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Chemistry of chromium-selenium complexes. Thermolytic degradation of $Cp_2Cr_2(CO)_4Se$, and the crystal structures of the cubane-like clusters $Cp_4Cr_4(\mu_3\text{-}CO)_2(\mu_3\text{-}Se)_2$ and $Cp_4Cr_4(\mu_3\text{-}O)_2(\mu_3\text{-}Se)_2$

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Abstract

Thermolysis of $Cp_2Cr_2(CO)_4Se$ (**1**) solution gave initially $Cp_4Cr_4(CO)_2Se_3$ (**3**), and a thermally labile unidentified species, which on further degradation afforded a mixture of products, from which more of **3**, and the cubane-like complexes $Cp_4Cr_4(CO)_2Se_2$ (**2**) and $Cp_4Cr_4O_2Se_2$ (**4**) were isolated. A more prolonged thermolysis in THF yielded $Cp_4Cr_4Se_4$ (**5**) as the main product. Crystal data: **2**, monoclinic, space group $C2/c$, a 17.656(5), b 8.232(1), c 18.079(6) Å, β 126.15(2)°, $Z = 4$, $R = 0.075$ for 1499 observed Mo-K_α data; **4**, monoclinic, space group $P2_1/c$, a 14.08(1), b 10.306(8), c 15.212(6) Å, β 103.55(2)°, $Z = 4$, $R = 0.082$ for 1711 observed Mo-K_α data. Both complexes possess a cubane-like structure with triply bridging Se and CO or O ligands at alternating corners of the cuboid.

Introduction

Rational synthetic approaches in cluster chemistry often involve main-group non-metal elements as bridging ligands [1–3]. Vahrenkamp [1,4,5], Adams [6], and Markó [7] have made extensive use of the uncoordinated electron pairs of the sulfido ligand to couple together small metal carbonyl units in order to build up and expand the cluster framework (eq. 1).

$$M_mE:\ + M_n' \rightarrow M_m(\mu\text{-}E)M_n' \qquad (1)$$

We have previously shown [8] that the self-condensation of $Cp_2Cr_2(CO)_4S$ and $Cp_2Cr_2(CO)_5S_2$ under thermolytic conditions, to form $Cp_4Cr_4(CO)_2S_2$ and

$Cp_4Cr_4S_4$, respectively, can be rationalised on the basis of the above postulated mechanistic pathway. We now describe the thermolysis of $Cp_2Cr_2(CO)_4Se$ (**1**), which yields the stable clusters $Cp_4Cr_4(CO)_2Se_2$ (**2**), $Cp_4Cr_4(CO)_2Se_3$ (**3**), $Cp_4Cr_4O_2Se_2$ (**4**) and $Cp_4Cr_4Se_4$ (**5**), and present the X-ray structures of **2** and **4**.

Experimental

All general procedures and spectral recordings were as described previously [8]. Elemental analysis were performed by the Analytical unit of the Australian National University, or Pascher Laboratories of Bonn, Germany. Cr was sometimes determined spectrophotometrically as CrO_4^{2-} [9] in our laboratory.

$Cp_2Cr_2(CO)_6$ was prepared as described by Manning [10]. Elemental black selenium was H & W analar grade. Silica gel, Merck Kieselgel 60, and Silanised Kieselgel 60 were activated at 140 °C overnight before chromatographic use.

Thermolysis of 1. An orange-brown solution of **1** in toluene (60 ml), prepared [11,12] in situ from $Cp_2Cr_2(CO)_6$ (1.0 g, 2.49 mmol) and black Se_8 (400 mg, 5.07 mmol), was filtered to remove residual Se_8 and refluxed under argon for 30 min. The resultant mixture consisted of fine black solids of $Cp_4Cr_4(CO)_2Se_3$ (**3**) (182 mg, 0.239 mmol, 19% yield), suspended in a brownish-green solution. Anal. Found for **3**: C, 34.21; H, 2.68; Cr, 27.51; Se, 31.27. $(C_5H_5)_4Cr_4(CO)_2Se_3$. $C_{22}H_{20}Cr_4O_2Se_3$ calcd.: C, 34.71; H, 2.65; Cr, 27.32; Se, 31.12%. On thermolysis or prolonged standing at ambient temperature, a solution of **3** in C_6D_6 was found to be converted into mainly $Cp_4Cr_4Se_4$ (**5**).

The NMR spectrum of the mother-liquor showed the signals from **3**, along with two other C_5H_5 resonances, δ 4.24 and δ 5.24 ($\nu_{\frac{1}{2}}$ 33 Hz), respectively, with relative integrals of 1/4/12. Tests showed that this product mixture was still thermally labile, and so the reaction was allowed to proceed for a further 1.5 h at 60–70 °C until the solution had turned brown-black. This solution now showed the resonances of **2** and **3** and δ 4.24, 5.12 ($\nu_{1/2}$ 40 Hz) and −5.6, with relative intensities of ca. 2/2/1/1/0.4. Filtration removed a green insoluble solid (60 mg), presumably either condensed Cr_mSe_n solids or paramagnetic $(CpCr)_mSe_n$ species, since it possessed neither proton resonances in the NMR nor any characteristic bands in the IR spectra. Chromatography of the filtrate on a silica-gel column (34 × 2.5 cm) gave three fractions: (i) a yellowish green eluate in n-hexane/toluene (60 ml); (ii) a black eluate in 1/1 toluene/ether (60 ml); and (iii) a brownish green eluate in THF (40 ml).

