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The effect of electron deficit on the geometry of sulphide bridged methylcyclopentadienylmetal tetrahedra. Synthesis, physicochemical characteristics, and molecular structures of $Cp'_3Cr_3(\mu_3\text{-}S)_4Co(CO)$, $Cp'_4Cr_4(\mu_3\text{-}O)(\mu_3\text{-}S)_3{}^+$ $ZnCl_3\cdot C_4H_8O^-$, and $Cp'_4V_4S_4$ ($Cp' = \pi\text{-}CH_3C_5H_4$)

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Abstract

A diamagnetic electron-saturated cluster, $Cp'_3Cr_3(\mu_3\text{-}S)_4Co(CO)$ (I), was obtained by heating a heterotrinuclear cluster, $Cp'_2Cr_2SCMe_3(\mu_3\text{-}S)_2Co(CO)_2$ ($Cp' = \pi\text{-}CH_3C_5H_4$), in heptane in the presence of diphenylacetylene. The treatment of $(Cp'CrSCMe_3)_2S$ with anhydrous $ZnCl_2$ in THF led to an electron-deficient cationic cluster, $Cp'_4Cr_4(\mu_3\text{-}O)(\mu_3\text{-}S)_3^+$ (II), with one unpaired electron ($ZnCl_3\cdot thf^-$ is the anion). Interaction between Cp'_2V and t-butylmercaptan in boiling heptane gives $Cp'_4V_4S_4$ (III) which is a new member in the family of cubane clusters, $Cp_4M_4S_4$, and contains an electron-deficient metal tetrahedral skeleton with two unpaired electrons. The structure of compounds I–III was determined by an X-ray diffraction study. I contains the metal tetrahedral Cr_3Co skeleton which is flattened down the axis joining Co and the centre of the Cr_3 base (Cr–Co 2.692(4), Cr–Cr 2.816(3) Å). The μ_3-S bridge is located above each face (Co–S average, 2.171(6) Å; Cr–S average, 2.255(5) Å). The Co atom is also linked to the terminal CO group (Co–C 1.82(2) Å), and each Cr atom is bonded to the $\pi\text{-}CH_3C_5H_4$ (Cr–C average, 2.29(2) Å. The cationic cluster in II is a distorted tetrahedron in which the Cr–Cr bonds at the sulphide bridge faces (average, 2.765(2) Å) are longer than those at the oxygen bridge face (average, 2.687(2) Å). The Cr–O bonds (average, 1.994(5) Å) are shorter than the Cr–S bonds (average, 2.224(3) Å), and both are shorter than their counterparts in the neutral cluster, $Cp'_4Cr_4(\mu_3\text{-}O)(\mu_3\text{-}S)_3 \cdot CuBr_2$ described previously, presumably because of the enhancement of π-bonding in both O–Cr and S–Cr bonds. This interaction is particularly noticeable in III, which has a strongly electron-deficient metal V_4 skeleton (V–S average, 2.292(3) Å) which gives rise to short V–V distances (average, 2.867(3) Å). The molecule of III is sterically not strained, the V–C distances (average, 2.28(1) Å) being close to distances expected for ordinary bonds. The physicochemical properties of I–III and the specific features of bonding peculiar to these clusters in relation to the electron deficit of their metal skeletons are discussed.

Introduction

Sulphide bridge clusters with a metal tetrahedral skeleton have attracted much attention as the synthetic analogues of 4Fe and 8Fe ferredoxins and also as the iron-molybdenum cofactor of nitrogenase. An exhaustive list of these clusters has been given in a recent review by Garner [1]. The metal skeleton in practically all of these compounds is either electron-saturated, that is having six ordinary M–M bonds, or electron-excessive which leads to weakening of some or even all of the M–M bonds. The first group of clusters includes, $[(NO)FeS]_4$ (Fe–Fe 2.634(1) Å) [2], $[(CN)_3Re(\mu_3\text{-}S)]_4{}^{4-}$ (Re–Re 2.755(5) Å) [3], $Cp_4Mo_4S_4$ [4], and $[i\text{-}PrC_5H_4Mo(\mu_3\text{-}S)]_4$ (Mo–Mo 2.904(3) Å) [5]. The second group of clusters is exemplified by the iron or cobalt cyclopentadienylsulphides $(CpMS)_4{}^{n+}$. The M–M bonds are totally absent in these compounds at M = Co and $n = 0$ (Co–Co 3.30(4) Å) whereby, according to Dahl's scheme [6], 6 bonding $(a_1 + e + 1t_1)$ and 6 antibonding $(2t_1 + t_2)$ orbitals of the metal skeleton are occupied. A gradual decrease of the number of electrons in the antibonding orbitals brings about, and enhances, the bonding interactions in the metal skeleton (Table 1).

It was of interest to analyse a situation in which further decrease in the number of electrons induces their withdrawal from the bonding orbitals of the metal skeleton. As a matter of principle, this should have weakened the M–M bonds as compared with complexes whose metal skeleton is electron-saturated. However, recent study of the products of oxidation of $(i\text{-}PrC_5H_4)_4Mo_4S_4$ [5] has shown that the transition to the mono- and di-cation had in fact exerted no influence on the Mo–Mo distances (Table 1). In our studies we examined the changes that occurred in the geometry and in the physicochemical properties of metal tetrahedral clusters on going from the uncharged cluster $Cp'_4Cr_4OS_3 \cdot CuBr_2$ [7] ($Cp' = \pi\text{-}CH_3C_5H_4$) to the mono-cationic cluster $Cp'_4Cr_4OS_3{}^+(ZnCl_3thf)^-$ and also from the chromium cluster $Cp'_4Cr_4S_4$ [7] to a similar vanadium cluster $Cp'_4V_4S_4$ having 4 electrons less. The choice of methylcyclopentadienyl clusters was determined by solubility; clusters studied previously $Cp_4Cr_4S_4$ [8] and $Cp_4V_4S_4$ [9], had poor solubility and could not be obtained as single crystals suitable for X-ray structure analysis. However, we recently found that the introduction of electron-donating methyl groups into the rings strengthens slightly the metal skeleton in the triangular cluster $Cp'_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ (Cr–Cr 2.590 Å; Cr–Co (average) 2.550 Å; Cr–S 2.28 Å) [10] as opposed to $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ (2.617, 2.592, and 2.24 Å,

Table 1

Distances between metal atoms in the $(\text{CpMS})_4^{n+}$ clusters

Anion	M	n	Number of electrons on antibonding orbitals	M ··· M (Å)	Reference
–	Co	0	12	3.30(4)	1
PF_6^-	Co	1	11	2×3.330(5) 4×3.172(5)	1
–	Fe	0	8	4×3.363(10) 2×2.650(6)	1
Br^-	Fe	1	7	2×3.319(3) 2×3.188(3) 2×2.652(4)	1
$(PF_6^-)_2$	Fe	2	6	2×3.254(3) 4×2.834(3)	1
–	Cr [a]	0	0	6×2.822(1)	7
–	Mo	0	0		
–	Mo [b]	0	0	6×2.904(3)	5
PF_6^-	Mo [b]	+1	0	6×2.894(3)	5
$(I^-)_2$	Mo [b]	+2	0	6×2.858(2)	5

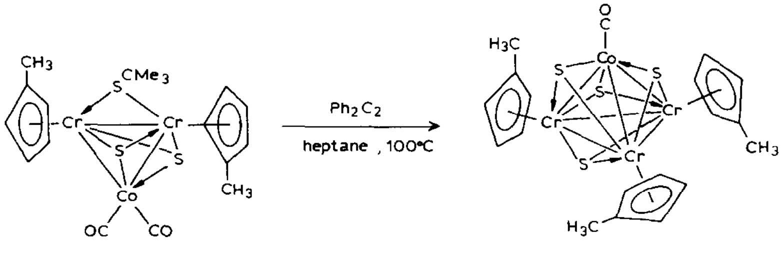
[a] Cp = $CH_3C_5H_4$. [b] Cp = i-PrC_5H_4.

respectively) [11] with simultaneous emergence of a staggered ring conformation instead of one which is eclipsed. For this reason, and in order to elucidate the effect of methyl groups in the rings on the geometry of tetrahedral clusters we synthesized and studied the heterometallic cluster $Cp'_3Cr_3S_4Co(CO)$, similar to the $Cp_3Cr_3S_4Co(CO)$ cluster studied previously [12].

