Hard/Soft Interactions in Early Transition Metal Thioether Macrocyclic Chemistry: Synthesis and Single Crystal Structure of *cis*-$[CrCl_2([14]aneS_4)]PF_6$ ($[14]aneS_4$ = 1,4,8,11-tetrathiacyclotetradecane)

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Introduction

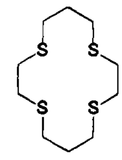
In contrast to the wide range of chromium(III) complexes with hard nitrogen and oxygen donor ligands,[1] very few examples of complexes with soft donor ligands such as phosphines[2−4] or thioethers[3−6] are known. This is principally due to the severe incompatability of the hard Cr(III) center with the soft phosphine or thioether functions.

The chemistry of thioether macrocycles has remained an area of extensive interest due to the ability of these ligands to stabilize unusual oxidation states and geometries, for example Au(II), Rh(II), Pd(I), and Pd(III). Thus thioether macrocyclic chemistry is dominated by middle and late d-block and p-block complexes.[7] In contrast the coordination of these macrocyclic thioether donors to first-row, early transition metals has received comparatively little investigation; examples being limited to the reactions of $[9]aneS_3$ with Cr(III)[6] (to give $CrCl_3([9]aneS_3)$, $[Cr(SO_3CF_3)_3([9]aneS_3)]$, and $[Cr([9]aneS_3)_2]^{3+}$, none of which have been structurally characterized and the latter of which has been prepared only in the solid state and loses ligand immediately upon contact with solvent) and V(IV)[8] (to give $[VCl_2O([9]aneS_3)]$). It has been assumed that the unique coordinating properties of $[9]aneS_3$ are largely responsible for the fact that these early transition metal complexes can be isolated.

We have been pursuing the reactions of $CrCl_3(thf)_3$ with various thioether macrocycles to determine whether the incorporation of other macrocyclic environments would render such hard/soft interactions accessible and to establish the nature of the S(thioether) to Cr(III) interaction. We now show Cr(III) thioether macrocyclic chemistry is not limited to $[9]aneS_3$, but that $[14]aneS_4$ forms a tetradentate complex with Cr(III) which is sufficiently stable to allow full solution and solid-state characterization. We report the preparation, redox behavior, and X-ray structure of the complex $[CrCl_2([14]aneS_4)]PF_6$.

Table 1. Crystal Data for *cis*-$[CrCl_2([14]aneS_4)]PF_6$

formula	$C_{10}H_{20}Cl_2$-$CrS_4{\cdot}PF_6$	λ/Å	0.71073 (Mo)
		μ (cm^{-1})	14.33
mol wt	536.4	*F(000)*	1084
color, morphology	blue/green prisms	transm factors: max; min	0.9969; 0.9472
cryst size/mm	0.20 × 0.10 × 0.25	no. of unique data	2164
		no. of obsd data with $F > 5\sigma(F)$	1567
cryst syst	monoclinic		
a/Å	10.699(2)	scan type	$\omega-2\theta$
b/Å	11.268(2)	$2\theta_{max}$/deg	54.0
c/Å	15.685(1)	final $\Delta\varrho$/(eÅ^{-3})	0.53
β/deg	92.685(10)	final Δ/σ	0.00
V/Å^3	1888.9(4)	*R*	0.041
space group	C2/c	R_w	0.055
Z	4	temp/K	120
D_{calc} (g cm^{-3})	1.886		



$[14]aneS_4$

Experimental Section

Infrared spectra were measured as KBr or CsI disks using a Perkin-Elmer 983 spectrometer over the range 200−4000 cm^{-1}. Mass spectra were run by fast-atom bombardment (FAB) using 3-NOBA (3-nitrobenzyl alcohol) as matrix on a VG Analytical 70-250-SE Normal Geometry Double Focusing Mass Spectrometer. Solution UV/visible spectra were recorded in 1 cm path length quartz cells using a Perkin-Elmer Lambda 19 spectrophotometer. Cyclic voltammetric experiments used an EG&G Princeton Applied Research Model 362 scanning potentiostat with 0.1 M $^nBu_4NBF_4$ supporting electrolyte, using a double platinum electrode as working and auxiliary electrode and a Ag/AgCl reference electrode. All potentials are quoted versus ferrocene/ferrocenium (Fc/Fc^+). ESR spectra were recorded as MeCN glasses (77 K) using a Bruker ECS106 X-band spectrometer. MeCN and $MeNO_2$ were dried and stored over molecular sieves; diethyl ether was dried over Na wire. Ligands were purchased from Aldrich and used as provided; $CrCl_3(thf)_3$ was prepared by the literature method.[9]

