [18]aneS$_6$ in a 2:1 molar ratio yields the binuclear species [(CrX$_3$)$_2$(μ-[18]aneS$_6$)]. We found that in order to promote co-ordination through the thioether donors it was necessary to remove the thf from the reaction mixture, otherwise the harder O-donor thf ligand would bind preferentially. These neutral, highly coloured products proved to be very poorly soluble in both chlorinated and organic solvents, and attempts to dissolve them in dimethyl sulfoxide (dmso) resulted in decomposition.

They are relatively stable in the solid state when stored in a dry atmosphere, hence all were stored in an N_2-purged glove-box. The IR spectra of these species provided evidence for the presence of co-ordinated thioether, and in the case of the chloro and bromo derivatives peaks were observed in most cases in the region 200–400 cm^{-1}, which might be assigned tentatively to ν(Cr–X). However, given that in some cases these peaks were rather weak, and since ν(Cr–S) would also be expected to appear in this region, definitive assignments were not possible. Owing to their poor solubilities and sensitivity to moisture, FAB and electrospray mass spectra proved unhelpful. However, microanalytical data and UV/VIS spectroscopic data consistent with the proposed formulations were obtained in all cases.

Reaction of $[CrX_3(thf)_3]$ (X = Cl or Br) with [14]aneS_4 or [16]aneS_4 in dry $MeNO_2$ solution in the presence of 1 molar equivalent of $TlPF_6$ resulted in the formation of an intense blue-green or green solution for [14]aneS_4 and [16]aneS_4 respectively, and a white precipitate of TlCl. Following removal of the TlCl by filtration, the complexes $[CrX_2([14]aneS_4)]PF_6$ and $[CrX_2([16]aneS_4)]PF_6$ were isolated by reducing the volume of solvent to *ca.* 3 cm^3 *in vacuo* and addition of dry diethyl ether. The complexes $[CrI_2([14]aneS_4)]BF_4$ and $[CrI_2([16]aneS_4)]BF_4$ were obtained by addition of the tetrathioether macrocycle to a solution of $[Cr(thf)_6][BF_4]_3$ in dry $MeNO_2$. This precursor was generated *in situ* by treatment of $[CrCl_3(thf)_3]$ with 3 molar equivalents of $AgBF_4$ in thf solution, followed by removal of the AgCl by filtration, addition of $MeNO_2$ and removal of the thf *in vacuo.*[16] Treatment of this $MeNO_2$ solution with 2 molar equivalents of NEt_4I gave a green-brown solution from which the products were obtained by addition of diethyl ether. These cationic tetrathioether compounds are considerably more soluble than the neutral species described above, dissolving readily in dry MeCN and $MeNO_2$ and partially in dry acetone. Also, the ionic products are noticeably more sensitive to hydrolysis, especially in solution. Attempts to prepare similar cationic species using the smaller tetrathioether macrocycle [12]aneS_4 (1,4,7,10-tetrathiacyclododecane) under similar conditions were not successful, yielding only a purple insoluble product thought to be $[CrX_3([12]aneS_4)]$ involving tridentate co-ordination of the macrocycle.

The IR spectra of the cationic tetrathioether complexes confirmed the presence of PF_6^- anion [$\nu(PF_6^-)$ 840, $\delta(PF_6^-)$ 558 cm^{-1}] and co-ordinated macrocycle in each case. For X = Cl and Br the spectra also revealed weak features in the range 200–400 cm^{-1} which can tentatively be assigned to ν(Cr–X) [ν(Cr–I) is expected to occur below 200 cm^{-1}]. The fast atom bombardment (FAB) or electrospray mass spectra showed that the most intense peaks had the correct isotopic distributions at m/z = 480 corresponding to $[Cr^{79}Br^{81}Br([14]aneS_4)]^+$, 418 to $[Cr^{35}Cl_2([16]aneS_4)]^+$ and 508 to $[Cr^{79}Br^{81}Br([16]aneS_4)]^+$, as well as peaks at lower m/z due to loss of Cl or Br. No useful information was obtained from the mass spectra of the iodo derivatives, possible due to the increased sensitivity of these particular species to hydrolysis. Satisfactory microanalytical data were obtained for each of these compounds, confirming the proposed formulations.