Results

Synthesis and properties

The $Cp'_3Cr_3S_4Co(CO)$ cluster (I) ($Cp' = MeC_5H_4$) was obtained by use of a technique similar to that for the synthesis of $Cp_3Cr_3S_4Co(CO)$ [12], i.e. by heating $(Cp'CrS)_2SCMe_3Co(CO)_2$ in heptane in the presence of diphenylacetylene:



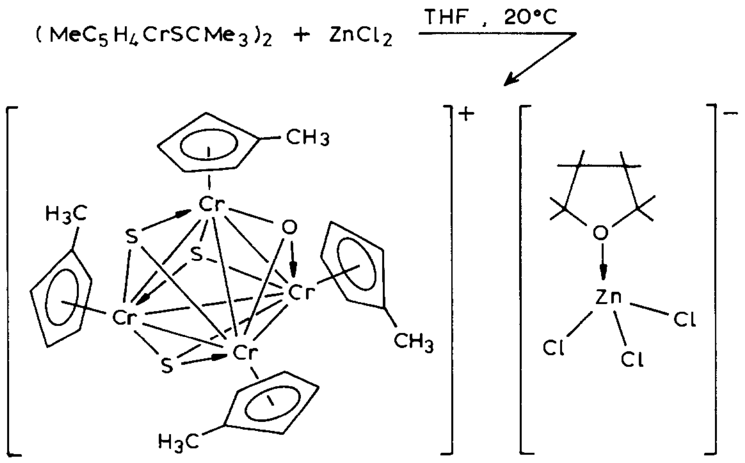
(I)

I was isolated pure by recrystallization from heptane in the form of air-stable, brown crystals, which were soluble in organic solvents. Its IR spectrum shows an intense stretching vibration band of the CO group at 1900 cm^{-1}, and bands at 2960–2830, 1485, 1440, 1360, 1015, and 805 cm^{-1} characteristic of the $CH_3C_5H_4$

Table 2

Atomic coordinates for $(MeC_5H_4)_3Cr_3(\mu_3\text{-}S)_4Co(CO)$ ($\times 10^3$; except for Co, Cr and S; $\times 10^4$). Anisotropic temperature factors are as: $T = \exp - 1/4(B_{11}a^{\star}n + B_{22}b^{\star}k + B_{33}c^{\star}l + 2B_{12}a^{\star}b^{\star}hk + 2B_{13}a^{\star}c^{\star}hl + 2B_{23}b^{\star c\star}kl)$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	−2169(3)	2468(2)	2667(2)	1.8(1)	1.7(1)	3.3(1)	0.0(1)	−0.34(9)	0.2(1)
Cr(1)	115(3)	1408(2)	2327(2)	0.23(9)	0.39(9)	1.0(1)	0.03(9)	0.04(8)	0.0(1)
Cr(2)	−1980(3)	1333(1)	3834(2)	−0.24(8)	0.05(9)	0.74(9)	−0.01(8)	0.04(7)	0.27(1)
Cr(3)	597(3)	2408(1)	3739(2)	0.11(9)	0.4(1)	1.2(1)	0.06(9)	−0.08(8)	0.0(1)
S(1)	830(6)	1169(3)	3775(4)	1.6(2)	1.7(2)	3.6(3)	−0.3(2)	−0.3(2)	0.3(2)
S(2)	381(6)	2661(3)	2236(4)	1.9(2)	2.3(2)	3.8(3)	0.0(2)	0.4(2)	0.3(2)
S(3)	−2732(6)	1314(3)	2342(4)	2.0(2)	1.7(2)	3.3(3)	0.0(2)	−0.5(2)	0.1(2)
S(4)	−2122(6)	2579(3)	4114(4)	2.0(2)	2.1(2)	3.2(3)	−0.3(2)	0.2(2)	−0.4(2)
O	−464(2)	347(1)	183(1)	3.1(8)	3.3(8)	7(1)	1.8(6)	−1.7(8)	1.5(8)
C	−374(3)	308(1)	216(2)	2(1)	4(1)	10(2)	−1.6(9)	−4(1)	2(1)
C(11)	14(3)	43(1)	134(2)	2.0(9)	6(1)	4(1)	1.6(9)	0.7(9)	−2(1)
C(12)	148(2)	36(1)	196(1)	3(1)	3(1)	1.3(9)	1.2(8)	0.0(8)	−0.3(8)
C(13)	258(3)	95(1)	179(1)	2.5(9)	4(1)	2(1)	−0.5(9)	0.1(8)	−0.7(9)
C(14)	187(3)	141(1)	115(2)	4(1)	5(1)	3(1)	0(1)	1.0(9)	0(1)
C(15)	34(3)	112(1)	88(2)	4(1)	4(1)	4(1)	−1.0(9)	−0.5(9)	1(1)
C(16)	−131(3)	−16(2)	123(2)	3(1)	6(2)	13(3)	−3(1)	3(1)	−6(2)
C(21)	−361(2)	119(1)	507(1)	1.5(8)	4(1)	3(1)	0.3(8)	0.2(8)	0.0(9)
C(22)	−448(2)	89(1)	432(1)	1.5(8)	3(1)	3(1)	−0.1(8)	0.7(8)	1.4(9)
C(23)	−366(2)	24(1)	399(1)	1.8(9)	3(1)	3(1)	0.4(8)	0.4(7)	0.6(9)
C(24)	−218(2)	21(1)	455(1)	1.9(9)	4(1)	2.0(9)	0.2(8)	−0.2(7)	1.4(9)
C(25)	−225(3)	82(1)	519(2)	3(1)	5(1)	3(1)	−0.1(9)	0.6(9)	−1(1)
C(26)	−416(3)	−25(1)	323(2)	4(1)	3(1)	4(1)	−0.2(9)	0.1(9)	−1(1)
C(31)	336(2)	263(1)	405(1)	3.0(9)	4(1)	2(1)	−0.3(9)	−1.8(8)	−0.8(9)
C(32)	256(2)	245(1)	488(1)	2.5(8)	2.3(9)	4(1)	−1.0(8)	−0.4(8)	−0.2(9)
C(33)	136(2)	295(1)	509(1)	3(1)	5(1)	1.4(9)	1.3(9)	−1.2(8)	−0.5(9)
C(34)	140(2)	352(1)	438(2)	4(1)	1.1(9)	4(1)	−0.2(8)	−0.8(9)	0(9)
C(35)	268(2)	333(1)	371(2)	2.0(9)	2.3(9)	5(1)	−0.7(8)	0.5(9)	−0.6(9)
C(36)	28(3)	422(1)	437(2)	3(1)	2(1)	8(2)	0.9(9)	0(1)	−1(1)



(II)

ligands. From magnetic susceptibility measurements, I was found to be diamagnetic. The mass spectrum of the complex features a peak with the highest mass of 580 corresponding to $[P-\mathrm{CO}]^+$ along with peaks of the products of the successive

Table 3

Bond lengths (Å) for $(\mathrm{MeC_5H_4})_3\mathrm{Cr_3}(\mu_3\text{-S})_4\mathrm{Co(CO)}$

Co–Cr(1)	2.692(4)	Cr(3)–S(2)	2.287(6)
Co–Cr(2)	2.688(4)	Cr(3)–S(4)	2.268(5)
Co–Cr(3)	2.695(3)	Cr(3)–C(31)	2.28(2)
Co–S(2)	2.169(5)	Cr(3)–C(32)	2.29(2)
Co–S(3)	2.181(6)	Cr(3)–C(33)	2.30(2)
Co–S(4)	2.164(6)	Cr(3)–C(34)	2.31(2)
Co–C	1.82(2)	Cr(3)–C(35)	2.35(2)
Cr(1)–Cr(2)	2.827(3)	O–C	1.11(3)
Cr(1)–Cr(3)	2.791(4)	C(11)–C(12)	1.41(3)
Cr(1)–S(1)	2.260(6)	C(11)–C(15)	1.43(3)
Cr(1)–S(2)	2.273(6)	C(11)–C(16)	1.57(3)
Cr(1)–S(3)	2.273(5)	C(12)–C(13)	1.41(3)
Cr(1)–C(11)	2.30(2)	C(13)–C(14)	1.38(3)
Cr(1)–C(12)	2.26(2)	C(14)–C(15)	1.38(3)
Cr(1)–C(13)	2.29(2)	C(21)–C(22)	1.42(3)
Cr(1)–C(14)	2.26(2)	C(21)–C(25)	1.28(3)
Cr(1)–C(15)	2.22(2)	C(22)–C(23)	1.42(3)
Cr(2)–Cr(3)	2.829(3)	C(23)–C(24)	1.42(3)
Cr(2)–S(1)	2.260(5)	C(23)–C(26)	1.49(3)
Cr(2)–S(3)	2.290(6)	C(24)–C(25)	1.47(3)
Cr(2)–S(4)	2.291(6)	C(31)–C(32)	1.44(3)
Cr(2)–C(21)	2.29(2)	C(31)–C(35)	1.46(3)
Cr(2)–C(22)	2.27(2)	C(32)–C(33)	1.36(3)
Cr(2)–C(23)	2.39(2)	C(33)–C(34)	1.47(3)
Cr(2)–C(24)	2.29(2)	C(34)–C(35)	1.49(3)
Cr(2)–C(25)	2.24(2)	C(34)–C(36)	1.54(3)
Cr(3)–S(1)			

