

Antiferromagnetic complexes with metal–metal bonds

XXI *. Reactions of $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2$ with chalcogens (S, Se, Te). Syntheses and molecular structures of $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2(\mu\text{-S}_4)$ and $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2(\mu\text{-Se})$

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Abstract

Reactions of $\text{Cp}_2\text{Cr}_2(\mu\text{-OR})_2$ (I) ($\text{R} = \text{CMe}_3$) with chalcogens have been studied. It is shown that reaction of I with S_8 (benzene-heptane, 20°C) results in the formation of a green complex $\text{Cp}_2\text{Cr}_2(\mu\text{-OR})_2(\mu\text{-S}_4)$ (III), which from its X-ray diffraction data (space group $P4_12_12$, $a = b = 18.20(5)$, $c = 30.14(3)$ Å) was found to possess two chromium atoms (with a Cr–Cr distance of $2.955(4)$ Å) and four sulfur atoms in a six-membered Cr_2S_4 metal cycle (Cr–S, $2.323(6)$, $2.354(6)$ Å, S–S $2.077(9)$, $1.976(12)$, $2.053(9)$ Å). The Cp rings are *cis* relative to the Cr–Cr bond (the CpCrCr angle is 134.5°). Reaction of I with the metals Se or Te under the same conditions yields the complexes $\text{Cp}_2\text{Cr}_2(\mu\text{-OR})_2(\mu\text{-E})$ ($\text{E} = \text{Se}$ (IV), Te (IVa)). The X-ray diffraction data (space group $P\bar{1}$, $a = 8.3983(8)$, $b = 9.2732(9)$, $c = 14.3254(10)$ Å, $\alpha = 76.977(7)$, $\beta = 77.326(7)$, $\gamma = 64.653(7)^\circ$) show that the Cr–Cr bond in IV is shortened to $2.617(6)$ Å, and that the CpCrCrCp moiety has a linear configuration (CpCrCr 172.5°). Complexes III, IV and IVa are thermally unstable and at 60°C , and undergo disproportionation to give $\text{Cp}_2\text{Cr}_2(\mu\text{-OR})_2(\text{OR})_2$ (V) and the corresponding tetrahedral clusters $\text{Cp}_4\text{Cr}_4\text{E}_4$. Binuclear complexes III, IV, and IVa are antiferromagnetic, the exchange parameter $-2J$ depends primarily on the geometry of the Cp_2Cr_2 fragment.

* For part XX see ref. 3.

Introduction

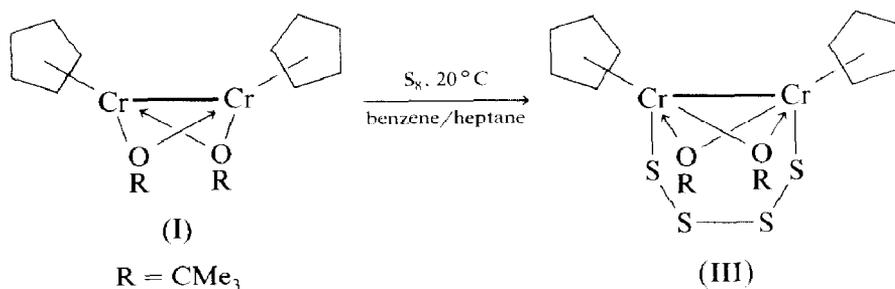
We have recently shown that the binuclear complex $\text{Cp}_2\text{Cr}_2(\mu\text{-OR})_2$ (I, $\text{R} = \text{CMe}_3$ [1]), formed by the interaction of chromocene with $\text{HO}(\text{CMe}_3)$, can be readily oxidized by CH_2X_2 ($\text{X} = \text{Cl, Br, I}$) to $\text{Cp}_2\text{Cr}_2\text{X}_2(\mu\text{-OR})_2$ (II), which causes considerable elongation of the Cr–Cr distance to 2.917, 2.971, 2.967 Å for $\text{X} = \text{Cl, Br, I}$, respectively, as compared with complex I (2.635 Å). This is a consequence of a decrease in the Cp(centre)CrCr angle from 145° in complex I to $126.6, 131.6, 131.7^\circ$ for $\text{X} = \text{Cl, Br, I}$ respectively. This angle determines the degree of σ -bonding which is due to the overlap of d_{z^2} orbitals at the metal atoms [2].

