Pergamon

S0277–5387(97)00227–1

Polyhedron Vol. 16, No. 24, pp. 4253–4256, 1997

0277–5387/97 $17.00+0.00

Chromium(III) complexes of polydentate and macrocyclic selenoethers—synthesis, spectroscopic and exafs studies

William Levason, Gillian Reid* and Stephen M. Smith

Department of Chemistry, University of Southampton, Southampton SO17 1BJ, U.K.

(Received 24 April 1997; accepted 26 May 1997)

Abstract—The reaction of $[CrX_3(thf)_3]$ (X = Cl or Br) with the isomeric triselenoethers $MeC(CH_2SeMe)_3$ and $Se(CH_2CH_2CH_2SeMe)_2$ (L) forms the very moisture sensitive $[CrX_3L]$ complexes. The macrocycle $[16]aneSe_4$ (1,5,9,13-tetraselenacyclohexadecane) forms $[CrX_2([16]aneSe_4)]PF_6$. The complexes have been characterized by analysis, IR and UV-visible spectroscopy and electrospray mass spectrometry. The UV-visible spectra have been analysed and the low 10Dq and large B values, are consistent with weak binding of the soft selenium ligands to the hard Cr^{III}. Chromium K-edge EXAFS data has been recorded and analysed for the chromium chloride complexes to produce Cr—Se and Cr—Cl distances, which provide further strong evidence for weak Cr^{III}-selenoether interactions. © 1997 Elsevier Science Ltd

Keywords: chromium macrocycle; selenoether; exafs.

INTRODUCTION

Chromium(III) is one of the harder acceptors among 3d metal centres, forming complexes readily with charged anions and nitrogen and oxygen donor ligands [1]. Relatively few complexes with soft ligands such as phosphines or thioethers are known, and these are hydrolytically unstable [2–4]. We are currently exploring the coordination chemistry of polydentate and macrocyclic selenium donor ligands, and have reported elsewhere examples with later transition metals including the platinum metal halides, Cu^I, Ag^I and Co^{III}, which are classed as soft acceptors [5]. No examples of hard, early 3d metal halides with selenoether ligands have been reported [6]. We describe below the synthesis of the first examples of Cr^{III} selenoether complexes, their spectroscopic study and structural data derived *via* chromium K-edge EXAFS studies.

EXPERIMENTAL

The ligands 1,5,9,13-tetraselenacyclohexadecane, ($[16]aneSe_4$), 1,5-diselenacyclooctane, ($[8]aneSe_2$) 1,1,1-tris(methylselenomethyl)ethane (L^1) and 2,6,10-triselenaundecane (L^2) [7,8], and chromium trihalide tetrahydrofuran adducts [9,10], were synthesised by literature methods. Infra-red spectra were recorded as Nujol mulls between CsI plates on a Perkin Elmer 983G spectrometer over the range 4000–180 cm^{-1}. Diffuse reflectance UV/visible spectra were recorded on powdered samples diluted with $BaSO_4$ or in solution using sealed quartz cells, on a Perkin Elmer Lambda 19 spectrometer. Electrospray mass spectra were obtained using a Hewlett-Packard Series 1050 mass spectrometer operating in positive electrospray mode. EXAFS measurements were made at the Daresbury Synchroton Radiation Source operating at 2.0 GeV with typical ring currents of 200 mA. Chromium K-edge data were collected on station 7.1 using a silicon 111 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 powdered samples diluted with boron nitride and mounted using Kapton tape in 1 mm thick aluminium holders. Typically, two or three data sets were recorded for each compound and these datasets were averaged prior to analysis. Sample integrity was checked after data collection by rerecording the diffuse reflectance spectra. Data treatment used the programs PAXAS and EXCURV92 [11] and was carried out as described elsewhere [12].

---

* Author to whom correspondence should be addressed.