Table 4

Bond angles (°) for $(\mathrm{MeC_5H_4})_3\mathrm{Cr_3}(\mu_3\text{-S})_4\mathrm{Co(CO)}$

Cr(1)CoCr(2)	63.38(9)	Cr(3)Cr(1)S(1)	51.5(1)
Cr(1)CoCr(3)	62.41(9)	Cr(3)Cr(1)S(2)	52.5(1)
Cr(1)CoS(2)	54.5(2)	Cr(3)Cr(1)S(3)	99.4(2)
Cr(1)CoS(3)	54.4(2)	S(1)Cr(1)S(2)	103.0(2)
Cr(1)CoS(4)	104.8(2)	S(1)Cr(1)S(3)	102.0(2)
Cr(1)CoC	144.5(8)	S(2)Cr(1)S(3)	99.7(2)
Cr(2)CoCr(3)	63.42(9)	CoCr(2)Cr(1)	58.38(9)
Cr(2)CoS(2)	105.9(2)	CoCr(2)Cr(3)	58.41(9)
Cr(2)CoS(3)	54.9(2)	CoCr(2)S(1)	96.7(2)
Cr(2)CoS(4)	55.1(2)	CoCr(2)S(3)	51.2(1)
Cr(2)CoC	139.3(8)	CoCr(2)S(4)	50.8(1)
Cr(3)CoS(2)	54.8(2)	Cr(1)Cr(2)Cr(3)	59.14(9)
Cr(3)CoS(3)	104.8(2)	Cr(1)Cr(2)S(1)	51.3(1)
Cr(3)CoS(4)	54.3(2)	Cr(1)Cr(2)S(3)	51.5(1)
Cr(3)CoC	144.7(8)	Cr(1)Cr(2)S(4)	97.4(2)
S(2)CoS(3)	106.1(2)	Cr(3)Cr(2)S(1)	50.9(1)
S(2)CoS(4)	106.4(2)	Cr(3)Cr(2)S(3)	97.9(2)
S(2)CoC	114.9(8)	Cr(3)Cr(2)S(4)	51.3(1)
S(3)CoS(4)	108.0(2)	S(1)Cr(2)S(3)	101.5(2)
S(3)CoC	110.5(8)	S(1)Cr(2)S(4)	100.9(2)
S(4)CoC	110.7(8)	S(3)Cr(2)S(4)	100.2(2)
CoCr(1)Cr(2)	58.24(9)	CoCr(3)Cr(1)	58.75(9)
CoCr(1)Cr(3)	58.84(9)	CoCr(3)Cr(2)	58.18(9)
CoCr(1)S(1)	96.6(2)	CoCr(3)S(1)	96.9(2)
CoCr(1)S(2)	50.9(2)	CoCr(3)S(2)	50.8(2)
CoCr(1)S(3)	51.3(1)	CoCr(3)S(4)	50.8(1)
Cr(2)Cr(1)Cr(3)	60.48(9)	Cr(1)Cr(3)Cr(2)	60.38(9)
Cr(2)Cr(1)S(1)	51.3(1)	Cr(1)Cr(3)S(1)	52.0(1)
Cr(2)Cr(1)S(2)	98.8(2)	Cr(1)Cr(3)S(2)	52.0(1)
Cr(2)Cr(1)S(3)	52.0(1)	Cr(1)Cr(3)S(4)	99.0(2)
Cr(2)Cr(3)S(1)	51.3(1)	C(12)C(11)C(16)	124(2)
Cr(2)Cr(3)S(2)	98.4(2)	C(15)C(11)C(16)	129(2)
Cr(2)Cr(3)S(4)	52.0(1)	C(11)C(12)C(13)	106(2)
S(1)Cr(3)S(2)	103.0(2)	C(12)C(13)C(14)	110(2)
S(1)Cr(3)S(4)	102.0(2)	C(13)C(14)C(15)	108(2)
S(2)Cr(3)S(4)	99.3(2)	C(11)C(15)C(14)	108(2)
Cr(1)S(1)Cr(2)	77.4(2)	C(22)C(21)C(25)	108(2)
Cr(1)S(1)Cr(3)	76.6(2)	C(21)C(22)C(23)	111(2)
Cr(2)S(1)Cr(3)	77.8(2)	C(22)C(23)C(24)	103(2)
CoS(2)Cr(1)	74.6(2)	C(22)C(23)C(26)	129(2)
CoS(2)Cr(3)	74.4(2)	C(24)C(23)C(26)	128(2)
Cr(1)S(2)Cr(3)	75.5(2)	C(23)C(24)C(25)	108(2)
CoS(3)Cr(1)	74.4(2)	C(21)C(25)C(24)	110(2)
CoS(3)Cr(2)	73.9(2)	C(32)C(31)C(35)	109(2)
Cr(1)S(3)Cr(2)	76.6(2)	C(31)C(32)C(33)	112(2)
CoS(4)Cr(2)	74.2(2)	C(32)C(33)C(34)	106(2)
CoS(4)Cr(3)	74.9(2)	C(33)C(34)C(35)	110(2)
Cr(2)S(4)Cr(3)	76.7(2)	C(33)C(34)C(36)	124(2)
CoCO	177(2)	C(35)C(34)C(36)	126(2)
C(12)C(11)C(15)	108(2)	C(31)C(35)C(34)	103(2)

detachments of the $\mathrm{CH_3C_5H_4}$ ligands from three chromium atoms, and finally give the $\mathrm{Cr_3CoS_4}^+$ ion (*m/e* 343).

Cyclic voltammetry of I in DMF ($\mathrm{NaBF_4}$ as background electrolyte) reveals 4 oxidation waves, three of which (−1.07, −0.23, +0.23 V) are reversible one-electron steps and the last (+0.80 V) is a two-electron irreversible process.

The cationic cluster $Cp'_4Cr_3OS_3{}^+(ZnCl_3 \cdot thf)^-$ (II) was obtained from the reaction of $(Cp'CrSCMe_3)_2S$ with anhydrous zinc chloride in tetrahydrofuran at 20 °C. Analytically pure II was isolated as dark blue needle-like crystals stable in air. The IR spectrum of II contains bands characteristic of π-$CH_3C_5H_4$ ligands at 810, 1010,

Table 5

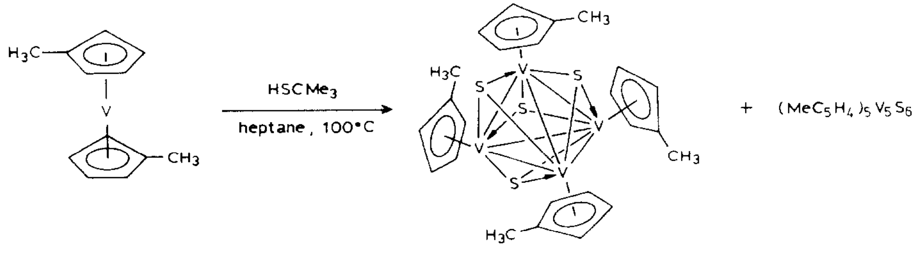
Atomic coordinates for $[(MeC_5H_4)_4Cr(\mu_3\text{-}S)_3(\mu_3\text{-}O)]^+[ZnCl_3 \cdot thf]^-$ ($\times 10^4$; except for Zn, Cr, S and Cl, $\times 10^5$) [a]