Complex I can be also oxidized by binuclear carbonyls, e.g. by cobalt carbonyl with the formation of $\text{Cp}_2\text{Cr}_2(\mu\text{-OR})_2(\text{OCCo}_3(\text{CO})_9)$, in which only one chromium atom is oxidized to Cr^{III} as a result of the addition of $(\mu_3\text{-OC})(\text{Co}_3(\text{CO})_9)$ fragment to the oxygen atom at the bridging CO group [3]. This results in a considerable decrease of the Cp(centre)CrCr angle at Cr^{III} as compared to Cr^{II} (117.2° and 155.7° , respectively). In this case the Cr–Cr bond is weakened to a lesser extent (to 2.766 Å) and the $-2J$ value is decreased to 180 cm^{-1} , which lies between the values for I, (204 cm^{-1}) and those for II ($150\text{--}160 \text{ cm}^{-1}$). Finally, if the $\text{Fe}(\text{CO})_4$ fragment is added to I by two Cr–Fe bonds (2.691 and 2.702 Å) the CpCrCrCp system becomes linear. It enhances the overlap of d_{z^2} orbitals. The Cr–Cr bond become shorter (2.635 Å) and the exchange parameter $-2J$ increases to 304 cm^{-1} [4]. Since the frontier orbitals of the $\text{Fe}(\text{CO})_4$ fragment resemble those of the chalcogen (S, Se, Te) atoms the same geometry and electronic effects on their bonding with complex I were expected.

Furthermore, it was of interest to compare the properties of the expected chalcogen derivatives of the complex I with the characteristics of the sulfidethiolate complex we described previously— $\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)_2(\mu\text{-S})$ —which had a short Cr–Cr bond (2.689 Å) in the linear fragment CpCrCrCp (CpCrCr $\sim 180^\circ$) [5], and the increased as compared to I value of the exchange parameter ($-2J 430 \text{ cm}^{-1}$).

Results and discussion

The outcome of the interaction of $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2$ (I) with sulfur (S_8) or metallic selenium or tellurium depends on the nature of the element. Thus, reaction of complex I with S_8 in benzene/heptane mixture at 20°C gives the complex $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2(\mu\text{-S}_4)$ (III) in as large green prisms.



The X-ray diffraction data (Table 1) show that in molecule III the S_4 group (half of the initial S_8 molecule), having S–S distances of 2.053(9), 1.976(12), 2.077(9) Å,

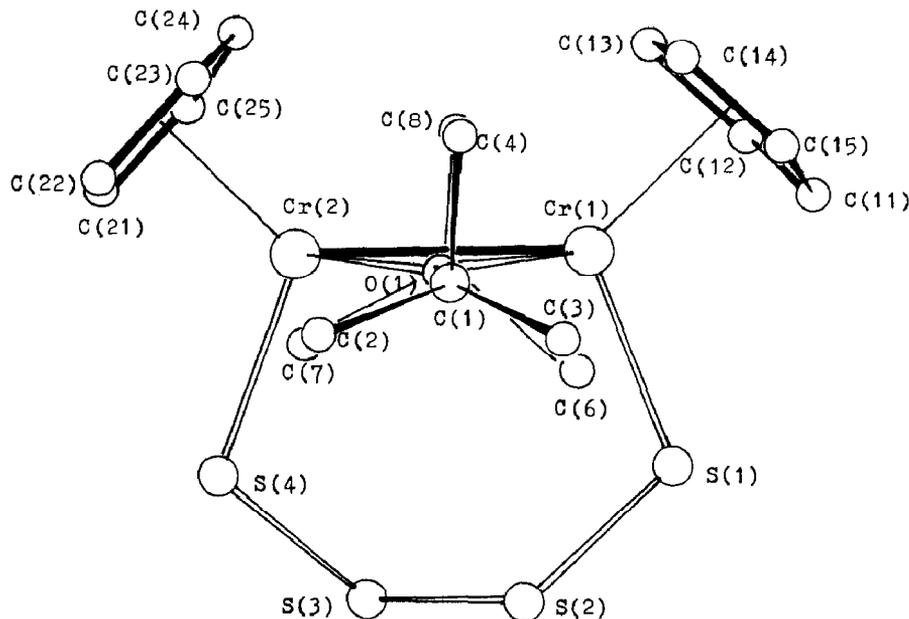
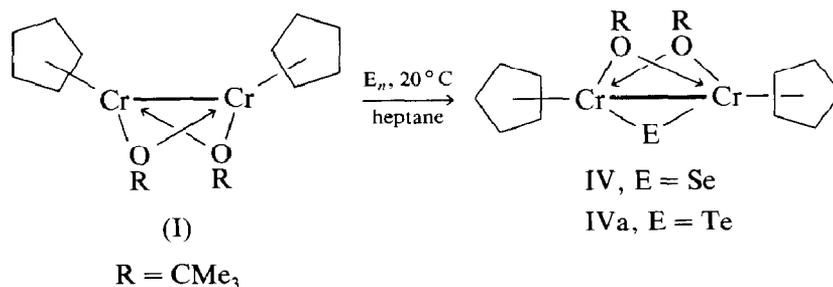