Fraction (i). Removal of solvents gave a deep green oily residue, (180 mg, 33% yield, based on 29.5% Cr content), possessing proton resonances at δ 4.25 and −5.61 (relative intensity ca. 5/1) in the NMR spectrum. This species was unstable in solution and attempted recrystallisation in n-hexane/ether at −30 °C gave several degradation species including **3**.

Fraction (ii). Concentration to dryness gave a black residue (296 mg) consisting of a 5/2 molar mixture of **2** and **3** together with small amounts of two other unidentified Cp-containing species. Rechromatography of this mixture on silanised silica gel column (20 × 2.5 cm), involving elution with n-hexane/toluene (60 ml), gave black solids, consisting mainly of **3**, (200 mg, 0.26 mmol, 21% yield) contaminated with an unidentified carbonyl Cp-containing species. Further elution with 1/1 toluene/ether gave a brown solution (50 ml), which afforded impure **2** as black crystals (60 mg, 0.088 mmol, 7.0%). The next fraction in 1/2 toluene-ether (30 ml), brown-black in colour, gave a further amount of **2** (40 mg, 0.060 mmol, 4.8%). Both batches of **2** were contaminated with trace quantities of **3** and other species. Recrystallisation from n-hexane/THF at −30 °C gave pure **2** as fine black crystals. Anal. Found for **2**: C, 37.04; H, 3.17; Cr, 30.16; Se, 23.0. $(C_5H_5)_4Cr_4(CO)_2Se_2$. $C_{22}H_{20}Cr_4O_2Se_2$, calcd.: C, 38.73; H, 2.95; Cr, 30.48; Se, 23.15%. A solution in C_6D_6 was found to have deposited solids of **5** after 16 h ambient temperature or 2 h at 50 °C.

Fraction (iii). This gave a deep green solid, **4** (62 mg, 0.094 mmol, 7.6% yield). Anal. Found for **4**: C, 37.01; H, 3.02, Cr, 32.46. $(C_5H_5)_4Cr_4O_2Se_2$. $C_{20}H_{20}Cr_4O_2Se_2$, calcd.: C, 36.49; H, 3.06; Cr, 31.60%.

In a separate thermolysis reaction of $Cp_2Cr_2(CO)_4Se$ (212 mg, 0.5 mmol) in THF (30 ml), 3 h reflux produced a black precipitate consisting mainly of **5** (82 mg, ca. 0.1 mmol, 40%). Anal. Found for **5**: C, 30.83; H, 2.63; Cr, 26.12; Se, 40.2. $(C_5H_5)_4Cr_4Se_4$, $C_{20}H_{20}Cr_4Se_4$, calcd.: C, 30.63; H, 2.57; Cr, 26.52; Se, 40.28%. The NMR spectrum of the mother liquor showed the presence of a 1/1/2 molar mixture of **2**, **3** and **5**, along with a small amount of the unstable intermediate (δ 4.24, −5.6).

Crystal structure analysis

Diffraction-quality crystals of **2** (diamond-shaped plates) and **4** (chunky polyhedra) were deposited from saturated solutions in toluene/THF during 5 weeks at ambient temperature in a dry box. Diffraction measurements were made on a Nicolet R3m four-circle diffractometer (graphite-monochromatized Mo-K_α radiation, λ 0.71069 (Å), and the crystal class, orientation matrix, and accurate unit-cell parameters were determined by standard procedures [13]. Intensities were recorded at 22 °C, and data collection and processing parameters are summarized in Table 1. Application of absorption corrections was based on a pseudo-ellipsoidal fit to azimuthal scans of selected strong reflections over a range of 2θ values [14,15]. The intensities were processed by the learnt-profile procedure [16].

Structure solution of **4** was accomplished by means of Patterson superposition and Fourier methods. In compound **2**, which is isomorphous with its S analogue [8], the tetranuclear molecule lies on a two-fold axis, and the triply-bridging ligands are statistically distributed over four sites in such a way that the Se and C atoms are superposed on each other. The scattering power of the disordered groups is accounted for by half-oxygen atoms O(1) and O(2), and fractional selenium atoms Se(1) and Se(2), each tied to a variable site occupancy factor which necessarily exceeds 1/2. All non-hydrogen atoms in the asymmetric unit were subjected to anisotropic refinement. The hydrogen atoms of the cyclopentadienyl groups were generated geometrically (C–H fixed at 0.96 Å) and included in structure factor calculations with assigned isotropic thermal parameters.