Atom	*x*	*y*	*z*
Zn	49760(12)	53922(6)	69292(6)
Cr(1)	2782(15)	81097(7)	50391(7)
Cr(2)	−13547(14)	69229(7)	50892(7)
Cr(3)	−23654(15)	80007(8)	41333(7)
Cr(4)	−20842(16)	82370(8)	55273(8)
S(1)	−35402(24)	74443(14)	48325(13)
S(2)	−4929(30)	72874(16)	42215(16)
S(3)	−14066(29)	89643(14)	47733(14)
Cl(1)	42414(29)	59496(16)	59209(15)
Cl(2)	34484(32)	45769(17)	71755(17)
Cl(3)	61773(37)	60568(20)	77971(18)
O	−326(5)	7630(2)	5812(3)
O_t(1)	6590(6)	4708(4)	6737(3)
C_t(1)	6318(12)	4202(6)	6168(6)
C_t(2)	7660(17)	3827(9)	6222(9)
C_t(3)	8692(13)	4105(8)	6762(8)
C_t(4)	8023(9)	4656(6)	7109(5)
C(11)	2233(11)	8184(6)	4643(5)
C(12)	2569(9)	7817(5)	5268(6)
C(13)	2383(9)	8295(6)	5810(5)
C(14)	1896(11)	8956(5)	5465(6)
C(15)	1830(11)	8861(6)	4774(6)
C(16)	2658(12)	8140(9)	6546(5)
C(21)	14(10)	5920(4)	5251(5)
C(22)	−424(9)	6040(4)	5858(5)
C(23)	−1966(9)	6015(5)	5701(5)
C(24)	−2399(11)	5834(5)	5003(7)
C(25)	−1208(14)	5793(5)	4727(5)
C(26)	587(10)	6174(6)	6545(5)
C(31)	−4429(11)	8010(7)	3365(5)
C(32)	−3894(12)	8725(6)	3427(5)
C(33)	−2638(13)	8707(7)	3225(5)
C(34)	−2346(13)	8040(8)	3042(5)
C(35)	−3422(12)	7561(6)	3131(5)
C(36)	−4690(21)	9368(10)	3679(9)
C(41)	−1838(14)	9121(7)	6312(6)
C(42)	−3139(12)	9217(7)	5867(6)
C(43)	−3925(11)	8613(8)	5932(7)
C(44)	−2996(18)	8166(7)	6419(7)
C(45)	−1697(14)	~~8494~~(9)	6628(7)
C(46)	−2833(35)	7552(10)	6841(14)

[a] Atoms with t-index constitute the THF ligand.

1425, and 3070 cm^{-1}. The mass spectrum of II reveals the presence of a peak (*m/e* 636) corresponding to the $(MeC_5H_4)_4Cr_4S_3O^+$ cation. The complex contains 1 unpaired electron: μ_{eff} (1.68 BM) does not change with temperature. Cyclic voltammetry in DMF reveals that there are two reversible waves of one-electron oxidations (at −0.16 and +0.60 V) for II.

The tetrahedral cluster of vanadium $Cp'_4V_4S_4$ (III) was obtained in the same way of that for $Cp_4V_4S_4$ [9], i.e. by boiling Cp'_2V with t-butylmercaptan in heptane:



(III)

In addition to III, a pentanuclear cluster, $Cp'_5V_5S_6$ resulted and was separated from III by chromatography on Al_2O_3. The cluster is a trigonal bipyramid and will be described later. The dark brown crystals of III, which were isolated, are relatively stable in air and readily soluble in organic solvents. Differential thermal analysis shows that under pure argon and in the presence of an Al_2O_3 filter, III melts at

Table 6

Bond lengths (Å) for $[(MeC_5H_4)_4Cr_4(\mu_3\text{-}S)_3(\mu_3\text{-}O)]^+ [ZnCl_3\cdot thf]^-$

Zn–Cl(1)	2.225(3)	Cr(2)–C(25)	2.193(9)
Zn–Cl(2)	2.221(3)	Cr(3)–Cr(4)	2.784(2)
Zn–Cl(3)	2.208(4)	Cr(3)–S(1)	2.242(3)
Zn–O_t(1)	2.092(7)	Cr(3)–S(2)	2.189(3)
Cr(1)–Cr(2)	2.681(2)	Cr(3)–S(3)	2.237(3)
Cr(1)–Cr(3)	2.757(2)	Cr(3)–C(31)	2.20(1)
Cr(1)–Cr(4)	2.686(2)	Cr(3)–C(32)	2.22(1)
Cr(1)–S(2)	2.214(3)	Cr(3)–C(33)	2.20(1)
Cr(1)–S(3)	2.214(3)	Cr(3)–C(34)	2.20(1)
Cr(1)–O	1.984(6)	Cr(3)–C(35)	2.181(9)
Cr(1)–C(11)	2.21(1)	Cr(4)–S(1)	2.248(3)
Cr(1)–C(12)	2.203(9)	Cr(4)–S(3)	2.221(3)
Cr(1)–C(13)	2.260(9)	Cr(4)–O	1.983(5)
Cr(1)–C(14)	2.21(1)	Cr(4)–C(41)	2.22(1)
Cr(1)–C(15)	2.18(1)	Cr(4)–C(42)	2.23(1)
Cr(2)–Cr(3)	2.753(2)	Cr(4)–C(43)	2.22(1)
Cr(2)–Cr(4)	2.694(2)	Cr(4)–C(44)	2.18(2)
Cr(2)–S(1)	2.247(3)	Cr(4)–C(45)	2.21(1)
Cr(2)–S(2)	2.203(3)	O_t(1)–C_t(1)	1.44(1)
Cr(2)–O	2.015(6)	O_t(1)–C_t(4)	1.40(1)
Cr(2)–C(21)	2.225(8)	C_t(1)–C_t(2)	1.44(2)
Cr(2)–C(22)	2.259(9)	C_t(2)–C_t(3)	1.38(2)
Cr(2)–C(23)	2.219(9)	C_t(3)–C_t(4)	1.45(2)
Cr(2)–C(24)	2.21(1)		

95 °C, and decomposes endothermally at 105 °C accompanied by the condensation of a colourless organic oil on the walls of the quartz cell. The IR spectrum of III features the bands peculiar to the π-$CH_3C_5H_4$ ligands. The mass spectrum of III contains a peak of the molecular ion (m/e 648) and the peaks of the products of the successive detachments of Cp′ ligands, to result in the $V_4S_4^+$ ion (m/e 332). III is paramagnetic and has two unpaired electrons with μ_{eff} (2.76 BM), close to a purely spin value and temperature-independent). By cyclic voltammetry, it was found that

Table 7

Bond angles (°) for $[(MeC_5H_4)_4Cr_4(\mu_3\text{-}S)_3(\mu_3\text{-}O)]^+ [ZnCl_3 \cdot thf]^-$

Cl(1)ZnCl(2)	115.0(1)	Cr(3)Cr(2)S(1)	52.09(8)
Cl(1)ZnCl(3)	117.7(1)	Cr(3)Cr(2)S(2)	50.94(9)
Cl(1)ZnO$_t$(1)	101.0(2)	Cr(3)Cr(2)O	94.7(2)
Cl(2)ZnCl(3)	115.9(1)	Cr(4)Cr(2)S(1)	53.22(8)
Cl(2)ZnO$_t$(1)	101.7(2)	Cr(4)Cr(2)S(2)	99.69(9)
Cl(3)ZnO$_t$(1)	101.5(2)	Cr(4)Cr(2)O	47.1(2)
Cr(2)Cr(1)Cr(3)	60.82(5)	S(1)Cr(2)S(2)	101.4(1)
Cr(2)Cr(1)Cr(4)	60.24(5)	S(1)Cr(2)O	99.7(2)
Cr(2)Cr(1)S(2)	52.43(9)	S(2)Cr(2)O	99.7(2)
Cr(2)Cr(1)S(3)	99.94(9)	Cr(1)Cr(3)Cr(2)	58.23(5)
Cr(2)Cr(1)O	48.4(2)	Cr(1)Cr(3)Cr(4)	58.00(5)
Cr(3)Cr(1)Cr(4)	61.51(5)	Cr(1)Cr(3)S(1)	98.02(9)
Cr(3)Cr(1)S(2)	50.82(9)	Cr(1)Cr(3)S(2)	51.65(9)
Cr(3)Cr(1)S(3)	52.10(8)	Cr(1)Cr(3)S(3)	51.35(8)
Cr(3)Cr(1)O	95.3(2)	Cr(2)Cr(3)Cr(4)	58.21(5)
Cr(4)Cr(1)S(2)	99.60(9)	Cr(2)Cr(3)S(1)	52.24(8)
Cr(4)Cr(1)S(3)	52.85(8)	Cr(2)Cr(3)S(2)	51.40(9)
Cr(4)Cr(1)O	47.4(2)	Cr(2)Cr(3)S(3)	97.25(9)
S(2)Cr(1)S(3)	101.4(1)	Cr(4)Cr(3)S(1)	51.79(8)
S(2)Cr(1)O	100.2(2)	Cr(4)Cr(3)S(2)	97.37(9)
S(3)Cr(1)O	99.4(2)	Cr(4)Cr(3)S(3)	51.10(8)
Cr(1)Cr(2)Cr(3)	60.95(5)	S(1)Cr(3)S(2)	102.0(1)
Cr(1)Cr(2)Cr(4)	59.98(5)	S(1)Cr(3)S(3)	101.1(1)
Cr(1)Cr(2)S(1)	100.12(9)	S(2)Cr(3)S(3)	101.5(1)
Cr(1)Cr(2)S(2)	52.82(9)	Cr(1)Cr(4)Cr(2)	59.78(5)
Cr(1)Cr(2)O	47.4(2)	Cr(1)Cr(4)Cr(3)	60.49(5)
Cr(3)Cr(2)Cr(4)	61.47(5)	Cr(1)Cr(4)S(1)	99.91(9)
Cr(1)Cr(4)S(3)	52.59(8)	Cr(1)S(2)Cr(3)	77.5(1)
Cr(1)Cr(4)O	47.4(2)	Cr(2)S(2)Cr(3)	77.7(1)
Cr(2)Cr(4)Cr(3)	60.32(5)	Cr(1)S(3)Cr(3)	76.6(1)
Cr(2)Cr(4)S(1)	53.15(8)	Cr(1)S(3)Cr(4)	74.6(1)
Cr(2)Cr(4)S(3)	99.37(9)	Cr(3)S(3)Cr(4)	77.3(1)
Cr(2)Cr(4)O	48.1(2)	Cr(1)OCr(2)	84.2(2)
Cr(3)Cr(4)S(1)	51.58(8)	Cr(1)OCr(4)	85.3(2)
Cr(3)Cr(4)S(3)	51.60(8)	Cr(2)OCr(4)	84.7(2)
Cr(3)Cr(4)O	94.5(2)	ZnO$_t$(1)C$_t$(1)	121.5(6)
S(1)Cr(4)S(3)	101.4(1)	ZnO$_t$(1)C$_t$(4)	128.1(6)
S(1)Cr(4)O	100.6(2)	C$_t$(1)O$_t$(1)C$_t$(4)	110.4(8)
S(3)Cr(4)O	99.2(2)	O$_t$(1)C$_t$(1)C$_t$(2)	105(1)
Cr(2)S(1)Cr(3)	75.67(9)	C$_t$(1)C$_t$(2)C$_t$(3)	110(1)
Cr(2)S(1)Cr(4)	73.63(9)	C$_t$(2)C$_t$(3)C$_t$(4)	108(1)
Cr(3)S(1)Cr(4)	76.64(9)	O$_t$(1)C$_t$(4)C$_t$(3)	106.3(9)
Cr(1)S(2)Cr(2)	74.8(1)		