Fig. 1. The structure of $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2(\mu\text{-S}_4)$ (III).

links two chromium atoms (Cr-S 2.323(6), 2.354(6) Å), to form a six-membered cycle Cr_2S_4 in the distorted chair conformation* (Fig. 1). The geometry of the binuclear fragment $\text{Cp}_2\text{Cr}_2(\mu\text{-OR})_2(\text{X})_2$ (X = terminal sulfur atoms of the S_4 chain) in III (Cr-Cr 2.955(4), Cr-S_{av} 2.338 Å, CpCrCr 134.5°) closely resembles that observed in the halogen-containing complexes $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2\text{X}_2$ ($\text{X} = \text{Cl, Br, I}$) [2]. The only significant difference lies in the values of dihedral angle between the wings of the Cr_2O_2 butterfly (164.6° in III, and 151.3°, 156.4 and 158.9° in II for $\text{X} = \text{Cl, Br, I}$, respectively), however, in all these cases the X atoms are located in the bisecting plane of this angle. Nevertheless this difference does not influence the magnetic properties of II (μ_{eff} changes from 2.19 to 0.93 BM in the temperature range of 289–77 K, $-2J = 164 \text{ cm}^{-1}$) as compared with the halogen derivatives II ($-2J = 148\text{--}168 \text{ cm}^{-1}$ [2]).

Unlike the reaction with S_8 , an interaction of complex I with the powdered selenium or tellurium metal (in pentane at 20°C) results in addition of only one bridging chalcogen atom:



* The unit cell contains two independent molecules $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2(\mu\text{-S}_4)$, one of them has a disordered S_4 group and slightly disordered OCMe_3 bridges. Therefore only characteristics of the first (ordered) molecule are given in the text.

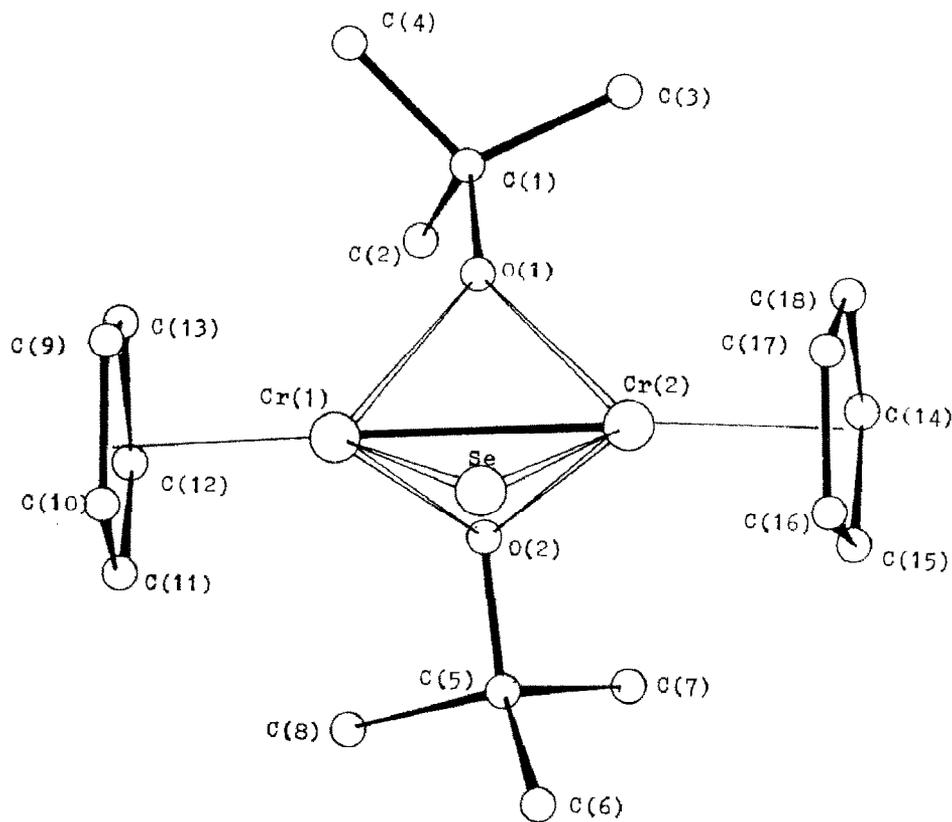


Fig. 2. The structure of $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2(\mu\text{-Se})$ (IV).