All computations were performed on a Data General Nova 3/12 minicomputer with the SHELXTL system [17]. Analytic expressions of neutral-atom scattering factors incorporating the real and imaginary components of anomalous dispersion were employed [18]. Blocked-cascade least-squares refinements [19] converged to the R indices and other parameters listed in Table 1.

Tables of hydrogen cation coordinates thermal parameters and lists of observed and calculated structure factors are available from the authors.

Table 1

Data collection and processing parameters

	2		4	
Molecular formula	$(\eta^5\text{-}C_5H_5)_4Cr_4(\mu_3\text{-}CO)_2(\mu_3\text{-}Se)_2$		$(\eta^5\text{-}C_5H_5)_4Cr_4(\mu_3\text{-}O)_2(\mu_3\text{-}Se)_2$	
Molecular weight	682.30		658.28	
Cell constants	a 17.656(5) Å	β 126.15(2)°	a 14.08(1)	β 103.55(2)°
	b 8.232(1)	V 2121.8(8) Å^3	b 10.306(8)	V 2146(2) Å^3
	c 18.079(6)	$Z = 4$	c 15.212(6)	$Z = 4$
		$F(000) = 1327.7$		$F(000) = 1279.3$
Density (exptl)	2.094 g cm^{-3} (flotation in $CCl_4/BrCH_2CH_2CH_2Br$)		>1.99 g cm^{-3} (dissolving in $CCl_4/BrCH_2CH_2Br$)	
Density (calcd)	2.136 g cm^{-3}		2.037 g cm^{-3}	
Space Group	$C2/c$		$P2_1/c$	
Radiation	graphite-monochromatized Mo-K_α, λ 0.71069 Å		graphite-monochromatized Mo-K_α, λ −0.71069 Å	
Absorption coefficent	53.65 cm^{-1}		53.01 cm^{-1}	
Crystal size	0.28×0.16×0.12 nm		0.20×0.16×0.14 nm	
Mean μr	0.583		0.457	
Transmission factors	0.396 to 0.894		0.290 to 0.354	
Scan type and speed	ω-2θ; 2.02–8.37 deg min^{-1}		ω-2θ; 2.02–8.37 deg min^{-1}	
Scan range	1° below K_{α_1} to 1° above K_{α_2}		1° below K_{α_1} to 1° above K_{α_2}	
Background counting	stationary counts for one-half of scan time at each end of scan		stationary counts for one-half of scan time at each end of scan	
Collection range	$h, k, \pm l$; $2\theta_{max}$ 52°		$h, k, \pm l$; $2\theta_{max}$ 48°	
Unique data measured	1763		2440	
Observed data with $\|F_0\| > 3\sigma(\|F_0\|)$, n	1499		1711	
Number of variables, p	146		253	
$R_F = \Sigma\|\|F_0 - F_c\|\|/\Sigma\|F_0\|$	0.075		0.082	
Weighting scheme	$w = [\sigma^2(F_0) + 0.0003\|F_0\|^2]^{-1}$		$w = [\sigma^2(F_0) + 0.0018\|F_0\|^2]^{-1}$	
$R_G = [\Sigma w(\|F_0\| - \|F_c\|)^2/\Sigma w\|F_0\|^2]^{1/2}$	0.083		0.089	
$S = [\Sigma w(\|F_0\| - \|F_c\|)^2/(n-p)]^{1/2}$	2.582		1.429	
Residual extrema in final difference map	+1.90 to −0.72 eÅ^{-3}		+1.36 to −1.06 eÅ^{-3}	

Results and discussion

Thermolytic degradation of 1

Thermolysis of an orange-brown solution of **1** in refluxing toluene for 0.5 h, produced **3**, in 19% yield, as a fine black solid suspended in a brownish green solution of a thermally labile cyclopentadienylchromium carbonyl species with δ(Cp) 4.24 and 5.24. On further thermolysis, a mixture of **2**, **3**, and other labile Cp-containing species was formed, along with some green insoluble non-characteriseable solids, presumably of polymeric Cr_mSe_n or some paramagnetic cyclopentadienyl chromium compounds.

Chromatography on silica gel initially separated 3 fractions, which gave: (a) a deep green unstable oil (33% yield), with proton resonances at δ 4.24, -5.61 (relative intensity 5/1); (b) a dark brown mixture of $Cp_4Cr_4(CO)_2Se_2$ (**2**) and $Cp_4Cr_4(CO)_2Se_3$ (**3**), with minor unidentified contaminants; and (c) dark green crystals of $Cp_4Cr_4O_2Se_2$ (**4**) (7.6% yield). Since the NMR spectral characteristics of **4** were not observed in the thermolysis product solution prior to chromatography, it must have arisen from the reaction of the intermediate "δ 5.12, $\nu_{1/2}$ 40 Hz" with H_2O or OH groups present in the silica gel of the column. The formation of μ_3-oxo clusters from the reaction of cyclopentadienyl-transition metal carbonyls with H_2O is not unprecedented [20].