Synthesis of $[CrX_2([16]aneSe_4)][PF_6]$, (X = Cl or Br)

To a stirred solution of $[CrX_3(thf)_3]$ (0.1 mmol) in anhydrous $MeNO_2$ under N_2, was added $TlPF_6$ (0.035 g, 0.1 mmol), followed by $[16]aneSe_4$ (0.050 g, 0.1 mmol) and the mixture stirred for 1 h to afford a deep blue (X = Cl), or blue/green (X = Br) solution. The mixture was then allowed to stand overnight to let the TlX precipitate settle. The solution was transferred by syringe into a stirring solution of anhydrous diethyl ether (50 cm^3), whereupon $[CrX_2([16]aneSe_4][PF_6]$ precipitated as a deep blue powder and was isolated by Schlenk filtration. $[CrCl_2([16]aneSe_4)][PF_6]$, 0.029 g, 38%. Found: C, 19.1; H, 3.2; calc. for $C_{12}H_{24}Cl_2CrF_6PSe_4$: C, 19.1; H, 3.2%. Electrospray mass spectrum (MeCN): $m/z = 608$; calc. for $[^{52}Cr^{35}Cl_2([16]ane^{80}Se)_4]^+$ 610. $[CrBr_2([16]aneSe_4)][PF_6]$, 0.023 g, 27%. Found: C, 17.3; H, 3.0; calc. for $C_{12}H_{24}Br_2CrF_6PSe_4$: C, 17.1; H, 2.9%. Electrospray mass spectrum (MeCN): $m/z = 698$; calc. for $[^{52}Cr^{79}Br_2([16]ane^{80}Se)_4]^+$ 698.

Synthesis of $[CrX_3(L)]$, (X = Cl *or* Br *and* L = L^1 or L^2)

To a stirred solution of $[CrX_3(thf)_3]$ (0.14 mmol) in anhydrous CH_2Cl_2 (10 cm^3) under N_2, was added a solution of L (0.050 g, 0.14 mmol) in anhydrous CH_2Cl_2 (5 cm^3). The solution was stirred for 2 h, during which time the required $[CrX_3(L)]$ complex began to precipitate. The mixture was added, under N_2, to a stirring solution of anhydrous diethyl ether (50 cm^3), and the pale green complex was isolated by Schlenk filtration. $[CrCl_3(L^1)]$ 0.053 g, 74%. Found: C, 19.1; H, 3.6; calc. for $C_8H_{18}Cl_3CrSe_3$: C, 18.8; H, 3.6%. Far IR/cm^{-1} (Nujol): 350sh, 325. $[CrCl_3(L^2)]$ 0.051 g, 71%. Found: C, 18.4; H, 3.6; calc. for $C_8H_{18}Cl_3CrSe_3$: C, 18.8; H, 3.6%. Far IR/cm^{-1} (Nujol): 365, 340, 315sh. $[CrBr_3(L^1)]$ 0.061 g, 68%. Found: C, 15.3, H, 2.9; calc. for $C_8H_{18}Br_3CrSe_3$: C, 14.9; H, 2.8%. Far IR/cm^{-1} (Nujol): 300, 270sh. $[CrBr_3(L^2)]$ 0.057 g, 63%. Found: C, 15.3, H, 2.9; calc. for $C_8H_{18}Br_3CrSe_3$: C, 14.9; H, 2.8%. Far IR/cm^{-1} (Nujol): 320sh, 289, 270sh.