There are very few structurally characterised examples of chromium(III) complexes involving thioether co-ordination. Gahan and co-workers[17] reported the structure of a Cr^{III}–S (thioether) complex. In their system the metal ion is encapsulated by an N_5S donor caging ligand which enforces the thioether co-ordination [Cr–S 2.399(2) Å]. Chakravorty and co-workers[18] have reported the preparation of a series of octahedral chromium(III) compounds involving $S_2N_2O_2$ chelating ligands, including a crystal structure of one example which shows d(Cr–S) = 2.417(3) and 2.445(3) Å. Both of these systems involve much harder donor sets than those of the present macrocyclic thioether complexes. Of more direct relevance to our work, the structure of the mononuclear complex $[CrCl_3([18]aneS_6)]$ which involves an S_3Cl_3 donor set has been reported, Cr–S 2.459(3), 2.442(5), 2.440(5), Cr–Cl 2.305(5), 2.279(5), 2.291(5) Å.[8] The Cr–S and Cr–Cl bond lengths compare well with those in *cis*-$[CrCl_2([14]aneS_4)]PF_6$, the structure of which we have reported, in which the geometry at Cr^{III} is a distorted octahedron, with *cis*-chloride ligands and the tetrathia macrocycle adopting a folded conformation, Cr–Cl(1) 2.295(1), Cr–S(1) 2.393(1), Cr–S(2) 2.407(2) Å.[9] We noted previously that the trend in d(M–Cl) *vs.* d(M–S) in this compound is opposite to that observed in complexes of [14]aneS_4 with late transition-metal ions. Thus, in *cis*-$[CrCl_2([14]aneS_4)]^+$ d(Cr–S) > d(Cr–Cl) (by *ca.* 0.1 Å), whereas in *cis*-$[RhCl_2([14]aneS_4)]^+$,[19] *cis*-$[IrCl_2([14]aneS_4)]^+$[20] and *cis*-$[RuCl_2([14]aneS_4)]$[21] d(M–S) < d(M–Cl) (by *ca.* 0.1 Å), suggesting rather more favourable M–S interactions in the later transition-metal complexes compared to the chromium species.

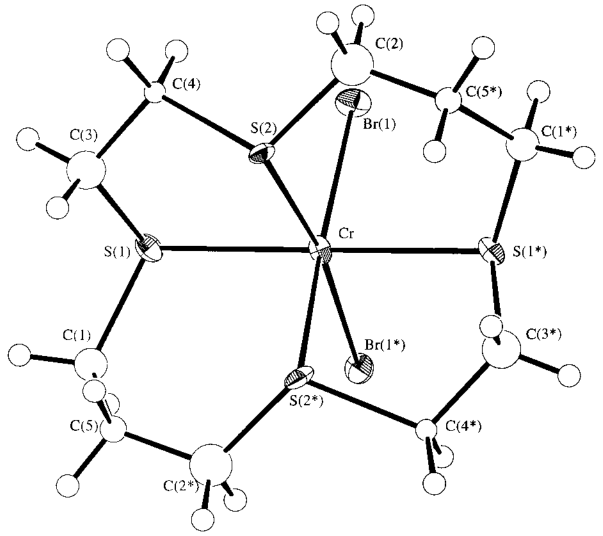


Fig. 1 View of the structure of *cis*-$[CrBr_2([14]aneS_4)]^+$ with the numbering scheme adopted (atoms marked with * are related by a crystallographic two-fold axis) [Cr–Br(1) 2.441(8), Cr–S(1) 2.41(1), Cr–S(2) 2.39(1) Å; Br(1)–Cr–Br(1*) 95.9(3), S(1)–Cr–S(1*) 179.7(8), S(1)–Cr–S(2) 84.5(4), S(1)–Cr–S(2*) 95.2(5), S(2)–Cr–S(2*) 80.5(6)°]

In an attempt to confirm the stereochemistry at the Cr^{III} single-crystal X-ray diffraction data were collected† on a small, very weakly diffracting crystal of $[CrBr_2([14]aneS_4)]PF_6$. The data were very weak and hence the final residuals rather high and it was not possible to refine the F and C atoms anisotropically due to the low data : parameters ratio. However, the analysis was sufficient to establish the stereochemistry of the $[CrBr_2([14]aneS_4)]^+$ cation. The structure of this species shows (Fig. 1) a very similar arrangement to that seen previously for $[CrCl_2([14]aneS_4)]^+$, with distorted-octahedral co-ordination at Cr^{III} *via* two mutually *cis*-bromide ligands and the four