Rechromatography of the middle fraction on silanised silica-gel, separated **3** from **2**, which was recrystallised from THF/n-hexane at $-30\,^\circ$C to give pure fine black crystals (11.8% yield). The total overall yield of **3** was ca. 40%.

A more exhaustive thermolysis reaction involving 3 h refluxing in THF produced ca. 60% yield of **5** mixed with **2**, **3** and the unstable species (δ 4.24, -5.6). The high yield of **5** is in agreement with the NMR spectral observations that **2** and **3**, are all converted mainly into **5** on prolonged standing in solution either at ambient or elevated temperatures. Thus, unlike the formation of $Cp_4Cr_4(CO)_2S_2$, the S-analogue of **2**, which was suggested to occur via a simple intermolecular coupling of two molecules of $Cp_2Cr_2(CO)_4S$ [8], the thermolytic breakdown of $Cp_2Cr_2(CO)_4Se$ (**1**) involves more complicated pathways, involving several labile intermediates.

Spectra

The spectra data for the various complexes are given in Table 2. It will be noted that there is a striking similarity between the mass spectral fragmentation pattern and the NMR and IR spectroscopic data of $Cp_4Cr_4(\mu_3\text{-CO})_2(\mu_3\text{-Se})_2$ (**2**) and its S analogue, which possessed Cp resonances at δ 9.95, 5.65 (^{1}H); and 99.29 and 91.88 (^{13}C) and $\nu(\mu_3\text{-CO})$ 1645 vs cm^{-1} [8]. Like its S analogue, **2** also exhibits variable temperature (VT) NMR behaviour. As the temperature is lowered, the Cp proton singlet resonances sharpen and approach, but do not coalesce even at $-90\,^\circ$C. The origin of this VT behaviour, also shown by **3** and **4**, is not clear and is under further investigation. Like **2**, $Cp_4Cr_4(CO)_2Se_3$ (**3**) also possesses two non-equivalent Cp rings, and a μ_3-CO bridging group is observed in the IR spectrum at 1620s,br cm^{-1}. In contrast, $Cp_4Cr_4O_2Se_2$ (**4**) shows only one broad Cp resonance throughout the range $-90\,^\circ$C (δ -13.52, $\nu_{1/2}$ 171 Hz) to $60\,^\circ$C (δ 6.02, $\nu_{1/2}$ 55 Hz). Judging from the broad appearance of these resonances, **4** could possibly possess some degree of paramagnetism, as was found for the antiferromagnetic distorted cubane $Cp_4Cr_4O_4$

Table 2

Spectral data

Complex	NMR [a]		IR (KBr) cm^{-1} [b]	Mass spectra [c], m/e (for ^{80}Se) [assignments]
	^1H (δ)	^{13}C (δ)		
2	(9.73 ($\nu_{1/2}$, 31Hz), 5.49) [d]	98.79, 90.25	ν(CO) 1630vs; other bands, 1420m, 1010m, 835m sh, 800 vs, 560vw vbr (unresolved), 495m	788 [$Cp_4Cr_4Se_4$], 723 [$Cp_3Cr_4Se_4$], 708 [$Cp_4Cr_4Se_3$], 684 [$Cp_4Cr_4(CO)_2Se_2$], 656 [$Cp_4Cr_4(CO)Se_2$], 628 [$Cp_4Cr_4Se_2$], 591 [$Cp_3Cr_4(CO)Se_2$], 511 [$Cp_3Cr_3Se_2$], 446 [$Cp_2Cr_3Se_2$], 329 [$CpCr_2Se_2$], 184 [Cr_2Se], 182 [Cp_2Cr],
3	(17.7 ($\nu_{1/2}$ 70 Hz), 3.72 ($\nu_{1/2}$ 12 Hz)) [e]	93.64, 83.95	ν(CO) 1620vs, br; other bands, 1420m, br; 1005m 800vs	788 [$Cp_4Cr_4Se_4$], 723 [$Cp_3Cr_4Se_4$], 708 [$Cp_4Cr_4Se_3$], 656 [$Cp_4Cr_4(CO)Se_2$], 643 [$Cp_3Cr_4Se_3$], 591 [$Cp_3Cr_4(CO)Se_2$], 511 [$Cp_3Cr_3Se_2$], 446 [$Cp_2Cr_3Se_2$], 394 [$Cp_2Cr_2Se_2$], 342 [$Cp_2Cr_2(CO)Se$], 184 [Cr_2Se], 182 [Cp_2Cr]
	(17.62 ($\nu_{1/2}$ 70 Hz), 3.66 ($\nu_{1/2}$ 10 Hz)) [f]	(99.18, 91.00) [g]		
4	2.44 ($\nu_{1/2}$ 70 Hz) [h]; (−13.52 ($\nu_{1/2}$ 171 Hz), −0.80 ($\nu_{1/2}$ 64 Hz), and 4.44 ($\nu_{1/2}$ 57 Hz) 6.02 ($\nu_{1/2}$ 55 Hz)) [i]		1645w, vbr; 1430m; 1386w; 1355vw; 1264w; 1110w (unresolved from 1057 and 1052), 1010s; 843m sh, 794vs; 572m, sh; 554s.	660 [$Cp_4Cr_4O_2Se_2$], 595 [$Cp_3Cr_4O_2Se_2$], 580 [$Cp_4Cr_4O_2Se$], 530 [$Cp_2Cr_4O_2Se_2$], 515 [$Cp_3Cr_4O_2Se$], 465 [$CpCr_4O_2Se_2$], 450 [$Cp_2Cr_4O_2Se$], 400 [$Cr_4O_2Se_2$], 332 [Cr_3OSe_2], 184 [Cr_2Se], 182 [Cp_2Cr]
5	5.13		1620w, vbr; 1420m; 1350vw; 1060vw; 1015w; 1000m; 890vw sh; 880m; 920m sh, 790vs	788 [$Cp_4Cr_4Se_4$], 723 [$Cp_3Cr_4Se_4$], 658 [$Cp_2Cr_4Se_4$, 593 [$CpCr_4Se_4$], 528 [Cr_4Se_4]