Table 8

Atomic coordinates for $(MeC_5H_4)_4V_4(\mu_3\text{-}S)$ ($\times 10^4$; except for V, $\times 10^5$). Anisotropic temperature factors are given as: $T = \exp[-1/4(B_{11}h^2a^{\star 2} + \ldots 2B_{12}hka^{\star}b^{\star}\ldots)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
V	31183(8)	43230(9)	5589(9)	1.14(5)	1.56(7)	1.40(6)	0.32(5)	−0.15(5)	−0.06(5)
S	1730(1)	4165(1)	689(1)	1.28(8)	1.41(9)	1.79(9)	0.14(6)	0.13(8)	0.259
C(1)	3329(6)	3021(6)	1009(6)	2.2(4)	2.3(4)	2.6(5)	0.4(4)	0.0(4)	0.8(4)
C(2)	4012(6)	3259(6)	542(6)	1.8(4)	2.6(5)	2.2(4)	0.5(3)	−0.3(3)	0.3(4)
C(3)	4367(7)	3912(6)	1005(7)	1.8(4)	2.6(5)	3.7(5)	0.7(4)	−0.7(4)	−0.0(4)
C(4)	3906(6)	4056(6)	1688(6)	2.5(5)	2.4(5)	2.6(5)	0.6(4)	−1.5(4)	0.1(4)
C(5)	3298(7)	3539(7)	1694(7)	4.3(7)	3.3(5)	2.3(5)	2.3(5)	0.4(4)	1.2(4)
C(6)	2756(7)	2321(7)	769(8)	3.2(5)	2.9(5)	4.9(7)	0.3(4)	1.1(5)	1.2(5)

III is oxidized in DMF in 4 reversible one-electron steps at −1.16, −0.22, +0.56, +1.02 V.

Structures

The $Cp'_3Cr_3S_4Co(CO)$ cluster (I) is crystallized in a monoclinic system; space group $P2_1/n$; *a* 7.959(4), *b* 18.043(1), *c* 14.891(9) Å; *β* 91.19(5)°, *V* 2137.9 Å^3, $Z = 4$. The atomic coordinates are listed in Table 2, bond lengths and valence angles, in Tables 3 and 4, respectively.

The metal skeleton of I is a distorted Cr_3Co tetrahedron because of shorter Co–Cr distances (2.692(4) Å (av.)), compared with Cr–Cr separations (2.816(3) Å (av.)). The tridentate sulphide bridges (average bond lengths of Co–S 2.171(6), Cr–S(1) 2.255(5), Cr–S 2.280(6) Å) are located above the faces of the Cr_3Co tetrahedron so that a pseudocubane structure, Cr_3CoS_4, arises. Also, each Cr atom is linked to the π-coordinated $CH_3C_5H_4$ ligand (Cr–C (av.) 2.29(2) Å, C–C (in Cp′) 1.42(3) Å (av.)), and the Co atom to the terminal carbonyl group (Co–C separation is 1.82(2) Å, (C–O 1.11(3) Å). The presence of methyl groups in the Cp′ ligands ($C_{C_5H_4}$–C_{CH_3} 1.53(3) Å (av.)) gives rise to short $CH_3 \cdots S$ contacts (2.90–3.15 Å).

The ionic cluster $Cp'_4Cr_4OS_3{}^+ZnCl_3 \cdot thf^-$ (II) is crystallized in a monoclinic system; space group $P2_1/n$; *a* 9.6002(9), *b* 18.1621(8), *c* 20.1040(20) Å, *β* 103.738(8)°, *V* 3405.0 Å^3, $Z = 4$. The atomic coordinates are listed in Table 5, bond lengths and valence angles, in Tables 6 and 7, respectively. The metal skeleton in the cation is a distorted tetrahedron composed of Cr atoms; each of which is coordinated to a π-$CH_3C_5H_4$ (Cr–C 2.21(1) Å (av.); $C_{C_5H_4}$–$C_{C_5H_4}$ 1.38(2) Å (av.); C_{CH_3}–$C_{C_5H_4}$ 1.48(s) Å (av.)). Tridentately bound sulphur atoms are located above the three tetrahedron faces (Cr–S 2.224(3) Å (av.)), and the tridentately bound oxygen atom is located above the fourth face (Cr–O 1.994(5) Å (av.)). The Cr–Cr bonds at the oxygen-bridge face (2.687(2) Å (av.)) are shorter than at the sulphide-bridge faces (2.765(2) Å (av.)). Short $CH_3 \cdots S$ contacts (2.90–3.10 Å) are present. The zinc atom in the $(ZnCl_3 \cdot thf)^-$ anion is pseudotetrahedrally surrounded by three Cl atoms (Zn–Cl 2.218(3) Å (av.)) and one oxygen atom of the coordinated tetrahydrofuran molecule (Zn–O 2.092(7), O–C 1.42(1) (av.), C–C 1.42(2) Å (av.)). The ClZnCl angles are on average, 116.3(1)°, the ClZnO angles are 101.4(2)° (av.).

The vanadium cluster $Cp'_4V_4S_4$ (III) has a cubic crystal system (space group $P\bar{4}3n$, *a* 16.348(4) Å, $Z = 6$). The atomic coordinates are listed in Table 8, bond lengths in Table 9 and valence angles in Table 10. The metal skeleton in III is a symmetric tetrahedron (V–V 2.867(3) Å (av.) with tridentately bound sulphur atoms above each face (V–S 2.29(4) Å (av.)). Each vanadium atom is coordinated with

Table 9

Bond lengths (Å) for $(MeC_5H_4)_4V_4(\mu_3\text{-}S)_4$ [a]

V–V′	2.870(2)	V–C(1)	2.28(1)	C(1)–C(5)	1.41(2)
V–V″	2.865(2)	V–C(2)	2.272(9)	C(1)–C(6)	1.53(2)
V–V‴	2.865(2)	V–C(3)	2.27(1)	C(2)–C(3)	1.43(1)
V–S	2.294(3)	V–C(4)	2.29(1)	C(3)–C(4)	1.37(1)
V–S′	2.291(3)	V–C(5)	2.27(1)	C(4)–C(5)	1.30(2)
V–S″	2.292(3)	C(1)–C(2)	1.41(1)		

[a] The atoms V′, V″, V‴, are related to V by a two-fold axis. The atoms S, S′, S″, are similarly related to S by a two-fold axis; see also Fig. 3.