RESULTS AND DISCUSSION

The reaction of $[CrX_3(thf)_3]$ (X = Cl or Br, thf = tetrahydrofuran) with the isomeric triselenoethers, $MeC(CH_2SeMe)_3$ (L^1) and $Se(CH_2CH_2CH_2SeMe)_2$ (L^2), in CH_2Cl_2 under rigorously anhydrous conditions gave green powders $[CrX_3(L)]$. IR spectroscopy confirms the presence of the appropriate selenium ligand, the absence of thf, and the presence of pseudo-octahedral Cr^{III} is demonstrated by the UV-visible spectra (below). The identification of the geometric isomer present is less certain; monomeric complexes of L^1 are constrained to be *fac* by the ligand geometry, but L^2 imposes no constraints. From the far IR spectra (Experimental Section) the tentatively assigned ν(Cr—X) modes are consistent with *fac* geometry for complexes of L^1 and *mer* for those of L^2. The complexes are indefinitely stable under dry dinitrogen, but are hydrolysed rapidly on exposure to the laboratory atmosphere. They are very poorly soluble in chlorocarbons and decomposed by oxygen or nitrogen donor solvents, reflecting the preference of the chromium centre for harder donors. The reaction of $[16]aneSe_4$ with $[CrX_3(thf)_3]$ and 1 equivalent of $TlPF_6$ gave blue $[CrX_2([16]aneSe_4)]PF_6$, which were more soluble in organic solvents, but also hydrolytically unstable. The electrospray mass spectra of those showed strong peaks with the correct isotope distribution for $[CrX_2([16]aneSe_4]^+$ (Fig. 1). Attempts to prepare complexes of type $[CrX_2([8]aneSe_2)_2]PF_6$ by reaction of the ligand with $[CrX_3(thf)_3]$ and $TlPF_6$ failed, presumably reflecting the weaker coordinating power of the diselenoether compared with $[16]aneSe_4$.

The UV-visible data (Table 1) were analysed using the appropriate Tanabe-Sugano diagram, and based upon an O_h geometry, since no splittings of the major bands were observed. This suggests that the $[16]aneSe_4$ complexes are probably *cis* isomers, since *trans* isomers usually exhibit marked splittings of ν_1 and ν_2 [2]. The Dq values are slightly lower than those reported for thioether analogues [2,4], and the relatively low values are consistent with weak interaction between the soft selenium ligands and the hard metal centre.

Due to the poor solubility and stability in most solvents, out attempts to grow single crystals for an X-ray structure determination were unsuccessful. However, we have used chromium K-edge EXAFS (extended X-ray absorption fine structure) data to obtain Cr—Se and Cr—Cl bond lengths for the chloro-complexes. Combined with the spectroscopic evidence of metal centre coordination number (6 in this case and fixed as an Se_3X_3 or Se_4X_2 donor set as appropriate), the EXAFS technique provides a satisfactory structural characterisation of unstable metal

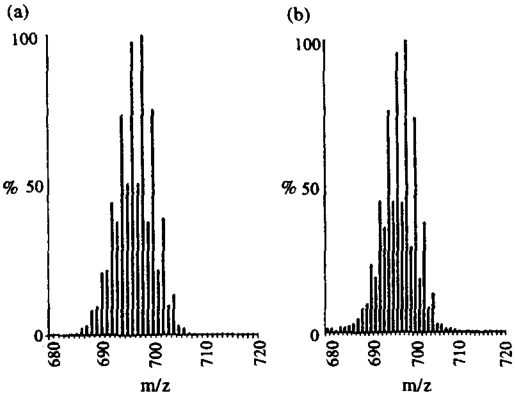

Fig. 1. Positive ion electrospray mass spectrum of $[Cr([16]aneSe_4)Br_2]^+$ in MeCN, (a) calculated, (b) experimental.

Table 1. UV-Visible Data[a]

Complex	ν_1 ($^4A_{2g} \rightarrow {}^4T_{2g}$)	ν_2 ($^4A_{2g} \rightarrow {}^4T_{1g}$)	LMCT[b]	Dq	B[c]	β[d]
$[CrCl_3(L^1)]$	14 490	20 500	27 700	1 449	617	0.67
$[CrBr_3(L^1)]$	14 450	20 830	26 040	1 445	660	0.72
$[CrCl_3(L^2)]$	14 620	20 300	28 900	1 462	567	0.62
$[CrBr_3(L^2)]$	14 470	20 600	26 310	1 447	630	0.69
$[CrCl_2([16]aneSe_4)]^{+}$[e]	15 580	20 920	—	1 558	511	0.56
$[CrBr_2([16]aneSe_4)]^{+}$[e]	15 770	21 440	—	1 577	550	0.59

[a] All energies in cm^{-1} diffuse reflectance spectra from powdered solids, except e,

[b] Ligand to metal charge transfer, probably $\pi(Se) \rightarrow t_{2g}(Cr)$,

[c] Racah parameter,

[d] Free ion B for Cr^{III} is 918 cm^{-1},

[e] $MeNO_2$ solution, solvent absorption obscures LMCT transition.