Synthesis of $[CrCl_2([14]aneS_4)][PF_6]$. To a solution of $CrCl_3(thf)_3$ (89 mg, 0.24 mmol) in $MeNO_2$ (20 cm^3) $[14]aneS_4$ (64 mg, 0.24 mmol) and $TlPF_6$ (85 mg, 0.24 mmol) were added in succession and the mixture was stirred for 24 h. Over this period the solution changed in color from pink to blue, and a white precipitate of TlCl formed. The TlCl was allowed to settle and the blue solution syringed from this precipitate into stirred dry Et_2O producing a dark blue precipitate. The product was then filtered using Schlenk apparatus, and dried *in vacuo* (44 mg, 34%). (Anal. Calcd for $C_{10}H_{20}Cl_2CrF_6PS_4$: C, 22.4; H, 3.7. Found: C, 22.2; H, 4.0). UV−vis spectrum {$MeNO_2$; $\nu/cm^{-1}(\epsilon/dm^3\ mol^{-1}\ cm^{-1})$}: 16 500 (210), 22 420 (150). FAB mass spectrum (3-NOBA matrix): found M^+ − 390, 355, 268; calculated for $[^{52}Cr^{35}Cl_2([14]aneS_4)]^+$ M^+ = 390, $[^{52}Cr^{35}Cl([14]aneS_4)]^+$ M^+ = 355, $[[14]aneS_4]^+$ M^+ = 268. IR spectrum (KBr disk/cm^{-1}) 2960 m, 1450 m, 1275 m, 1055 m, 840 s, 560 m, 380 m, 360 m.

Single Crystal Structure Determination on $[CrCl_2([14]aneS_4)]PF_6$. Small dark blue/green single crystals of the complex were obtained by vapor diffusion of diethyl ether into a solution of the complex $MeNO_2$. The selected crystal was coated in silicone oil and mounted on a glass fiber. Crystal data are given in Table 1.

Data collection used a Rigaku AFC7R four-circle diffractometer, with graphite-monochromated Mo Kα X-radiation. The structure was solved by direct methods[10] and developed by using iterative cycles of

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Table 2. Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) for *cis*-$[CrCl_2([14]aneS_4)]^+$

	Bond Lengths		
Cr(1)−Cl(1)	2.295(1)	C(1)−C(5)	1.536(8)
Cr(1)−S(1)	2.393(1)	C(3)−C(4)	1.513(7)
Cr(1)−S(2)	2.407(2)	S(1)−C(2)	1.814(6)
S(1)−C(1)	1.828(5)	S(2)−C(5)	1.813(5)
S(2)−C(4)	1.804(6)	C(2)−C(3)	1.524(8)
	Bond Angles		
Cl(1)−Cr(1)−Cl(1)*	97.39(8)	Cl(1)−Cr(1)−S(1)	90.07(5)
Cl(1)−Cr(1)−S(1)*	90.60(5)	Cl(1)−Cr(1)−S(2)	91.38(4)
Cl(1)−Cr(1)−S(2)*	169.59(5)	S(1)−Cr(1)−S(1)*	178.97(9)
S(1)−Cr(1)−S(2)	94.99(5)	S(1)−Cr(1)−S(2)*	84.22(5)
S(1)−C(1)−C(5)*	109.7(4)	S(1)−C(2)−C(3)	118.8(4)
C(2)−C(3)−C(4)	115.9(5)	S(2)−C(4)−C(3)	109.3(4)
S(2)−C(5)−C(1)*	107.1(4)	C(4)−S(2)−C(5)	105.5(3)
S(2)−Cr(1)−S(2)*	80.48(7)	Cr(1)−S(1)−C(1)	104.9(2)
Cr(1)−S(1)−C(2)	111.5(2)	C(1)−S(1)−C(2)	103.9(3)
Cr(1)−S(2)−C(4)	107.4(2)	Cr(1)−S(2)−C(5)	99.6(2)
	Torsion Angles		
S(1)−C(1)−C(5)−S(2)	61.9(4)	S(1)−C(2)−C(3)−C(4)	71.7(6)
S(2)−C(4)−C(3)−C(2)	−86.3(5)	C(1)−S(1)−C(2)−C(3)	69.7(5)
C(1)−C(5)−S(2)−C(4)	−170.4(4)	C(2)−S(1)−C(1)−C(5)	−149.0(4)
C(3)−C(4)−S(2)−C(5)	174.5(4)		