Table 10

Bond angles (°) for $(MeC_5H_4)_4V_4(\mu_3\text{-}S)_4$ [a]

V′VV″	59.93(5)	SVS″	101.42(9)
V′VV‴	59.93(5)	S′VS″	101.08(9)
V″VV‴	60.13(5)	VSV′	77.32(9)
V′VS	98.37(8)	VSV″	77.33(9)
V″VS	51.23(7)	VSV‴	77.56(9)
V‴VS	51.21(7)	C(2)C(1)C(5)	107.1(9)
V′VS′	51.31(7)	C(2)C(1)C(6)	123.6(9)
V″VS′	51.37(7)	C(5)C(1)C(6)	129.3(9)
V‴VS′	98.58(8)	C(1)C(2)C(3)	104.0(9)
V′VS″	51.29(7)	C(2)C(3)C(4)	109.6(9)
V″VS″	98.59(8)	C(3)C(4)C(5)	108.4(9)
V‴VS″	51.37(7)	C(1)C(5)C(4)	111(1)
SVS′	101.44(9)		

[a] See footnote *a* of Table 9.

$\pi\text{-}CH_3C_5H_4$ (V–C 2.28(1) Å (av.), $C_{C_5H_4}$–$C_{C_5H_4}$ 1.40(2) Å (av.), C_{CH_3}–$C_{C_5H_4}$ 1.55(2) Å); there are short $CH_3 \cdots S$ contacts (2.91–3.15 Å).

Discussion

Synthesis

The formation of the heterometallic tetrahedral cluster $Cp'_3 \cdot Cr_3S_4Co(CO)$ (I) from the triangular cluster $Cp'_2Cr_2SCMe_3(\mu_3\text{-}S)_2 \cdot Co(CO)_2$ during heating with tolan seems to involve, as is the case with the synthesis of $Cp_3Cr_3S_4Co(CO)$ [12], the binding of some cobalt atoms into typical acetylene-carbonyl complexes [13] (the composition of the products and the fate of the t-butyl group were not studied). It should be noted here that we recently obtained a mixed ligand cluster $Cp_3Cr_3Co(CO)_3(S_3O) \cdot HOOCCMe_3$with a strongly weakened Cr_3Co skeleton which is the result of the detachment of some of the cobalt atoms from the Cr_2Co skeleton in the form of Co^{II} trimethylacetate under the action of trimethylacetic acid which presumably acts as a source of oxygen atoms [14]. Further loss of two CO groups then gives rise to a mixed-ligand tetrahedral cluster $Cp_3Cr_3Co(CO)(S_3O)$. Formal analogues of this cluster, if Co(CO) is replaced by an isoelectronic Cp′Cr fragment, are the uncharged clusters $Cp'_4Cr_4(OS_3) \cdot CuBr_2$, in which the Cu^{II} atom is weakly bound to the tetradentate-bridge sulphur atom [7], and the ionic clusters $Cp'_4Cr_4(OS_3)^+ZnCl_3 \cdot thf^-$ (II) obtained from a reaction between $(Cp'CrSCMe_3)_2S$ and $ZnCl_2$ in THF. The scheme of the formation of these clusters is not yet clear, but traces of water seem to be a source of oxygen atoms. Also, pronounced hydrolyzability of $ZnCl_2$ with the formation of a strong complex acid $HZnCl_3$ may account for cluster oxidation to a mono-cation in a manner similar to the oxidation of $(i\text{-}PrC_5H_4)_4Mo_4S_4$ under the action of HBF_4 [5].

Finally, the synthesis of the tetrahedral cluster of vanadium, $Cp'_4V_4S_4$ (III), by heating Cp'_2V and t-BuSH in heptane is similar to the preparation of $Cp'_4Cr_4S_4$ from Cp'_2Cr and t-BuSH [6] but proceeds under milder conditions and is accompanied by a side reaction, that of the formation of a trigonal bipyramidal cluster $Cp'_5V_5S_6$ similar to a recently described oxygen-containing cluster $Cp_5V_5O_6$ [15]. In contrast

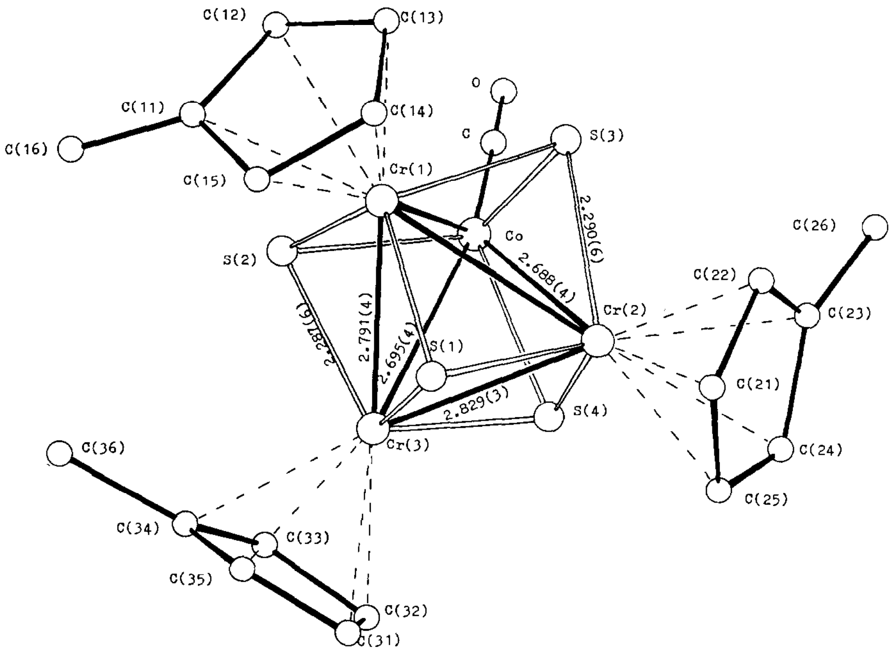


Fig. 1. The molecular structure of $(MeC_5H_4)_3Cr_3(\mu_3\text{-}S)_4Co(CO)$.

to its cyclopentadienyl analogue, studied previously [9], III is readily soluble in organic solvents and readily forms large well-shaped crystals. It is noteworthy that they are as stable in air as the crystals of the electron-saturated cluster $Cp_4Cr_4S_4$ although the vanadium cluster has 4 electrons less and is formally electron-deficient.

Structures

A comparison of the geometries of the heterometallic clusters $Cp'_3Cr_3(\mu_3\text{-}S)_4Co(CO)$ (I) (Fig. 1) and $Cp_3Cr_3(\mu\text{-}S)_4Co(CO)$ [12] reveals that the average Cr–Cr bond lengths are equal, 2.816 and 2.818 Å, respectively, and a minor growth of the Cr–S(1), Cr–S, Co–Cr, and Co–S average bond lengths (by 0.02, 0.03, 0.035, and 0.01 Å, respectively in I). This is due to steric effects induced by short $CH_3 \cdots S$ contacts (2.90–3.15 Å). In sterically less-strained triangular clusters $L_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ ($L = Cp'$ or Cp), the introduction of a CH_3 place of H into L caused strengthening of the metal skeleton although the degree of strengthening was almost insignificant [10]. Thus, the replacement of Cp by Cp′, while changing the relative orientation or the rings, leaves the structure of the metal skeleton almost unchanged. Although the Cr–Cr bond lengths (2.816 Å (av.)) and the Co–Cr bonds (2.692 Å (av.)) are close to the sums of their corresponding covalent radii of the elements [16], a pronounced shortening of the Cr–S (2.255 and 2.280 Å) and Co–S (2.171 Å) bonds as opposed to the sums of the corresponding covalent radii of the elements (2.40 and 2.25 Å) is noteworthy. This indicates considerable double bonding in Cr–S and Co–S by π interaction between the antibonding orbitals of the metal skeleton and the lone electron pair of each μ_3-sulphide bridge. Further shortening of the bridge M–S bonds does not increase the M–M distances, although

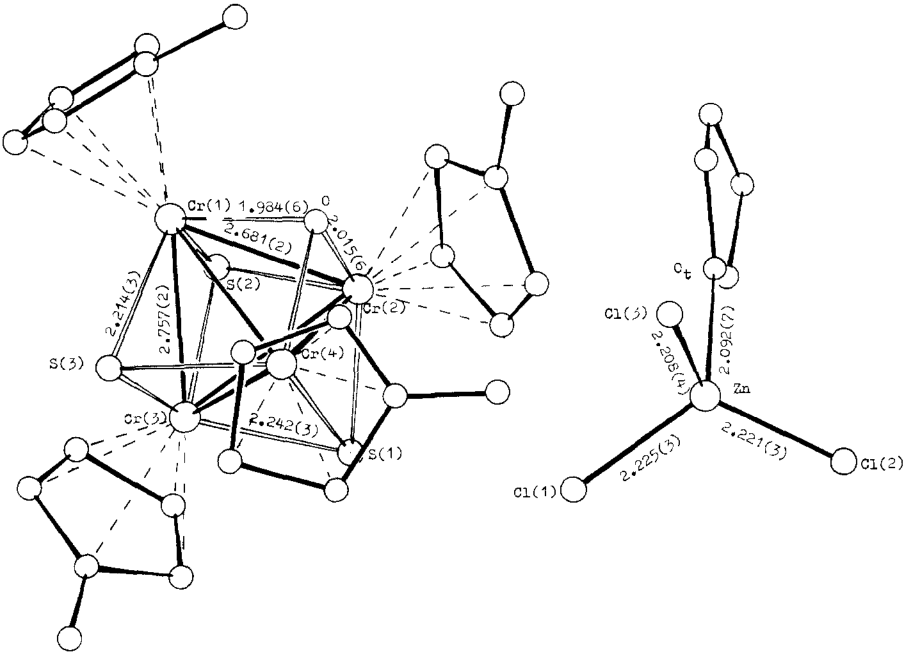


Fig. 2. The molecular structure of $[(MeC_5H_4)_4Cr_4(\mu_3\text{-}S)_3(\mu_3\text{-}O)]^+[ZnCl_3\cdot thf]^-$.