Table 2. EXAFS data

Complex	d(Cr-Se) (Å)[a]	$2\sigma^2$ ($Å^2$)[b]	d(Cr—Cl) (Å)	$2\sigma^2$ ($Å^2$)	R[c]	FI[d]
$[CrCl_3(L^1)]$	2.555(7)	0.023(1)	2.290(7)	0.016(1)	27.6	8.5
$[CrCl_3(L^2)]$	2.544(6)	0.012(1)	2.254(8)	0.011(1)	18.3	4.8
$[CrCl_2([16]aneSe_4)]^+$	2.566(5)	0.012(1)	2.318(9)	0.007(1)	23.0	6.2
$[CrCl_3(thf)_3]$	2.009(13)[e]	0.025(2)	2.295(3)	0.009(04)	23.3	4.1
$[CrCl_3(thf)_3]$[f]	2.03(av)		2.30(av)			

[a] Standard deviations in parenthesis. Note that systematic errors in bond distances arising from data collection and analysis procedures are *ca.* ±0.02 Å for well defined shells.

[b] Debye-Waller factor.

[c] R factors defined as $[\int (\chi^T - \chi^E)k^3 dk / \int \chi^E k^3 dk] \times 100\%$.

[d] Fit index defined as $\Sigma_i[(\chi^T - \chi^E)_i^3]^2$.

[e] d(Cr—O).

[f] X-ray crystallographic data from [14].

complexes [4,12]. The $[CrCl_3(thf)_3]$ complex was used as a model complex to check the data collection and refinement procedures, and as shown in Table 2 the data on this complex compare satisfactorily with the single crystal X-ray data. For the selenoether complexes, the EXAFS data refined to give the results shown in Table 2, and a typical example is shown in Fig. 2. The d(Cr—Cl) distances 2.25–2.32 Å may be compared with 2.295(1) Å in *cis*-$[CrCl_2([14aneS_4)]PF_6$ [4] and 2.316(1)–2.331(1) Å in $[CrCl_4(Ph_2PCH{=}CHPPh_2)]^-$ [2]. The d(Cr^{III}—Se) bond lengths of 2.54–2.57 Å are *ca.* 0.15–0.20 Å longer than Cr^{III}—S bonds in chromium(III) thioethers [4], reflecting the larger size of selenium. Similar differences in d(M—S) and d(M—Se) have been observed in thio- and selenoether macrocycles of later transition metals [5]. Sig-

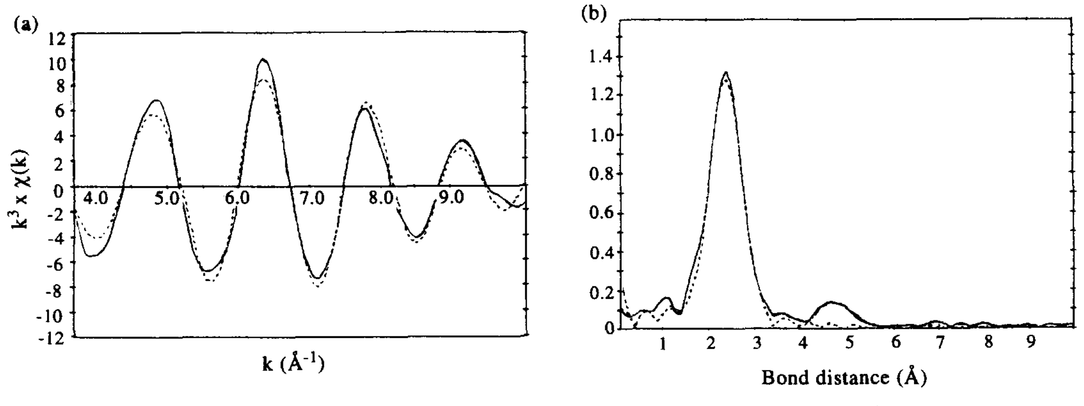

Fig. 2. (a) Background subtracted chromium K-edge EXAFS spectrum of $[CrCl_3\{MeC(CH_2SeMe)_3\}]$ and (b) corresponding Fourier transform (full line: experimental, broken line: theory).

nificantly, a comparison of the Cr—Se distances with M—Se bond lengths in complexes of later transition metals such as M = Rh^{III} or Ir^{III} [5], shows that the former are longer by *ca.* 0.1 Å, despite the smaller radius of Cr^{III} (Cr^{3+} = 0.62 Å, Rh^{3+} 0.66 Å, Ir^{3+} 0.68 Å) [13], consistent with weak Cr—Se bonding.