[a] Measured in benzene-d_6 at ambient temperature unless otherwise specified. Chemical shifts (singlets assigned to C_5H_5 unless otherwise stated) referenced to residual benzene in C_6D_6. [b] Abbreviations: vs very strong, s strong, m medium, w weak, vw very weak, sh shoulder, br broad, vbr very broad. [c] Electron-impact low resolution spectra. [d] Identical δ's in toluene-d_8. Exhibits variable-temperature behaviour. At −90 °C, δ 5.28 and 4.91. [e] Relative intensity 1.6/1. [f] In toluene-d_8. At −90 °C, δ 9.8 ($\nu_{1/2}$ 24 Hz), and 5.03, relative intensity ca. 2/1. [g] In toluene-d_8 at −90 °C. [h] Varies between δ 2.03 and 2.62. [i] In toluene-d_8 at −90 °C, 0 °C, 45 °C and 60 °C respectively.

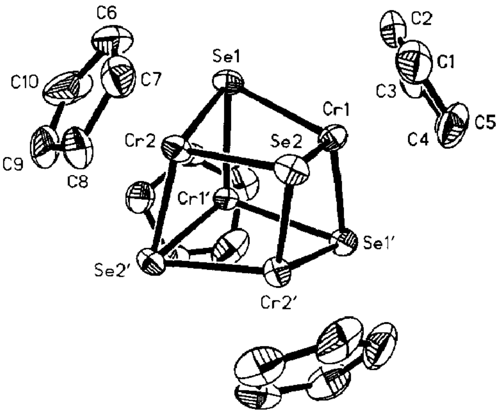

Fig. 1. Perspective view of the molecular structure of 2 with atom labelling. The thermal ellipsoids are drawn at the 30% probability level. The primed and unprimed atoms are related by two-fold rotation symmetry, and two cyclopentadienyl rings and the disordered O atoms have been omitted for clarity.

[21] and its derivative $Cp_4Cr_4O_3(\eta^2\text{-}C_5H_4)$ [22], which gave no signals or very broad featureless signals, respectively, in the NMR. Unlike **2** and **3**, both of which readily lose the μ_3-CO groups of the cuboid skeletal framework, the $Cr_4(\mu_3\text{-}O)_2(\mu_3\text{-}Se)_2$ core unit persists, as **4** successively loses its Cp rings in the mass fragmentation process. Bottomley [21b] has ascribed the observed instability of the Cp rings in $Cp_4Cr_4O_4$ to "the lack of electrons for π-backbonding to Cp". In the IR spectrum,

Table 3

Atomic coordinates ($\times 10^4$) and thermal parameters [a] ($Å^2 \times 10^3$) for $(\eta^5\text{-}C_5H_5)_4Cr_4(\mu_3\text{-}CO)_2(\mu_3\text{-}Se)_2$ (**2**)

Atom [b]	x	y	z	U_{eq}
Cr(1)	911(1)	498(2)	2716(1)	41(1)
Cr(2)	317(1)	−1865(2)	3424(1)	42(1)
Se(1)	506(2)	916(3)	3758(1)	46(1)
Se(2)	1240(2)	−2257(3)	2860(2)	47(1)
O(1)	769(1)	1656(25)	4189(12)	64(11)
O(2)	1596(18)	−2972(31)	3062(16)	76(20)
C(1)	2428(10)	664(22)	3340(10)	90(10)
C(2)	2232(12)	1945(24)	3669(11)	91(12)
C(3)	1551(11)	2883(18)	2909(11)	79(12)
C(4)	1438(10)	2271(18)	2195(8)	76(8)
C(5)	1967(10)	845(20)	2436(9)	85(10)
C(6)	1142(10)	−2088(8)	4939(8)	81(9)
C(7)	1322(9)	−3416(17)	4607(8)	75(8)
C(8)	503(11)	−4258(17)	4038(9)	81(10)
C(9)	−158(11)	−3477(24)	4078(10)	102(11)
C(10)	168(11)	−2118(26)	4566(9)	107(12)

[a] Equivalent isotropic temperature factor U_{eq} defined as 1/3 of the trace of the orthogonalised U matrix.