[a] Atoms marked with an asterisk are related to unasterisked atoms by the crystallographic 2-fold axis.

full-matrix least-squares refinement and difference Fourier syntheses which located all non-H atoms. The Cr atom of the complex cation occupies a site of 2-fold symmetry at (0, *y*, 0.25) and the P atom of the PF_6^- anion sits on a crystallographic inversion center at (0,0,0). The structure was therefore solved for a half $[CrCl_2([14]aneS_4)]^+$ cation and a half PF_6^- anion.[11] Both the cation and anion were ordered. All non-H atoms were refined anisotropically, while H-atoms were included in fixed, calculated positions. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses. Selected bond lengths, angles, and torsion angles are given in Table 2.

Results and Discussion

The reaction of $CrCl_3(thf)_3$ with [14]aneS_4 in dry $MeNO_2$ in the presence of 1 equiv of $TlPF_6$ yields a dark blue solid, $[CrCl_2([14]aneS_4)]PF_6$. This product is soluble in dry $MeNO_2$ and MeCN, but in the presence of moist solvents, or upon prolonged exposure (*ca.* 10 min) of solutions of the compund to atmospheric moisture, decomposition occurs. As a solid, $[CrCl_2([14]aneS_4)]PF_6$ is stable for days even in the open atmosphere.

The UV−vis spectrum of $[CrCl_2([14]aneS_4)]PF_6$ is typical of a Cr(III) complex with a L_4Cl_2 donor set, showing two d−d transitions at 16 500 and 22 420 cm^{-1} in $MeNO_2$ solution. For Cr(III) and an O_h environment three spin allowed d−d bands are predicted, ${}^4A_{2g} \rightarrow {}^4T_{2g}$, ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$, and ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$, of which the latter is rarely observed as it is often obscured by intense charge transfer bands.[12] Noticeable splitting of these bands usually occurs upon reducing the symmetry from O_h to D_{4h}.[17] The absence of any splitting in the UV−vis spectrum of $[CrCl_2([14]aneS_4)]PF_6$ suggests that this exists as the *cis* isomer in solution, the bands corresponding to ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (16 500 cm^{-1}) and ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ (22 420 cm^{-1}). Analysis of these data gives Dq = 1650 cm^{-1}. The observation of two bands tentatively assigned as Cr−Cl stretches in the IR spectrum of $[CrCl_2([14]aneS_4)]PF_6$ (ν_{Cr-Cl} = 360 and 380 cm^{-1}) is also consistent with a *cis*-dichloro stereochemistry.