The complexes $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2(\mu\text{-E})$ (IV, E = Se; IVa, E = Te) were isolated as green-brown and brick-red crystals, respectively. The X-ray diffraction study of IV (see also Fig. 2) shows that addition of Se atom to two chromium atoms (Cr–Se 2.394(6) Å) results in an almost linear Cp_2Cr_2 group (Cp(centre) Cr–Cr_{mean} 172.5°) which as shown previously [3], strengthens and shortens the Cr–Cr bond to 2.617(6) Å and increases the antiferromagnetic exchange parameter to $-2J = 290 \text{ cm}^{-1}$ (μ_{eff} decreases from 1.68 to 1.07 BM in the temperature range of 290–77 K). This value approaches the 304 cm^{-1} for $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2(\mu\text{-Fe}(\text{CO})_4)$ (V) whose binuclear fragment $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2$ (Cr–Cr 2.635 Å, CpCrCr 178°) [4] has a geometry very similar to that in IV. At the same time the $-2J$ value for IV is much lower than the 430 cm^{-1} for the isoelectronic antiferromagnetic analogue $\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)_2(\mu\text{-S})$ (VI), which also has a linear Cp_2Cr_2 (Cr–Cr 2.689 Å) fragment [5]. This difference is probably attributable to enhanced indirect exchange interactions via the two bridging thiolate and single sulfide ligands [5] relative to the exchange via the two alkoxide ligands and the single selenide bridge.

The thermally unstable complexes IV and IVa on heating above 60°C undergo disproportionation in solution to give the binuclear tetraalkoxide complex $\text{Cp}_2\text{Cr}_2(\text{OCMe}_3)_2(\mu\text{-OCMe}_3)_2$ [3] and the corresponding tetramers $\text{Cp}_4\text{Cr}_4\text{E}_4$ (E = Se, Te). The disproportionation probably occurs via an intermediate (A) which has a ligand geometry about each chromium atom close to that observed in the halogenide complexes $\text{Cp}_2\text{Cr}_2(\text{OR})_2\text{X}_2$. The tetrahedral clusters have been also independently