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† $C_{10}H_{20}Br_2CrF_6PS_4$, M = 625.3, monoclinic $C2/c$, a = 10.808(3), b = 11.514(2), c = 15.879(3) Å, β = 92.71(2)°, U = 1974 $Å^3$, Z = 4, D_c = 2.104 g cm^{-3}, T = 150 K, small dark blue block, 0.30 × 0.20 × 0.10 mm, μ = 51.91 cm^{-1}, $F(000)$ = 1228. Data collection used a Rigaku AFC7S four-circle diffractometer equipped with an Oxford Systems low-temperature attachment. ω–2θ Scans; 4571 unique reflections measured ($2\theta_{max}$ = 50°), 515 with $I > 2\sigma(I)$ used in all calculations. The structure was solved by direct methods[22] and refined (based on F) using iterative cycles of full-matrix least squares[23] which revealed one half cation (with the Cr atom lying on a two-fold axis) and one half PF_6^- anion (with the P atom occupying a crystallographic inversion centre) in the asymmetric unit. At isotropic convergence the data were corrected for absorption using DIFABS[24] (maximum, minimum transmission factors = 1.000, 0.582), and the Cr, Br, P and S atoms were then refined anisotropically and H atoms included in fixed, calculated positions. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses. This model refined to R, R' = 0.089, 0.090 respectively and S = 2.23 for 71 parameters and the final Fourier-difference map showed residual electron-density peaks of 1.19 and −1.18 e $Å^{-3}$.

Table 1 Chromium K-edge EXAFS structural data[a] for chromium(III) thioether macrocyclic compounds

Complex	d(Cr–S)[b]/Å	$2\sigma^{2c}$/Å^2	d(Cr–X)[b]/Å	$2\sigma^{2c}$/Å^2	R[d]	Fit index[e]
$[CrCl_3([9]aneS_3)]$	2.396(11)	0.0121(20)	2.306(9)	0.0119(16)	22.5	2.9
$[CrBr_3([9]aneS_3)]$	2.401(4)	0.0064(14)	2.450(3)	0.0095(6)	21.2	3.5
$[CrCl_3([10]aneS_3)]$	2.361(3)	0.0076(6)	2.239(8)	0.0257(23)	20.1	3.8
cis-$[CrCl_2([14]aneS_4)]PF_6$	2.394(5) 2.40 (average)[f]	0.0199(11)	2.291(4) 2.295(1)[f]	0.0086(6)	17.8	1.9
cis-$[CrBr_2([14]aneS_4)]PF_6$	2.409(3)	0.0133(7)	2.446(1)	0.0072(2)	16.3	1.4
$[Cr_2Cl_6([18]aneS_6)]$	2.424(4)	0.0162(10)	2.291(2)	0.0094(4)	19.8	1.9
$[CrCl_3(thf)_3]$	2.009(13)[g]	0.0245(20)	2.295(4)	0.0092(41)	23.3	4.1
$[CrBr_3(thf)_3]$	1.998(4)[g]	0.0105(8)	2.458(2)	0.0110(2)	18.6	3.3

[a] Recorded in transmission mode on station 7.1 or 8.1, using powdered samples diluted with BN; AFAC (a factor compensating for the reduction in amplitude due to multi-electron processes) = 0.80 for all refinements. [b] Standard deviations in parentheses. Note that the systematic errors in bond distances arising from data collection and analysis procedures are ±0.02–0.03 Å for well defined co-ordination shells. [c] Debye–Waller factor. [d] Defined as $[\int(\chi^T - \chi^E)k^3\,dk/\int\chi^E k^3\,dk]$ (where T is theoretical and E is experimental) 100%. [e] Defined as $\Sigma i[(\chi^T - \chi^E)k_i^3]^2$. [f] X-Ray crystallographic data from ref. 9. [g] d(Cr–O).