the efficiency of bonding in the metal skeleton by the electrons decreases. Similar double bonding in $\overset{\frown}{Cr-S}$ (2.25 Å) was observed for $Cp'_4Cr_4S_4$, thus Cr atoms are drawn together and a distance of 2.822(2) Å [7] which is close to the sum of covalent radii of the atoms then results. A traditional alternative description of this situation involves filling all six bonding orbitals in accordance with Dahl's scheme [4] with twelve electrons from four Cr^{III} ions (electron configuration d^3) which corresponds to the formation of six ordinary Cr–Cr bonds. However, this scheme does not account for shortening of the Cr–S bonds (or other M–S bonds) and assumes a weakened metal skeleton as a result of the withdrawal of electrons from the bonding orbitals. This is contrary to experimental fact [5], viz. the shortening of the Mo–Mo distances in the $(i\text{-}PrC_5H_4)_4MoS_4{}^{n+}$ clusters from 2.904 to 2.894 and 2.858 Å on going from the uncharged cluster on to a mono- and to a di-cation. It should be emphasized that irrespective of the value of n, the Mo–S bonds are shortened to 2.344 Å which is much less than the sum of the covalent radii of Mo and S (2.5 Å).

A comparison of the geometries of the tetrasulphide cluster, $Cp'_4Cr_4S_4$ [7], and of the neutral and cationic mixed ligand clusters, $Cp'_4Cr_4OS_3$ (adduct with $CuBr_2$) [7], and $Cp'_4Cr_4OS_3{}^+$ (with the $ZnCl_3\cdot thf^-$ anion) (Fig. 2), showed that the Cr–Cr distances depend first of all on the nature of the bridge ligand. Thus, a slight shortening of the Cr–S bonds (to 2.25, 2.24, and 2.22 Å, respectively) is observed; the distances between the chromium atoms, having sulphide bridges only, decrease from 2.82 to 2.76 Å. At the same time, the Cr–Cr distances at the oxygen bridge face decreased to 2.70 Å in the neutral cluster and to 2.687 Å in the mono-cation; the Cr–O bonds shortened from 2.08 to 1.994 Å. The greater dependence of the Cr–O bond length to growth of positive charge on the Cr atom corresponds to the

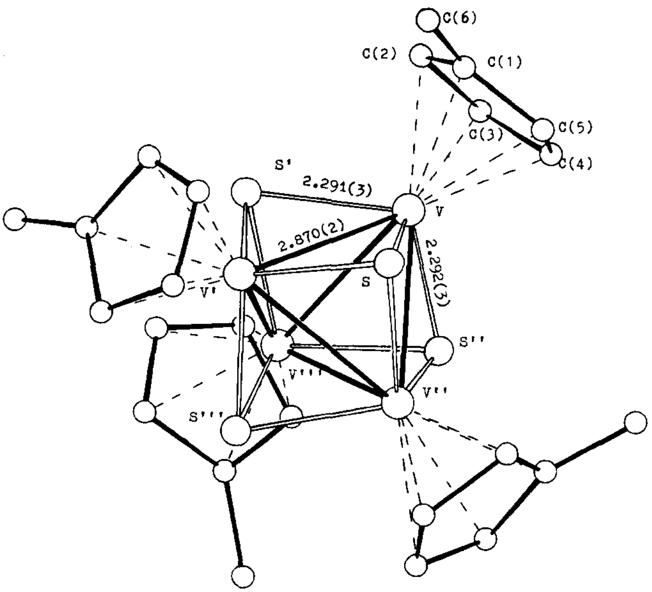


Fig. 3. The molecular structure of $(MeC_5H_4)_4V_4(\mu_3\text{-}S)_4$.

stronger ability of the Cr^{III} and Cr^{IV} ions to bond to O^{2-} as it is a harder Lewis base than S^{2-}. The role of the μ_3-S–M double bond is particularly prevalent in the vanadium cluster $Cp'_4V_4S_4$ (III) (Fig. 3) which is practically isostructural with $Cp'_4Cr_4S_4$ although, as was noted before, the metal tetrahedron composed of V^{III} ions (electron configuration d^2) contains 4 electrons less than that of Cr^{III}. A minor (by ~ 0.04 Å) increase of the V–S and V–V distances relative to the Cr–S and Cr–Cr distances is only observed; this increase corresponds to the difference of the covalent radii of V and Cr of 1.49 and 1.46 Å, respectively [16]. The lengths of the V–S bonds (2.291(4) Å (av.)) are 0.2 Å shorter than the sum of the covalent radii of V and S (2.5 Å).

Mass spectra

The proposal that an important part is played by the $\mu_3\text{-}\overset{\frown}{X\text{–}M}$ double bond (X = S or O; M = Cr or V) in the tetrahedral clusters $Cp'_4M_4X_4$ is in good agreement with the mass spectrometric data, which indicate the stepwise detachment of four methylcyclopentadienyl ligands, with conservation of the M_4X_4 fragment. As Simon and Dahl have already shown [6], it is noteworthy that the electron-excessive molecule $Cp_4Co_4S_4$, in which the 24 electrons of the metal skeleton occupy all 12 bonding and antibonding orbitals and thus prevent $\mu_3\text{-}\overset{\frown}{S\text{–}Co}$ double bonding (Co–S 2.23 Å), and Co–Co bonding (Co ··· Co 3.295 Å), decomposes under the electron impact mostly to give mainly mononuclear fragments.

Magnetic properties and electronic structure

Temperature dependent static magnetic susceptibility measurements on the clusters show that $Cp'_3Cr_3S_4Co(CO)$ (I) is diamagnetic, $Cp'_3Cr_4OS_3{}^+ZnCl_3 \cdot thf^-$ (II) has one unpaired electron, and $Cp'_4V_4S_4$ (III) has two unpaired electrons. These results are consistent with Dahl's qualitative MO scheme by which the bonding orbitals of the metal skeleton have $a_1^2e^4t_2^6$ symmetry [4]; the correctness of the scheme has been confirmed by photoelectron spectroscopy on $(\text{i-PrC}_5\text{H}_4)_4\text{Mo}_4\text{S}_4$ [5]. It has been found that the a_1 and e orbitals are strongly bonding and that the t_2 orbital is only slightly stable and loses electrons readily.

In the case of cluster I, 16 electrons from the 3 Cr^{III} ions (electron configuration d^3) and from the Co^{II} ion (electron configuration d^7) occupy all 6 bonding orbitals of the metal skeleton (Cr_3Co); in addition, 2 non-bonding orbitals of the Co atom are occupied. It should be noted that the isoorbital cluster $\text{Cp}_3\text{Cr}_3\text{S}_4\text{Fe}\cdot(\text{OOCCMe}_3)$ studied in our earlier experiments contained 2 electrons less; therefore, only 2 unpaired electrons were located in the non-bonding orbitals of the Fe ion [17].

Unlike the diamagnetic cluster $\text{Cp}'_4\text{Cr}_4\text{S}_4$ [6], the mixed ligand uncharged cluster $\text{Cp}'_4\text{Cr}_4\text{OS}_3\cdot\text{CuBr}_2$ shows antiferromagnetic properties [7], as do the oxygen bridge tetrahedra, $\text{Cp}_4\text{Cr}_4\text{O}_4$ [15] and $\text{Cp}'_4\text{Cr}_4\text{O}_4$ [7]. This seems to be due to stronger splitting of the singlet ($S = 0$) and triplet ($S = 1$) states for the sulphide bridge complexes than those for the oxygen bridge, which leads to the thermal population of the triplet level in the latter and hence to antiferromagnetic behaviour. The removal of an electron from II leaves only one unpaired electron ($S = 1/2$). The μ_{eff} value for II is independent of temperature.