This study has shown that despite the severe hard/soft mismatch between Cr^{III} and selenoether donors, complexes of polydentate selenoethers can be prepared and isolated. Further studies with other early transition metals are in progress.

Acknowledgements—We thank the Leverhulme Trust for a fellowship (S.M.S.) and the EPSRC and the Director of the Daresbury Laboratory for provision of facilities for the EXAFS study.

REFERENCES

1. Larkworthy, L. F., Nolan, K. B. and O'Brien, P., in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, England, 1987, vol. 3.
2. For examples see: Gray, L. R., Hale, A. L., Levason, W., McCullough, F. P. and Webster, M., *J. Chem. Soc., Dalton Trans.*, 1984, 47; 1983, 2573; Hale, A. L. and Levason, W., *J. Chem. Soc., Dalton Trans.*, 1983, 2569.
3. Kuppers, H.-J. and Wieghardt, K., *Polyhedron*, 1989, **8**, 1770.
4. Champness, N. R., Jacob, S. R., Reid, G. and Frampton, C. S., *Inorg. Chem.*, 1995, **34**, 396; Champness, N. R., Pope, S. J. A. and Reid, G., *J. Chem. Soc., Dalton Trans.*, 1997, 1639.
5. Champness, N. R., Kelly, P. F., Levason, W., Reid, G., Slawin, A. M. Z. and Williams, D. J., *Inorg. Chem.*, 1995, **34**, 445; Levason, W., Quirk, J. J. and Reid, G., *J. Chem. Soc., Dalton Trans.*, 1996, 3713; Black, J. R., Champness, N. R., Levason, W. and Reid, G., *Inorg. Chem.*, 1996, **35**, 1820, 4432, and references therein.
6. For reviews of selenoether coordination chemistry see, Gysling, H. J., in *The Chemistry of Organic Selenium and Tellurium Compounds*, vol. 1, eds Z. Rappoport and S. Patai, Wiley, New York, 1986, 679; E. G. Hope and W. Levason, *Coord. Chem. Rev.*, 1993, **122**, 109.
7. Batchelor, R. J., Einstein, F. W. B., Gay, I. D., Gu, J.-H., Johnston, B. D. and Pinto, B. M., *J. Am. Chem. Soc.*, 1989, **111**, 6582.
8. Gulliver, D. J., Hope, E. G., Levason, W., Murray, S. G., Potter, D. M. and Marshall, G. L., *J. Chem. Soc., Perkin Trans. III*, 1984, 429.
9. Herwig, W. and Zeiss, H. H., *J. Org. Chem.*, 1958, **23**, 1404.
10. Jones, P. J., Hale, A. L., Levason, W. and McCullough, F. P., *Inorg. Chem.*, 1983, **22**, 2642.
11. Binsted, N., *PAXAS: Program for the Analysis of X-ray Absorption Spectra*, Southampton University, 1988; Gurman, S. J., Binsted, N. and Ross, I. J., *J. Phys. C.*, 1984, **17**, 143; 1986, **19**, 1845.
12. Corker, J. M., Evans, J., Levason, W., Spicer, M. D. and Andrews, P., *Inorg. Chem.*, 1991, **30**, 331; Champness, N. R., Levason, W., Oldroyd, R. D. and Preece, S. R., *Inorg. Chem.*, 1994, **33**, 2060.
13. Shannon, R. D. and Prewitt, R. D., *Acta Crystallog. Sect. B*, 1970, **26**, 1046.
14. Cotton, F. A., Duraj, S. A., Powell, G. L. and Roth, W. J., *Inorg. Chim. Acta*, 1986, **113**, 81.