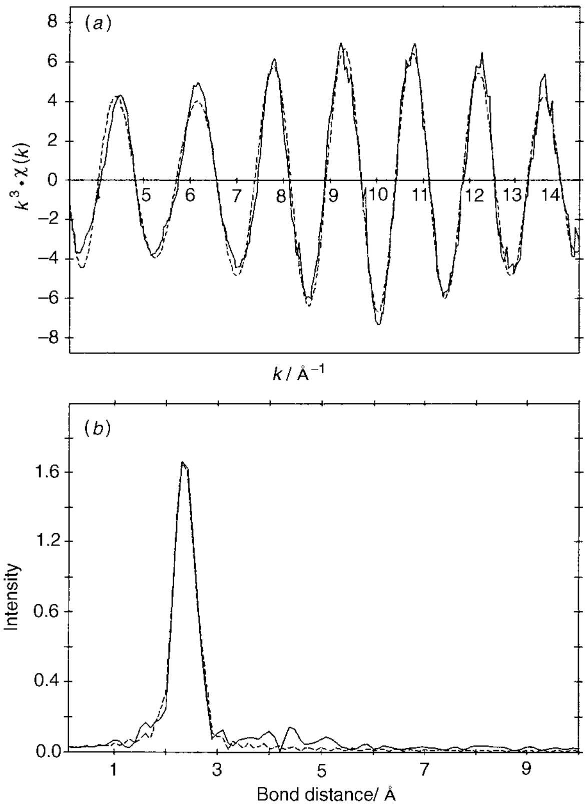

Fig. 2 Background-subtracted chromium K-edge EXAFS data (*a*) and the corresponding Fourier transform (*b*) for *cis*-$[CrBr_2([14]aneS_4)]PF_6$ (solid line, experimental; dashed line, calculated data)

thioether donors of the macrocycle, which adopts a folded arrangement, Cr–Br(1) 2.441(8), Cr–S(1) 2.41(1), Cr–S(2) 2.39(1) Å. As a result of the poor crystal quality the geometric parameters have high associated estimated standard deviations, and hence comparisons with related species require caution. However, the Cr–S distances are similar to those in both *cis*-$[CrCl_2([14]aneS_4)]^+$ [9] and $[CrCl_3([18]aneS_6)]$,[8] while d(Cr–Br) is *ca.* 0.15 Å longer than d(Cr–Cl) in these compounds. The angles subtended at Cr^{III} show a marked deviated from the 90 and 180° expected for a regular octahedron. Again this is similar to the case in *cis*-$[CrCl_2([14]aneS_4)]^+$.

Chromium K-edge EXAFS studies

Owing to the limited solubilities displayed by many of the compounds isolated, and their sensitivity to moisture, in most cases crystals suitable for an X-ray study could not be obtained. However, given the lack of structural data on compounds of this type, we proposed that chromium K-edge EXAFS data would provide useful information regarding the metal–ligand bond lengths for the first co-ordination sphere, *i.e.* d(Cr–S) and d(Cr–X). Importantly, the spectroscopic studies carried out in parallel provided key information concerning the donor sets involved in these products. Details of the refined EXAFS data for the complexes are given in Table 1 and Fig. 2 shows a typical example. Chromium K-edge EXAFS spectra were also recorded for the $[CrX_3(thf)_3]$ model compounds and for $[CrCl_2([14]aneS_4)]PF_6$ in order to compare the Cr–S and Cr–X distances derived from this method with the *average* values obtained from X-ray crystallographic studies. The EXAFS data for the thf adducts, $[CrX_3(thf)_3]$, were satisfactorily modelled to a first shell of three oxygens giving Cr–O distances of 2.01 and 2.00 Å for X = Cl and Br respectively, with a second shell of three halides giving d(Cr–Cl) = 2.29 and d(Cr–Br) = 2.46 Å. In the case of *cis*-$[CrCl_2([14]aneS_4)]PF_6$ the data were satisfactorily modelled to an S_4Cl_2 donor set with d(Cr–Cl) = 2.29, d(Cr–S) = 2.39 Å. These results correlate very well with the average Cr–S, Cr–O or Cr–X distances derived from the X-ray crystallographic studies.[9,25]

For $[CrX_3([9]aneS_3)]$, $[CrCl_3([10]aneS_3)]$ and $[(CrCl_3)_2(\mu\text{-}[18]aneS_6)]$ the EXAFS data were modelled for three sulfurs and three halogen atoms (Cl or Br as appropriate), while for *cis*-$[CrBr_2([14]aneS_4)]PF_6$ two shells were modelled, one with four sulfurs and one with two bromides. For the complexes *cis*-$[CrX_2([14]aneS_4)]PF_6$ no attempt was made to split the sulfur shell to take account of the slightly different distances expected for the Cr–S (*trans* to X) and Cr–S (*trans* to S) since X-ray structural studies have shown that the difference is very small (in this case only *ca.* 0.01 Å). In all cases the EXAFS data gave d(Cr–S) values very similar to those obtained crystallographically for chromium(III)–thioether interactions (*ca.* 2.4 Å) and significantly longer than d(Cr–Cl) (*ca.* 2.3 Å). This is consistent with the thioether interaction being rather weak, as might be anticipated for such a hard metal–soft ligand combination. The Cr–Br bond lengths of *ca.* 2.45 Å are in accord with the trend expected on the basis of the increased size of bromine over chlorine and also agree very well with d(Cr–Br) derived from the X-ray crystallographic study on *cis*-$[CrBr_2([14]aneS_4)]PF_6$ described above.