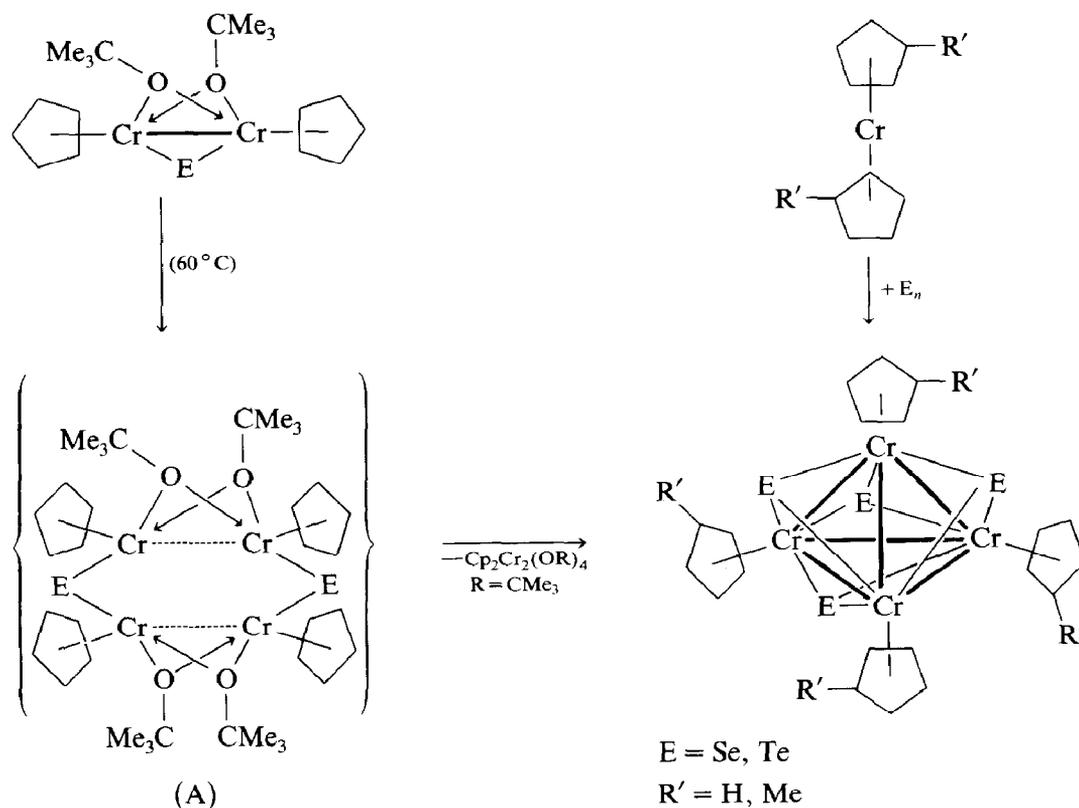
Table 1

Comparison of geometry and magnetic characteristics of $\text{Cp}_2\text{Cr}_2(\mu\text{-ECMe}_3)_2(\mu\text{-X})$ and $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2$

| | I E = O [1] | | IV E = O X = Se | | V E = O [4] X = Fe(CO) ₄ | | VI E = S [5] X = S | |
|--|----------------|-----|-----------------------|-----|---|-----|--------------------------|-----|
| Cr-Cr (Å) | 2.635 | | 2.617 | | 2.635 | | 2.689 | |
| Cr-μ-E (Å) | 1.983 | | 1.97 | | 1.979 | | 2.38 | |
| Cr-μ-X (Å) | - | | 2.394 2.707 | | 2.691 | | 2.24 | |
| CrXCr (°) | - | | 66.2 | | 83.3 | | 68.3 | |
| Cp*CrCl ^a (°) | 145 | | 170-175 | | 176 | | 178 | |
| S _{Cr1} /S _{Cr2} | 3/2 | 3/2 | 3/2 | 3/2 | 3/2 | 3/2 | 3/2 | 3/2 |
| -zJ _{Cr-Cr} (cm ⁻¹) | 204 | | 290 | | 304 | | 430 | |

^a Cp* = centre of the C₅H₅ ring.

synthesized by the reaction of $(\text{MeC}_5\text{H}_4)_2\text{Cr}$ and chalcogens and identified from their mass-spectra; the selenium-containing analogue has been also identified by an X-ray diffraction studies [6].



Experimental

All syntheses were carried out under pure argon in absolute solvents. The initial complexes $(\text{RC}_5\text{H}_4)_2\text{Cr}$ and $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2$ were synthesized by standard

Table 2

Positional parameters for complex $\text{Cp}_2\text{Cr}_2(\mu - \text{OCMe}_3)_2(\mu - \text{S}_4) \cdot \frac{1}{2} \text{C}_6\text{H}_6$