[b] Site occupancy factors are 1/2 for O(1) and O(2), 0.617 (4) (incorporating the scattering power of the superimposed C atom) for Se(1) and Se(2), and unity for the other atoms.

Table 4

Selected bond lengths (Å) and bond angles (deg) ^{a} for $(\eta^5\text{-}C_5H_5)_4Cr_4(\mu_3\text{-}CO)_2(\mu_3\text{-}Se)_2$ (2)

Cr(1)–Cr(2)	2.848(3)	Cr(1)–Cr(1′)	2.828(4)
Cr(1)–Cr(2′)	2.733(2)	Cr(2)–Cr(2′)	2.830(4)
Cr(1)–Se(1)	2.402(4)	Cr(1)–Se(1′)	2.369(2)
Cr(1)–Se(2)	2.317(3)	Cr(2)–Se(1)	2.341(3)
Cr(2)–Se(2)	2.400(5)	Cr(2)–Se(2′)	2.350(3)
Se(1)–O(1)	0.88(2)	Se(2)–O(2)	0.78(2)
Cr(1)–C(1)	2.21(2)	Cr(2)–C(6)	2.22(1)
Cr(1)–C(2)	2.26(2)	Cr(2)–C(7)	2.21(1)
Cr(1)–C(3)	2.19(2)	Cr(2)–C(8)	2.19(1)
Cr(1)–C(4)	2.22(2)	Cr(2)–C(9)	2.24(2)
Cr(1)–C(5)	2.22(2)	Cr(2)–C(10)	2.24(2)
C(1)–C(2)	1.35(3)	C(6)–C(7)	1.37(2)
C(2)–C(3)	1.41(2)	C(7)–C(8)	1.37(2)
C(3)–C(4)	1.29(3)	C(8)–C(9)	1.37(3)
C(4)–C(5)	1.40(2)	C(9)–C(10)	1.33(3)
C(5)–C(1)	1.34(2)	C(10)–C(6)	1.43(3)
Cr(2)–Cr(1)–Cr(1′)	57.6(1)	Cr(2)–Cr(1)–Cr(2′)	60.9(1)
Cr(1′)–Cr(1)–Cr(2′)	61.6(1)	Cr(1)–Cr(2)–Cr(1′)	60.9(1)
Cr(1)–Cr(2)–Cr(2′)	57.5(1)	Cr(1′)–Cr(2)–Cr(2′)	61.6(1)
Se(1)–Cr(1)–Se(1′)	104.8(1)	Se(1)–Cr(1)–Se(2)	102.9(1)
Se(2)–Cr(1)–Se(1′)	107.3(1)	Se(1)–Cr(2)–Se(2)	102.2(1)
Se(1)–Cr(2)–Se(2′)	107.1(1)	Se(2)–Cr(2)–Se(2′)	104.7(1)
Cr(1)–Se(1)–Cr(2)	73.8(1)	Cr(1)–Se(2)–Cr(2)	74.2(1)
Cr(1)–Se(1)–Cr(1′)	72.7(1)	Cr(1)–Se(2)–Cr(2′)	71.7(1)
Cr(2)–Se(1)–Cr(1′)	70.9(1)	Cr(2)–Se(2)–Cr(2′)	73.1(1)

^{a} Primed atoms are generated by the symmetry transformation $(-x,\ y,\ \frac{1}{2}-z)$.

the strongest vibrations at 794vs and 554s cm^{-1} can be attributed to core vibrations, equivalent to 750, 551 cm^{-1} [23] and 545 cm^{-1} [21b] observed for $Cp_4Cr_4O_4$.

Structure of 2

A perspective view of the molecular structure of **2** is illustrated in Fig. 1. Atomic coordinates are listed in Table 3. Bond lengths and selected bond angles are given in

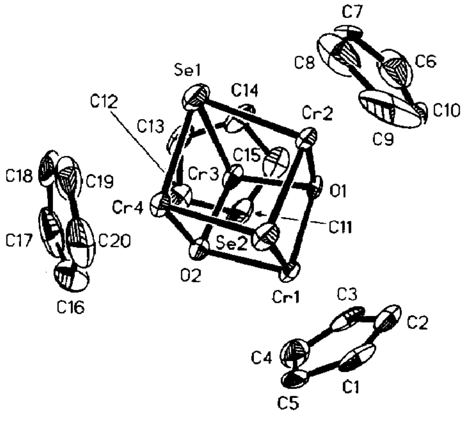

Fig. 2. Perspective view of the molecular structure of 4 with atom labelling. The thermal ellipsoids are drawn at the 30% probability level.