Electronic spectra

The UV/VIS spectra were recorded by diffuse reflectance (and also in solution for the soluble species), and the data for all of the new compounds are presented in Table 2. In an O_h environment, three spin-allowed d–d bands are predicted for chromium(III) species, ${}^4A_{2g} \longrightarrow {}^4T_{2g}$ (ν_1), ${}^4A_{2g} \longrightarrow {}^4T_{1g}$(F) ($\nu_2$) and ${}^4A_{2g} \longrightarrow {}^4T_{1g}$(P) ($\nu_3$), of which the latter is rarely observed as it is often obscured by intense charge-transfer bands.[26]

Table 2 Electronic spectroscopic data (cm^{-1})[a] for chromium(III) thioether macrocyclic compounds

Compound	Colour	ν_1	ν_2	*Dq*	*B*
$[CrCl_3([9]aneS_3)]$	Purple	14 450	20 080	1 445	556
$[CrBr_3([9]aneS_3)]$	Blue-purple	14 350	19 230	1 435	463
$[CrCl_3([10]aneS_3)]$	Purple	14 750	20 240	1 473	590
$[CrBr_3([10]aneS_3)]$	Dark purple	14 140	19 120	1 414	505
$[(CrCl_3)_2([18]aneS_6)]$	Pink-purple	14 450	19 530	1 445	516
$[(CrBr_3)_2([18]aneS_6)]$	Blue-purple	14 250	18 620	1 425	491
$[CrCl_2([14]aneS_4)]PF_6$[b]	Blue-green	16 500	22 400	1 650	536
$[CrBr_2([14]aneS_4)]PF_6$[b]	Dark blue	16 500	21 550	1 650	485
$[CrI_2([14]aneS_4)]PF_6$	Olive green	16 700 (sh)	—	—	—
$[CrCl_2([16]aneS_4)]PF_6$[b]	Green	15 820	21 790	1 582	546
$[CrBr_2([16]aneS_4)]PF_6$[b]	Dark green	15 510	20 940	1 551	554
$[CrI_2([16]aneS_4)]PF_6$	Light green	16 100	—	—	—

[a] Recorded for solid diluted with $BaSO_4$ by diffuse reflectance, except where indicated; sh = shoulder; $C = 4.5B$. [b] Recorded in $MeNO_2$ solution.

Noticeable splitting of these bands usually occurs upon reducing the symmetry from O_h to D_{4h} (*i.e.* a *trans*-L_4X_2 donor set), whereas reducing the symmetry to C_{2v} (*i.e.* a *cis*-L_4X_2 donor set) usually just results in some broadening of the transitions.[18] Also, reducing the symmetry from O_h to C_{3v} (*i.e.* a *fac*-L_3X_3 donor set as in the trithia and binuclear hexathia species) should theoretically result in splitting of the bands, although in practice only broadening of the bands is observed usually. Owing to the geometric constraints of the ligands used only the *fac* isomer is expected in each of the trithia species.

The UV/VIS spectra of the chromium(III) thioether species in this work are typical of chromium(III) complexes with an L_4Cl_2 donor set, showing two d–d transitions. The absence of any noticeable splitting in the UV/VIS spectra of $[CrX_2([14]aneS_4)]PF_6$ or $[CrX_2([16]aneS_4)]PF_6$ either in solution or the solid state suggests that these exist as the *cis* isomers. This has been confirmed for $[CrX_2([14]aneS_4)]^+$ through single-crystal structure analyses on the chloride and bromide derivatives, however in the absence of such data there is some uncertainty over the geometric arrangement (*cis vs. trans*) in the complexes of $[16]aneS_4$.