On going from $\text{Cp}'_4\text{Cr}_4\text{S}_4$ to $\text{Cp}'_4\text{V}_4\text{S}_4$, 4 electrons are withdrawn from the weakly bonding t_2 orbital and only 2 unpaired electrons are left (μ_{eff} is temperature-independent). The μ_3-$\overset{\curvearrowright}{\text{X–M}}$ double bond does not seem to affect the symmetry and relative location of the orbitals in the metal skeleton, although it does lead to its strengthening, particularly when the electrons of the skeleton are withdrawn by oxidation. Thus, the Co–S bonds in $\text{Cp}_4\text{Co}_4\text{S}_4^+$ are 0.012 Å shorter compared with those of $\text{Cp}_4\text{Co}_4\text{S}_4$ [4].

Electrochemical properties

It is probable that the μ_3-$\overset{\curvearrowright}{\text{X–M}}$ interaction underlies the remarkable ability of clusters I–III and that of $\text{Cp}'_4\text{Cr}_4\text{X}_4$ (X = O or S) to undergo reversible electrochemical processes of multistep oxidation or reduction in DMF or acetonitrile. Thus, cyclic voltammetry of $\text{Cp}'_4\text{V}_4\text{S}_4$ (III) in DMF gives 4 waves of diffusion-controlled reversible oxidations ($E^0 = -1.16$, -0.22, $+0.56$, $+1.02$ V relative to SCE). Formally this corresponds to the oxidation of each V^{III} ion into V^{IV}.

The electrochemical transformations of $\text{Cp}'_4\text{Cr}_4\text{S}_4$ (IV) proceed in a similar manner, although only three waves of reversible one-electron oxidations (-1.08, -0.16, $+0.50$ V) are observed in DMF and the fourth ($+1.4$ V) took place only in MeCN.

The oxygen bridge analogue, $\text{Cp}'_4\text{Cr}_4\text{O}_4$(V), behaves in a similar way. However, π-bonding of μ_3-$\overset{\curvearrowleft}{\ddot{\text{O}}\text{–Cr}}$ in this cluster is probably enhanced, because by analogy, in $\text{Cp}_4\text{Cr}_4\text{O}_4$ the Cr–O bonds are shortened to 1.97 Å [15]. For this reason V is more readily oxidised than IV and so 3 waves of reversible one-electron oxidations at $E^0 = -1.26$, -0.58 and $+0.32$ V were observed in DMF (an attempt to detect the fourth wave in DMF failed).

The electrochemical behaviour of the mixed ligand cationic cluster $\text{Cp}'_4\text{Cr}_4(\text{OS}_3)^+$ $\text{ZnCl}_3\cdot\text{thf}^-$ (II), as expected, is more similar to that of IV than of V. In DMF II gives only two reversible one-electron oxidation waves ($E^0 = -0.16$ and $+0.60$ V). It is evident that the oxidation wave at $E^0 \approx -1$ V, characteristic of oxidation of the uncharged cluster, is absent. In this case the first wave (−0.16 V) coincides with the second wave of oxidation of cluster IV which corresponds to the $IV^+ \rightleftarrows IV^{2+}$ transition. The third unclear oxidation wave at $E^0 = +1.6$ V is also detectable but observations in DMF in this region are difficult.

Finally, in addition to three reversible one-electron oxidation waves ($E^0 = -1.07$, -0.23 and $+0.23$ V), cyclic voltammetry of $Cp'_3Cr_3S_4Co(CO)$ (I) in DMF gives one wave of a two-electron irreversible oxidation at $E^0 = +0.80$ V.

Experimental

All procedures were carried out in a stream of pure argon. The starting compounds, $(CH_3C_5H_4)_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$, $(CH_3C_5H_4)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$, $(CH_3C_5H_4)_2V$, were obtained by use of techniques described previously [7,10,18]. Benzene and heptane were purified by distillation in an argon counterflow over a sodium dispersion. Acetonitrile was distilled over CaH_2 and P_2O_5. Dimethylformamide purified by fractional distillation at 5 Torr. Tetrahydrofuran was absolutised by distillation in argon counterflow in the presence of sodium benzophenoneketyl.

Cyclic voltammetry and microcoulometry were conducted in MeCN or DMFA with $NaBF_4$ as background electrolyte. A platinum point was used as the working electrode and a saturated calomel electrode was used as the reference. Platinum wire was the auxiliary electrode. Microcoulometric data were collected from a cell with two arms separated by a porous glass membrane. A platinum gauze electrode (Fischer's electrode) served as a working electrode and a saturated calomel electrode as reference; a platinum gauze electrode in the background solution served as the auxiliary electrode.

IR spectra of the complexes were recorded with a Specord IR-75 instrument. Magnetic measurements, carried out by use of the Faraday method, were made with a unit installed at the Institute of General and Inorganic Chemistry, U.S.S.R. Academy of Sciences. Mass spectra were recorded with an automatic DS-50 system. The X-ray diffraction data for clusters I and III were recorded with a four-circle automatic Syntex $P2_1$ diffractometer (λMo-K_α, λ 0.71069 Å, θ–2θ scan, $2 \leqslant \theta \leqslant 52°$, T −100 °C). The structures were solved by a direct method and refined in a full-matrix anisotropic approximation for all non-hydrogen atoms to $R_I = 0.085$, $R_w = 0.077$ for 2268 reflections with $I \geqslant 2\sigma(I)$ for I and to $R_I = 0.069$ and $R_w = 0.060$ for 722 reflections with $I \geqslant 2\sigma(I)$ for III. The experimental data for II were recorded with an automatic Hilger and Watts diffractometer (λMo-K_α, λ 0.71069 Å, θ–2θ scan, $2 \leqslant \theta \leqslant 60°$, T 20 °C). The structure was also solved by a direct method and refined in a blocked-diagonal anisotropic approximation for all non-hydrogen atoms to $R_I = 0.072$, $R_w = 0.050$ for 3258 reflections with $I \geqslant 2\sigma(I)$.

$(CH_3C_5H_4)_3Cr_3(\mu_3\text{-}S)_4Co(CO)$ (I)

A solution of 0.19 g (0.36 mmol) of $(CH_3C_5H_4)_2Cr_2(\mu\text{-}SCMe_3)\cdot(\mu_3\text{-}S)_2Co(CO)_2$ and 0.12 g (0.66 mmol) of Ph_2C_2 in 25 ml of heptane was heated at 75 °C for 2.5 h. The brown solution formed was filtered and then evaporated to dryness. The dry residue which remained, was dissolved in hot pentane (30 ml) and the filtrate cooled to −5 °C. The crystals which precipitated were separated from the solution, washed with cold pentane, and vacuum dried. Yield 0.12 g. IR spectrum (ν, cm^{-1}): 505m, 595w, 685m, 745m, 805s, 1015m, 1360m, 1440m, 1485m, 1900s, 2830–2960b.m, 3080w.

$[(CH_3C_5H_4)_4Cr_4(\mu_3\text{-}O)(\mu_3\text{-}S)_3]^+[Cl_3Zn\cdot OC_4H_8]^-$ (II)

To a violet solution of 1.24 g (2.62 mmol) of a solution of $(MeC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ in 30 ml of THF a solution of 0.18 g (1.31 mmol) of $ZnCl_2$ in 20 ml of THF was added. The dark violet solution obtained was boiled for 10 min until the colour turned into bright blue. The solvent was evaporated to dryness at 0.1 Torr and 60 ° C and the product was extracted with heptane, then with benzene (60–80 ml altogether). The combined blue extract was evaporated and the solid product recrystallized from hot THF. The large dark blue crystals were washed with cold THF and vacuum dried. Yield 0.9 g (70%). IR spectrum (ν, cm^{-1}): 585m, 810s, 1010m, 1100m, 1350w, 1425m, 1470w 3070w.

$(CH_3C_5H_4)_4V_4(\mu_3\text{-}S)_4$ (III)

To a violet solution of 3.45 g (16.51 mmol) $(CH_3C_5H_4)_2V$ in 60 ml of heptane was added 3.5 ml (33.3 mmol) of Me_3CSH and the mixture was boiled for 3 h. The resulting brown solution was subjected to chromatography on an Al_2O_3 column (3 × 30 cm) with the brown ($R_f \sim 0.8$) (A) and dark violet ($R_f \sim 0.2$) zones eluting with heptane. The brown solution of A thus obtained concentrated to ~ 1/6 of its initial volume and cooled to -5 ° C. The large dark brown crystals which precipitated were washed with cold pentane and vacuum dried. Yield 1.6 g (59.9%). IR spectrum (ν, cm^{-1}): 450w, 605w, 790s, 800m, 870m, 885w, 1035m, 1375m, 1450m, 1470w, 1630w, 2860w, 2910m, 2940w, 3060m.

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