Table 5

Atomic coordinates ($\times 10^4$) and thermal parameters [a] ($Å^2 \times 10^3$) for $(\eta^5\text{-}C_5H_5)_4Cr_4(\mu_3\text{-}O)_2(\mu_3\text{-}Se)_2$ (4)

Atom	x	y	z	U_{eq}
Cr(1)	2807(2)	34(3)	428(2)	38(1)
Cr(2)	2191(2)	2525(3)	1017(2)	39(1)
Cr(3)	1784(2)	−25(3)	1761(2)	42(1)
Cr(4)	3767(2)	911(3)	2323(2)	46(1)
Se(1)	2322(2)	1985(2)	2606(1)	60(1)
Se(2)	3839(1)	1944(2)	880(1)	46(1)
O(1)	1651(8)	868(11)	645(6)	38(4)
O(2)	3080(8)	−557(12)	1672(7)	46(5)
C(1)	3255(17)	−237(22)	−893(13)	74(10)
C(2)	2273(16)	−240(23)	−1064(12)	63(9)
C(3)	2015(18)	−1320(23)	−614(14)	64(10)
C(4)	2798(17)	−1967(22)	−168(14)	80(11)
C(5)	3613(19)	−1303(28)	−307(14)	94(12)
C(6)	864(21)	3717(22)	400(18)	106(13)
C(7)	1268(18)	4272(23)	1146(14)	97(12)
C(8)	2169(20)	4655(25)	1086(22)	124(15)
C(9)	2248(26)	4340(25)	224(27)	152(22)
C(10)	1435(25)	3635(22)	−135(14)	140(17)
C(11)	1017(15)	−1922(21)	1513(12)	69(9)
C(12)	1533(16)	−1896(20)	2422(13)	60(8)
C(13)	1100(16)	−888(23)	2805(13)	72(10)
C(14)	367(16)	−290(23)	2157(13)	71(10)
C(15)	287(13)	−916(18)	1375(13)	54(8)
C(16)	5194(21)	−59(25)	2874(17)	99(13)
C(17)	4629(19)	−289(29)	3459(17)	119(14)
C(18)	4437(19)	938(36)	3797(13)	159(18)
C(19)	4916(26)	1776(28)	3373(21)	145(18)
C(20)	5341(20)	1172(35)	2865(20)	106(16)

[a] Equivalent isotropic temperature factor U_{eq} defined as 1/3 of the trace of orthogonalised U matrix.

Table 4. The structure belongs to a class of cubane-like clusters of chromium of which $Cp_4Cr_4(\mu_3\text{-}S)_4$ [24] and $Cp_4Cr_4(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2$ [8] have recently been structurally characterised. Being isostructural with the latter, **2** has randomly distributed μ_3-Se and μ_3-CO groups alternating with Cr at the corners of a distorted cube. Such "cubane-like" assemblies of chalcogen atoms and CO ligands are still rare, and have not been noted for any other transition metal. A comparison of some selected bond lengths and angles of these and related complexes is given in Table 7. It is observed that the small difference between the bonding parameters of **2** and those of its S analogue are attributable to the size difference between Se and S; both show a greater distortion from a regular cube than the parent compound $Cp_4Cr_4S_4$ [24].

Structure of 4

The perspective view of the molecule (shown in Fig. 2) reveals a cubane-like structure with two μ_3-oxo ligands, two μ_3-Se atoms, and four μ_3-Cr atoms alter-

Table 6

Selected bond lengths (Å) and bond angles (deg) for $(\eta^5\text{-}C_5H_5)_4Cr_4(\mu_3\text{-}O)_2(\mu_3\text{-}Se)_2$ (4)