| Atom | Molecule A | | | Molecule B | | |
|-------------------|------------|-----------|-----------|------------|-----------|-----------|
| | x | y | z | x | y | z |
| Cr(1) | 0.5781(3) | 0.1416(3) | 0.0959(2) | 0.3078(4) | 0.8620(4) | 0.0728(2) |
| Cr(2) | 0.7219(3) | 0.1758(4) | 0.1364(2) | 0.3582(4) | 0.7920(5) | 0.1527(2) |
| S(1) | 0.5049(6) | 0.0779(7) | 0.1460(4) | 0.2030(8) | 0.7994(8) | 0.0467(5) |
| S(2) | 0.5675(9) | 0.0342(8) | 0.1972(4) | 0.200(1) | 0.694(1) | 0.0718(7) |
| S(3) | 0.6204(8) | 0.111(1) | 0.2310(4) | 0.185(1) | 0.710(2) | 0.1429(9) |
| S(4) | 0.7257(6) | 0.1277(7) | 0.2089(3) | 0.2837(8) | 0.6917(9) | 0.1706(5) |
| S(2) ^a | | | | 0.179(2) | 0.710(2) | 0.079(2) |
| S(3) ^a | | | | 0.209(2) | 0.670(2) | 0.126(1) |
| O(1) | 0.676(1) | 0.091(1) | 0.1045(7) | 0.370(2) | 0.773(2) | 0.093(1) |
| O(2) | 0.618(1) | 0.211(1) | 0.1352(7) | 0.281(2) | 0.862(2) | 0.1372(9) |
| C(1) | 0.699(2) | 0.018(2) | 0.090(1) | 0.398(2) | 0.726(2) | 0.064(1) |
| C(2) | 0.760(2) | 0.002(2) | 0.122(1) | 0.484(3) | 0.762(3) | 0.053(2) |
| C(3) | 0.641(3) | -0.034(2) | 0.088(1) | 0.402(3) | 0.653(3) | 0.085(2) |
| C(4) | 0.730(3) | 0.022(3) | 0.047(2) | 0.370(2) | 0.708(3) | 0.019(1) |
| C(5) | 0.593(3) | 0.278(3) | 0.151(2) | 0.240(3) | 0.895(3) | 0.158(2) |
| C(6) | 0.504(2) | 0.261(2) | 0.168(1) | 0.262(3) | 0.973(3) | 0.173(2) |
| C(7) | 0.640(3) | 0.301(3) | 0.198(2) | 0.210(3) | 0.864(3) | 0.205(2) |
| C(8) | 0.602(3) | 0.350(2) | 0.123(1) | 0.155(2) | 0.907(2) | 0.132(1) |
| C(11) | 0.475(2) | 0.141(2) | 0.054(1) | 0.364(3) | 0.895(3) | 0.004(2) |
| C(12) | 0.497(2) | 0.206(2) | 0.054(1) | 0.391(3) | 0.934(3) | 0.045(2) |
| C(13) | 0.570(2) | 0.211(2) | 0.034(1) | 0.369(3) | 0.982(3) | 0.075(2) |
| C(14) | 0.586(3) | 0.141(3) | 0.019(2) | 0.287(3) | 0.988(3) | 0.054(2) |
| C(15) | 0.525(2) | 0.101(2) | 0.032(1) | 0.275(4) | 0.932(3) | 0.014(2) |
| C(21) | 0.808(3) | 0.254(3) | 0.157(2) | 0.474(3) | 0.734(3) | 0.166(2) |
| C(22) | 0.835(3) | 0.190(3) | 0.136(2) | 0.489(3) | 0.800(4) | 0.174(2) |
| C(23) | 0.822(3) | 0.180(3) | 0.090(2) | 0.439(4) | 0.866(3) | 0.186(2) |
| C(24) | 0.792(3) | 0.234(3) | 0.080(2) | 0.379(4) | 0.860(4) | 0.220(2) |
| C(25) | 0.771(3) | 0.276(3) | 0.116(2) | 0.412(3) | 0.768(3) | 0.214(2) |
| CB(1) | 0.579(3) | 0.529(3) | 0.016(2) | 0.971(6) | 0.053(6) | 0.019(4) |
| CB(2) | 0.551(3) | 0.485(3) | 0.036(2) | 1.002(9) | 0.013(9) | 0.024(5) |
| CB(3) | 0.499(3) | 0.457(3) | 0.013(2) | 1.031(3) | -0.031(3) | 0.039(2) |

^a Data for one of the two independent molecules with disordered S_4 group S. O and C atoms were refined isotropically. The data listed are for the regular molecule with all the non-hydrogen atoms refined anisotropically.

procedures [7,1]. The IR spectra were recorded in KBr pellets with a Specord 75-IR instrument. Magnetic susceptibility was measured by the Faraday method with apparatus designed by the Institute of General and Inorganic Chemistry [8]. X-ray diffraction data for II and IV were obtained with the automatic diffractometers CAD-4 and Hilger & Watts, respectively (λMoK_α , $\theta-2\theta$ scan, 20°C (Table 8)). Structures of II and IV were solved by direct full-matrix (for III) and blockdiagonal (for IV) approximations for all non-hydrogen atoms (Tables 2–7).

$(\text{C}_5\text{H}_5)_2\text{Cr}_2(\mu\text{-OCMe}_3)_2(\mu\text{-S}_4)$ (III)

The red-brown solution of $(\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{OCMe}_3)$ (obtained from the reaction of Cp_2Cr (0.5 g, 2.74 mmol) with HOCMe_3) in 15 ml of heptane was carefully covered