For each of the chromium(III) compounds *Dq* is obtained directly from ν_1, while the Racah parameter (*B*) can be extracted from the appropriate Tanabe–Sugano diagram.[26] It should be noted, however, that there is a considerable error associated with *B* of *ca.* ±50 cm^{-1}. From the values of *Dq* obtained it can be seen that for the neutral chromium(III) species with S_3X_3 donor sets *Dq* is smaller than for the species with S_4X_2 donor sets, consistent with the replacement of π-donor halogen ligands with thioether donors (probably weak σ donors only in these compounds). Consistent with this, *Dq* is even smaller for the hexachloro species $[CrCl_6]^{3-}$ (1318).[27] The values of *Dq* for the thioether compounds are considerably smaller than for other chromium(III) species with harder N- and O-donor ligands, *e.g.* $[Cr(H_2NCH_2CH_2NH_2)_3]^{3+}$ ($Dq = 2180$), $[Cr(bipy)_3]^{3+}$ (bipy = 2,2′-bipyridine) ($Dq = 2340$), and $[Cr(H_2O)_6]^{3+}$ ($Dq = 1740$).[27,28] For chromium(III) compounds with other soft donor sets such as phosphines the *Dq* values generally compare well with those for the thioether species in this work, *e.g.* for $[CrCl_3\{MeC(CH_2PPh_2)_3\}]$ (P_3Cl_3 donor set) $Dq = 1600$.[3] The values are also very similar to those for the other chromium(III)–thioether species known, *e.g.* $[CrCl_3\{MeC(CH_2SMe)_3\}]$ (S_3Cl_3 donor set) $Dq = 1470$ cm^{-1}.[3] These trends are consistent with only weak interactions between the Cr^{III} and the soft thioether functions.

For all of the compounds studied *B* lies in the range 463–590 cm^{-1}. These values are rather smaller than those observed for $[Cr(H_2O)_6]^{3+}$ ($B = 710$) and $[Cr(dmso)_6]^{3+}$ ($B = 685$ cm^{-1}).[27]

Conclusion

These results confirm that, despite the anticipated incompatibility between hard chromium(III) centres and soft thioether functions, a series of relatively stable mono- and di-nuclear complexes involving S_3X_3 and S_4X_2 donor sets has been successfully synthesized, adding considerably to the previously very limited range of such compounds known. Chromium K-edge EXAFS studies have proved to be extremely useful, providing structural data on the Cr–S and Cr–X bond distances in this unusual series of compounds. The values derived from the EXAFS measurements compare very well with those from X-ray crystallographic studies where such information is available. In particular, the Cr–S bond lengths are apparently largely independent of the macrocycle ring size or number of donor atoms available, and the Cr–S bond lengths, together with the *Dq* values, indicate relatively weak Cr^{III}–S (thioether) interactions in these compounds. Current work investigating the possibility of substituting the halide ligand to generate organometallic chromium–thioether macrocyclic derivatives is underway.

Experimental

Infrared spectra were measured as KBr or CsI discs or as Nujol mulls between CsI plates using a Perkin-Elmer 983 spectrometer over the range 200–4000 cm^{-1}, mass spectra by FAB using 3-nitrobenzyl alcohol as matrix on a VG Analytical 70-250-SE normal-geometry double-focusing spectrometer or by electrospray using a Hewlett-Packard Series 1050 spectrometer and UV/VIS spectra in solution using 1 cm path length quartz cells or by diffuse reflectance using samples diluted with $BaSO_4$ on a Perkin-Elmer Lambda19 spectrophotometer. Microanalytical data were obtained using a F & M model 185 C, H and N analyser. The EXAFS measurements were made at the Daresbury Laboratory, operating at 2.0 GeV (*ca.* 3.2×10^{-7} J) with typical currents of 200 mA. Chromium K-edge data were collected on stations 7.1 and 8.1 using a silicon(111) order-sorting monochromator, with harmonic rejection achieved by stepping off the peak of the rocking curve by 50% of the full height level. Data were collected in transmission mode from samples diluted with boron nitride and mounted between Sellotape in 1 mm aluminium holders.

Diethyl ether was dried over sodium wire. The compounds $[CrCl_3(thf)_3]$,[29] $[CrBr_3(thf)_3]$, $[Cr(thf)_6][BF_4]_3$[16] and *cis*-$[CrCl_2([14]aneS_4)]PF_6$ [9] were prepared by the literature methods.

Preparations

***(a)* $[CrCl_3([9]aneS_3)]$.** To a solution of $[CrCl_3(thf)_3]$ (0.104 g, 0.28 mmol) in dry, degassed CH_2Cl_2 (15 cm^3) was added $[9]aneS_3$ (0.05 g, 0.28 mmol). The resulting purple solution was stirred at room temperature under N_2 for 2 h and Et_2O was added to afford a purple solid which was filtered off and dried *in vacuo*. Yield = 0.066 g, 70% (Found: C, 21.5; H, 3.7. $C_6H_{12}Cl_3CrS_3$ requires C, 21.3; H, 3.5%). IR (CsI disc): 2970w, 1445s, 1405s, 826m, 349 (br) m and 293w cm^{-1}.