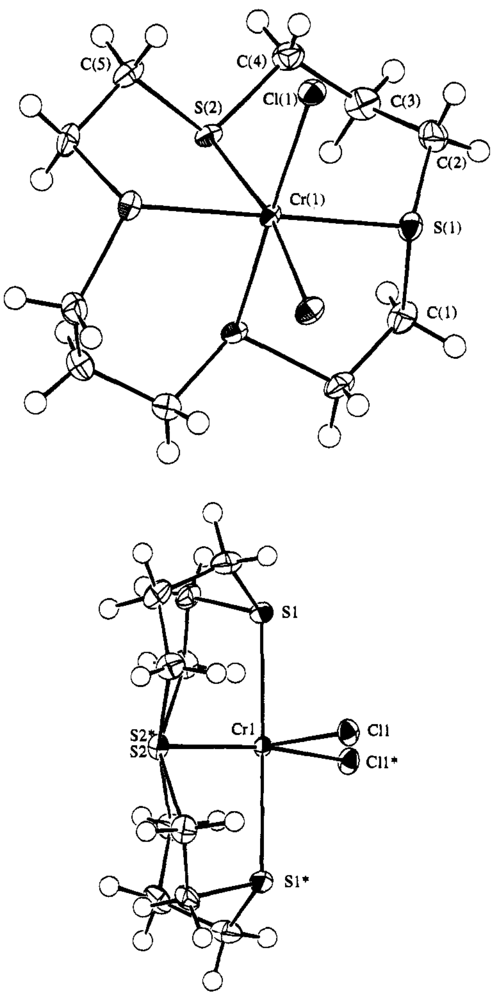

Figure 1. Top (a) and edge (b) view of the structure of *cis*-$[CrCl_2([14]aneS_4)]^+$ with numbering scheme adopted.

Since there has been only one structurally characterized example of Cr(III) bound to a thioether donor and very few examples of thioether complexes with other early transition metals, a single crystal structure determination on $[CrCl_2([14]aneS_4)]PF_6$ was undertaken. The structure determination shows the Cr atom occupying a crystallographic 2-fold axis. The geometry at Cr(III) is a distorted octahedron, with *cis*-dichloro ligands and the tetrathia macrocycle adopting a folded conformation: Cr−Cl(1) = 2.295(1) Å, Cr−S(1) = 2.393(1) Å, and Cr−S(2) = 2.407(2) Å. The structure is shown in Figure 1.

Gahan and co-workers reported the only previous structurally characterized example of a Cr(III)−S (thioether) complex. In their system the metal ion is encapsulated by a caging ligand which enforces the thioether coordination [Cr−S = 2.399(2) Å] and involves a much harder N_5S donor set compared to the tetrathia macrocyclic complex in this study.[13] The Cr−S bond lengths in *cis*-$[CrCl_2([14]aneS_4)]^+$, Cr−S (mean) = 2.400 Å, are in good agreement with the value reported by Gahan *et al.*[13] Comparisons of M−S and M−Cl bond lengths in *cis*-$[CrCl_2([14]aneS_4)]PF_6$ with late transition metal complexes of [14]aneS_4 show opposite trends, illustrating the reluctance of the hard Cr(III) center to bind to the soft thioether donors, e.g. *cis*-$[RhCl_2[14]aneS_4]^+$ {Rh−S = 2.29−2.33 Å, Rh−Cl = 2.38 Å[14]} *cis*-$[RuCl_2[14]aneS_4]$ {Ru−S = 2.26−2.33 Å, Ru−Cl = 2.47 Å[15]} and *cis*-$[IrCl_2[14]aneS_4]^+$ {Ir−S = 2.27−2.34 Å, Ir−Cl

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(mean) = 2.39 Å[17]}. This suggests that the relatively weak thioether to Cr(III) interactions involve little π-bonding character. This is consistent with the thioether to V(IV) bonding in $[VCl_2O([9]aneS_3)]$.[8]

A cyclic voltammogram was also recorded for $[CrCl_2([14]aneS_4)]PF_6$ in MeCN (0.1M $^nBu_4NBF_4$ supporting electrolyte) giving a broad irreversible reduction, at −0.75 V vs Fc/Fc^+. This is assigned as a $Cr^{III}-Cr^{II}$ redox couple. A further oxidative wave was observed at +0.76 V, vs Fc/Fc^+ following the reduction. This occurs at the same potential as the Cl^-/Cl^0 oxidation for $^nBu_4NCl$, thus indicating a possible decomposition route for the complex via loss of chloride. No significant improvement in reversibility of the Cr(III)−Cr(II) reductive couple was observed in the presence of a large excess of $^nBu_4NCl$. Similar behavior has been observed previously in the reduction of $[RhCl_2(Me_4[14]aneN_4)]^+$.[17] The ESR spectrum of $[CrCl_2([14]aneS_4)]PF_6$ (MeCN glass) shows a very broad signal, as expected for a system containing three unpaired electrons, with $g = 2.051$.

Further work to investigate the coordination of thioether and phosphine macrocyclic ligands to hard Cr, V, and Ti centers is underway.

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Supplementary Material Available: Tables of complete atomic coordinates (Table S1), full bond lengths, angles and torsion angles (Table S2), and anisotropic thermal parameters (Table S3) (5 pages). Ordering information is given on any current masthead page.

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