Table 3

Bond lengths in the complex $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2(\mu\text{-S}_4) \cdot \frac{1}{2}\text{C}_6\text{H}_6$ (molecule A)

| | | | |
|-------------|-----------|------------|----------|
| Cr(1)–Cr(2) | 2.955(4) | Cr(1)–S(1) | 2.323(6) |
| Cr(1)–O(1) | 2.02(1) | Cr(1)–O(2) | 1.88(1) |
| Cr(2)–S(4) | 2.354(6) | Cr(2)–O(1) | 2.01(1) |
| Cr(2)–O(2) | 2.00(1) | S(1)–S(2) | 2.077(9) |
| S(2)–S(3) | 1.976(12) | S(4)–S(3) | 2.053(9) |
| O(1)–C(1) | 1.45(2) | O(2)–C(5) | 1.38(3) |

Table 4

Bond angles ($^\circ$) in the complex $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2(\mu\text{-S}_4) \cdot \frac{1}{2}\text{C}_6\text{H}_6$ (molecule A)

| | | | |
|----------------|----------|----------------|----------|
| Cr(2)Cr(1)S(1) | 110.1(2) | S(4)Cr(2)O(1) | 99.8(4) |
| Cr(2)Cr(1)O(1) | 42.7(3) | S(4)Cr(2)O(2) | 99.5(3) |
| Cr(2)Cr(1)O(2) | 42.0(3) | O(1)Cr(2)O(2) | 81.2(5) |
| S(1)Cr(1)O(1) | 101.0(3) | Cr(1)S(1)S(2) | 111.1(3) |
| S(1)Cr(1)O(2) | 98.6(4) | S(1)S(2)S(3) | 112.4(5) |
| O(1)Cr(1)O(2) | 83.7(5) | S(2)S(3)S(4) | 113.1(5) |
| Cr(1)Cr(2)S(4) | 109.3(2) | Cr(2)S(4)S(3) | 109.3(3) |
| Cr(1)Cr(2)O(1) | 43.1(3) | Cr(1)O(1)Cr(2) | 94.3(5) |
| Cr(1)Cr(2)O(2) | 39.0(3) | Cr(1)O(2)Cr(2) | 99.1(5) |

Table 5

Positional parameters (for Se and Cr $\times 10^4$, for O and C $\times 10^3$) for $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2(\mu\text{-Se})$ (IV)

| Atom | x | y | z |
|-------|----------|---------|---------|
| Se | 920(4) | 2209(3) | 3387(2) |
| Cr(1) | 1127(5) | 734(4) | 2160(3) |
| Cr(2) | –1708(5) | 1772(4) | 3434(3) |
| O(1) | –16(2) | –43(2) | 313(1) |
| O(2) | –133(2) | 213(2) | 199(1) |
| C(1) | –47(4) | –176(3) | 300(2) |
| C(2) | –125(4) | –145(3) | 195(2) |
| C(3) | –220(3) | –199(3) | 370(2) |
| C(4) | 123(4) | –339(4) | 308(2) |
| C(5) | –228(3) | 366(3) | 131(2) |
| C(6) | –214(4) | 515(3) | 155(2) |
| C(7) | –427(3) | 387(3) | 138(2) |
| C(8) | –129(3) | 330(3) | 26(2) |
| C(9) | 321(3) | –122(3) | 127(2) |
| C(10) | 271(3) | 32(3) | 64(2) |
| C(11) | 316(3) | 136(3) | 97(2) |
| C(12) | 404(3) | 46(3) | 179(2) |
| C(13) | 410(3) | –107(3) | 202(2) |
| C(14) | –474(3) | 234(3) | 400(2) |
| C(15) | –439(3) | 382(3) | 389(2) |
| C(16) | –316(3) | 364(3) | 443(2) |
| C(17) | –261(3) | 203(2) | 504(2) |
| C(18) | –360(3) | 131(3) | 476(2) |

Table 6

Bond lengths in $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2(\mu\text{-Se})$ (IV).

| Atom | <i>x</i> | <i>y</i> | <i>z</i> |
|-------------|----------|------------|----------|
| Se–Cr(1) | 2.395(5) | Cr(2)–O(1) | 1.98(1) |
| Se–Cr(2) | 2.394(6) | Cr(2)–O(2) | 2.00(1) |
| Cr(1)–Cr(2) | 2.617(6) | O(1)–C(1) | 1.42(3) |
| Cr(1)–O(1) | 1.98(2) | O(2)–C(5) | 1.53(3) |
| Cr(1)–O(2) | 1.95(2) | | |