Cr(1)–Cr(2)	2.916(4)	Cr(1)–Cr(3)	2.748(4)
Cr(1)–Cr(4)	3.020(4)	Cr(2)–Cr(3)	2.970(4)
Cr(2)–Cr(4)	3.093(4)	Cr(3)–Cr(4)	2.887(4)
Cr(2)–Se(1)	2.445(3)	Cr(3)–Se(1)	2.462(4)
Cr(4)–Se(1)	2.441(4)	Cr(1)–Se(2)	2.447(3)
Cr(2)–Se(2)	2.452(4)	Cr(4)–Se(2)	2.462(3)
Cr(1)–O(1)	1.94(1)	Cr(2)–O(1)	1.90(1)
Cr(3)–O(1)	1.90(1)	Cr(1)–O(2)	1.94(1)
Cr(3)–O(2)	1.94(1)	Cr(4)–O(2)	1.94(1)
Cr(1)–C(1)	2.26(2)	Cr(2)–C(6)	2.25(3)
Cr(1)–C(2)	2.24(2)	Cr(2)–C(7)	2.26(3)
Cr(1)–C(3)	2.21(2)	Cr(2)–C(8)	2.20(3)
Cr(1)–C(4)	2.25(2)	Cr(2)–C(9)	2.24(3)
Cr(1)–C(5)	2.25(3)	Cr(2)–C(10)	2.15(2)
Cr(3)–C(11)	2.22(2)	Cr(4)–C(16)	2.23(3)
Cr(3)–C(12)	2.24(2)	Cr(4)–C(17)	2.24(3)
Cr(3)–C(13)	2.23(2)	Cr(4)–C(18)	2.22(2)
Cr(3)–C(14)	2.23(2)	Cr(4)–C(19)	2.18(3)
Cr(3)–C(15)	2.25(2)	Cr(4)–C(20)	2.19(3)
Cr(2)–Cr(1)–Cr(3)	63.2(1)	Cr(2)–Cr(1)–Cr(4)	62.8(1)
Cr(3)–Cr(1)–Cr(4)	59.8(1)	Cr(1)–Cr(2)–Cr(3)	55.7(1)
Cr(1)–Cr(2)–Cr(4)	60.3(1)	Cr(3)–Cr(2)–Cr(4)	56.8(1)
Cr(1)–Cr(3)–Cr(2)	61.2(1)	Cr(1)–Cr(3)–Cr(4)	64.8(1)
Cr(2)–Cr(3)–Cr(4)	63.7(1)	Cr(1)–Cr(4)–Cr(2)	57.0(1)
Cr(1)–Cr(4)–Cr(3)	55.4(1)	Cr(2)–Cr(4)–Cr(3)	59.4(1)
Cr(2)–Se(1)–Cr(3)	74.5(1)	Cr(2)–Se(1)–Cr(4)	78.6(1)
Cr(3)–Se(1)–Cr(4)	72.1(1)	Cr(1)–Se(2)–Cr(2)	73.1(1)
Cr(1)–Se(2)–Cr(4)	75.9(1)	Cr(2)–Se(2)–Cr(4)	78.0(1)
Cr(1)–O(1)–Cr(2)	98.9(5)	Cr(1)–O(1)–Cr(3)	91.5(5)
Cr(2)–O(1)–Cr(3)	102.7(5)	Cr(1)–O(2)–Cr(3)	90.3(5)
Cr(1)–O(2)–Cr(4)	102.4(6)	Cr(3)–O(2)–Cr(4)	96.2(6)
O(1)–Cr(1)–O(2)	87.5(5)	O(1)–Cr(3)–O(2)	88.4(5)
Se(1)–Cr(2)–Se(2)	100.1(1)	Se(1)–Cr(4)–Se(2)	99.9(1)
O(1)–Cr(1)–Se(2)	93.6(3)	O(2)–Cr(1)–Se(2)	90.6(4)
O(1)–Cr(2)–Se(1)	91.2(3)	O(1)–Cr(2)–Se(2)	94.4(4)
O(1)–Cr(3)–Se(1)	90.7(3)	O(1)–Cr(3)–Se(1)	95.5(4)
O(2)–Cr(4)–Se(1)	96.2(4)	O(2)–Cr(4)–Se(2)	90.1(4)

nately occupying the corners of a cuboid. Atomic coordinates are listed in Table 5. Bond lengths and selected bond angles are given in Table 6. Table 7 shows a comparison with other chalcogen cubane structures and with $Cp_4Cr_4O_4$ (D_2 symmetry) [21]. Molecule 4 conforms closely to C_2 symmetry, with a two fold axis passing through the mid-points of the Cr(1)–Cr(3) and Cr(2)–Cr(4) bonds. As one of the few examples of μ_3-oxo metal clusters known to date [20–23,25–33], 4 is the second known tetranuclear Cr cluster, after $Cp_4Cr_4O_4$, of which it can be considered a Se derivative. Interest in such μ_3-oxo complexes lies in their role as models for catalytically active metal oxides and in the similarity of their bonding mode to that of oxygen atoms bonded to surfaces [34].

Table 7

Comparison of selected bond lengths (Å) and angles (deg) in some related cubane-like structures [a]

	$Cp_4Cr_4S_4$ [b]	$Cp_4Cr_4(CO)_2S_2$ [c,d]	$Cp_4Cr_4(CO)_2Se_2$ [d,e] (2)	$Cp_4Cr_4O_2Se_2$ [e] (4)	$Cp_4Cr_4O_4$ [f]
Cr–Cr	2.818– 2.891	2.651– 2.773	2.733– 2.848	2.748– 3.093	2.702– 2.900
Cr–Cr–Cr	58.7 – 61.2	57.2 – 61.6	57.6 – 61.6	55.4 – 64.8	56.2 –63.4
E–Cr	2.255– 2.263	2.218– 2.267	2.317– 2.402	2.441– 2.462	
E′–Cr				1.90 – 1.94	1.918– 1.949
E–Cr–E	98.6 –102.3	100.8 –106.2	102.2 –107.3	99.9 –100.1	
E′–Cr–E′				87.5 – 88.4	83.1 –90.4
Cr–E–Cr	77.1 – 79.7	73.0 – 76.4	71.7 – 74.2	72.1 – 78.6	
Cr–E′–Cr				90.3 –102.7	88.4 –97.1

[a] E = S, Se; E′ = 0. [b] Ref. 24. [c] Ref. 8. [d] CO and E are indistinguishable due to disorder. [e] This work. [f] Ref. 21.

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