***(b)* [CrBr$_3$([9]aneS$_3$)].** Method as for (*a*), using [CrBr$_3$(thf)$_3$] (0.101 g, 0.20 mmol) and [9]aneS$_3$ (0.036 g, 0.20 mmol), giving a blue-purple solid. Yield = 0.059 g, 62% (Found: C, 14.9; H, 2.7. $C_6H_{12}Br_3CrS_3$ requires C, 15.3; H, 2.6%). IR (Nujol mull): 346m and 324m cm^{-1}.

***(c)* [CrCl$_3$([10]aneS$_3$)].** Method as for (*a*), using [CrCl$_3$(thf)$_3$] (0.108 g, 0.29 mmol) and [10]aneS$_3$ (0.056 g, 0.29 mmol), giving a purple solid. Yield = 0.077 g, 75% (Found: C, 24.0; H, 4.1. $C_7H_{14}Cl_3CrS_3$ requires C, 23.9; H, 4.0%). IR (Nujol mull): 359m and 346m cm^{-1}.

***(d)* [CrBr$_3$([10]aneS$_3$)].** Method as for (*a*), using [CrBr$_3$(thf)$_3$] (0.091 g, 0.018 mmol) and [10]aneS$_3$ (0.035 g, 0.18 mmol), giving a dark purple solid. Yield = 0.037 g, 68% (Found: C, 17.1; H, 3.0. $C_7H_{14}Br_3CrS_3$ requires C, 17.3; H, 2.9%). IR (Nujol mull): 342w, 325m and 300m cm^{-1}.

***(e)* [(CrCl$_3$)$_2$(μ-[18]aneS$_6$)].** Method as for (*a*), using [CrCl$_3$(thf)$_3$] (0.066 g, 0.18 mmol) and [18]aneS$_6$ (0.03 g, 0.09 mmol), giving a pink-purple solid. Yield = 0.080 g, 66% (Found: C, 21.6; H, 3.5. $C_{12}H_{24}Cl_6Cr_2S_6$ requires C, 21.3; H, 3.5%). IR (Nujol mull): 340 (br) m and 298w cm^{-1}.

***(f)* [(CrBr$_3$)$_2$(μ-[18]aneS$_6$)].** Method as for (*a*), using [CrBr$_3$(thf)$_3$] (0.07 g, 0.14 mmol) and [18]aneS$_6$ (0.025 g, 0.07 mmol), giving a blue-purple solid. Yield = 0.07 g, 52% (Found: C, 15.1; H, 2.6. $C_{12}H_{24}Br_6Cr_2S_6$ requires C, 15.3; H, 2.5%). IR (Nujol mull): 310m and 301w cm^{-1}.

***(g)* [CrBr$_2$([14]aneS$_4$)]PF$_6$.** To a solution of [CrBr$_3$(thf)$_3$] (0.12 g, 0.24 mmol) in dry, degassed $MeNO_2$ (15 cm^3) was added $TlPF_6$ (0.085 g, 0.24 mmol) and [14]aneS$_4$ (0.065 g, 0.24 mmol). After stirring for *ca.* 12 h the white TlCl precipitate was filtered off, leaving a blue-green solution. Addition of Et_2O gave a deep blue solid which was filtered off, washed with Et_2O and dried *in vacuo*. Yield = 0.06 g, 41% (Found: C, 18.8; H, 3.4. $C_{10}H_{20}Br_2CrF_6PS_4$ requires C, 19.2; H, 3.2%). Electrospray mass spectrum (MeCN solution): *m/z* = 480 {calc. for [Cr^{79}Br^{81}Br([14]aneS$_4$)]$^+$ *m/z* = 480}. IR (Nujol mull): 839vs, 557s, 346w and 323w cm^{-1}.

***(h)* [CrI$_2$([14]aneS$_4$)]BF$_4$.** The salt $AgBF_4$ (0.156 g, 0.80 mmol) and [CrCl$_3$(thf)$_3$] (0.10 g, 0.27 mmol) were stirred in dry thf (25 cm^3) for *ca.* 2 h to give a white AgCl precipitate which was filtered off to leave a pale green solution of [Cr(thf)$_6$][BF$_4$]$_3$. Dry $MeNO_2$ (25 cm^3) was then added and the thf removed *in vacuo*. The compounds [14]aneS$_4$ (0.072 g, 0.27 mmol) and NEt_4I (0.139 g, 0.54 mmol) were added and the deep green reaction mixture stirred for 1 h. The volume was then reduced *in vacuo* to <3 cm^3. Addition of Et_2O yielded an olive-green solid which was filtered off and dried. Yield = 0.04 g, 22% (Found: C, 21.1; H, 3.9. $C_{10}H_{20}BCrF_{12}I_2S_4$ requires C, 21.8; H, 3.6%). IR (Nujol mull): 1077s, 839m, 564m and 351w cm^{-1}.

***(i)* [CrCl$_2$([16]aneS$_4$)]PF$_6$.** As for (*g*), using [CrCl$_3$(thf)$_3$] (0.06 g, 0.16 mmol), $TlPF_6$ (0.056 g, 0.16 mmol) and [16]aneS$_4$ (0.048 g, 0.016 mmol), giving a light green solid. Yield = 0.03 g, 30% (Found: C, 25.0; H, 4.6. $C_{12}H_{24}Cl_2CrF_6PS_4$ requires C, 25.5; H, 4.3%). Electrospray mass spectrum (MeCN solution): *m/z* = 418 {calc. for [Cr^{35}Cl$_2$([16]aneS$_4$)]$^+$ *m/z* = 418}. IR (Nujol mull): 840vs, 558s and 366 (br) w cm^{-1}.

***(j)* [CrBr$_2$([16]aneS$_4$)]PF$_6$.** As for (*g*), using [CrBr$_3$(thf)$_3$] (0.08 g, 0.16 mmol), $TlPF_6$ (0.056 g, 0.16 mmol) and [16]aneS$_4$ (0.048 g, 0.016 mmol), giving a dark green solid. Yield = 0.03 g, 29% (Found: C, 22.4; H, 3.9. $C_{12}H_{24}Br_2CrF_6PS_4$ requires C, 22.0; H, 3.7%). Electrospray mass spectrum (MeCN solution): *m/z* = 508 {calc. for [Cr^{79}Br^{81}Br([16]aneS$_4$)]$^+$ *m/z* = 508}. IR (Nujol mull): 841vs, 558s and 302w cm^{-1}.

***(k)* [CrI$_2$([16]aneS$_4$)]BF$_4$.** Method as for (*h*), using [Cr(thf)$_6$][BF$_4$]$_3$ (0.25 mmol), [16]aneS$_4$ (0.08 g, 0.27 mmol) and NEt_4I (0.139 g, 0.54 mmol), giving a green solid. Yield = 0.03 g, 16% (Found: C, 21.5; H, 3.8. $C_{12}H_{24}BCrF_{12}I_2S_4$ requires C, 20.9; H, 3.5%). IR (Nujol mull): 1056s, 846m, 562m and 359w cm^{-1}.

EXAFS Refinements

Typically two or three data sets were collected for each complex and the analyses were carried out on the averaged spectra. The raw data were background-subtracted using the program PAXAS[30] by fitting a sixth- or eighth-order split polynomial to the pre-edge subtracted spectrum between $k = 2$ and to 13–15 Å^{-1}. Curve fitting was carried out using the program EXCURV 92.[31] Ground-state potentials of the atoms were calculated using Von Barth theory and phase shifts using Hedin–Lundqvist potentials. Two shells (either 3 S and 3 X or 4 S and 2 X) were fitted in each case. Refinements were also carried out using 6 S or 6 X, as well as other combinations, and in the case of X = Br the results clearly supported the S_3Br_3 or S_4Br_2 donor sets expected. In the case of the chloro derivatives the very similar backscattering from S and Cl made the assignment of the donor set difficult on the basis of the EXAFS data alone, although a better fit was obtained using two shells (either 3 S and 3 Cl or 4 S and 2 Cl as appropriate) and, in addition, the UV/VIS, IR and mass spectometric data provide very strong evidence for the donor sets chosen. The distances and Debye–Waller factors were refined for all the shells, as well as the Fermi energy difference. No attempt was made to refine the carbons of the ligand backbones since these occur over a range of distances and are not expected to be well defined.

Acknowledgements

We thank the EPSRC for an Earmarked Studentship (S. J. A. P.) and for funding the X-ray diffractometer, and the University of Southampton for support. We also thank the Director of the Synchrotron Radiation Source at Daresbury for the use of the facilities and we are indebted to Dr. W. Levason and Professor J. Evans (University of Southampton) for help in collecting the EXAFS data and the former for microanalytical measurements.

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Received 11*th December* 1996; *Paper* 6/08332C