Table 7

Bond angles (°) in $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2(\mu\text{-Se})$ (IV)

| | | | |
|----------------|---------|----------------|---------|
| Cr(1)SeCr(2) | 66.2(2) | SeCr(2)O(1) | 88.4(5) |
| SeCr(1)Cr(2) | 56.9(1) | SeCr(2)O(2) | 88.4(5) |
| SeCr(1)O(1) | 88.3(5) | Cr(1)Cr(2)O(1) | 48.7(5) |
| SeCr(1)O(2) | 89.7(5) | Cr(1)Cr(2)O(2) | 47.6(4) |
| Cr(2)Cr(1)O(1) | 48.5(5) | O(1)Cr(2)O(2) | 77.6(6) |
| Cr(2)Cr(1)O(2) | 49.4(5) | Cr(1)O(1)Cr(2) | 82.7(6) |
| O(1)Cr(1)O(2) | 78.9(6) | Cr(1)O(2)Cr(2) | 83.0(6) |
| SeCr(2)Cr(1) | 56.9(1) | | |

Table 8

Crystal data for $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2(\mu\text{-S}_4)$ (III) and $\text{Cp}_2\text{Cr}_2(\mu\text{-OCMe}_3)_2(\mu\text{-Se})$ (IV)

| | III | IV |
|---|----------------|-------------|
| Crystal system | tetragonal | triclinic |
| Space group | $P4_12_12$ | $P\bar{1}$ |
| <i>a</i> (Å) | 18.20(5) | 8.3983(8) |
| <i>b</i> (Å) | 18.20(5) | 9.2732(9) |
| <i>c</i> (Å) | 30.14(3) | 14.3254(10) |
| α (°) | 90 | 76.977(7) |
| β (°) | 90 | 77.326(7) |
| γ (°) | 90 | 64.653(7) |
| <i>V</i> (Å ³) | 9983.6 | 972.7 |
| <i>Z</i> | 8 ^a | 2 |
| Number of reflections measured | 2643 | 1726 |
| Number of reflections with $I > 3\sigma(I)$ | 1657 | 1102 |
| <i>R</i> ₁ | 0.10 | 0.12 |
| <i>R</i> _w | 0.12 | 0.10 |

^a Two independent molecules in the unit cell.

with a solution of S_8 (1 g, 3.9 mmol) in benzene (10 ml). The system was left to stand at room temperature for 4 d. Large green needle-shaped crystals were isolated by decantation, washed with heptane and dried at 60 °C/0.1 torr. Yield 0.4 g (57%).

IR spectrum (ν , cm^{-1}): 605 m., 670 w., 755 m., 800 s., 870 m., 1005 m., 1155 s., 1355 m., 1380 w., 1425 w.br., 290 w.br., 2970 w.br.

(C₅H₅)₂Cr₂(μ-OCMe₃)₂(μ-Se) (IV)

A twenty-fold excess of powdered selenium metal was added to the red-brown solution of Cp₂Cr₂(μ-OCMe₃)₂ (obtained from the reaction of Cp₂Cr (0.5 g, 2.74 mmol) with HOOCMe₃ in pentane (15 ml). The reaction mixture was stirred with a magnetic stirrer for 2 d to give a brown-green solution, which was evaporated to dryness at 22 °C/0.1 torr. The brown-green residue was washed with 25 ml of cold (−70 °C) pentane and dissolved in 30 ml of pentane. The brown-green solution was concentrated to 10 ml at 22 °C/0.1 torr and left to stand at −18 °C for 2 d. The brown-green single crystals were isolated from the mother liquor by decantation, washed with cold (−70 °C) pentane and dried in stream of argon flow at 22 °C. Yield 0.4 g.

IR spectrum (ν , cm^{−1}): 545 m.br., 810 s., 920 m.br., 1030 m.br., 1165 s., 1350 m., 1420 m.br., 2955 w.br.

Thermolysis of (C₅H₅)₂Cr₂(μ-OCMe₃)₂(μ-Se) (IV)

An excess of selenium metal was added to the red-brown solution of Cp₂Cr₂(μ-OCMe₃)₂ (obtained from the reaction of Cp₂Cr (0.5 g, 2.74 mmol) with HOOCMe₃) in toluene (25 ml). The reaction mixture was refluxed for 2 h, the brown-green solution thus formed was filtered and the solvent was evaporated in an argon flow at 120 °C. The solid residue was extracted by hot heptane until it became colourless (solution A) (40–60 ml altogether). Afterwards the green extract (A) was concentrated at 120 °C to 5–8 ml and cooled to −18 °C. After one day, the large green prisms Cp₂Cr₂(OCMe₃)₂(μ-OCMe₃)₂ [3] was isolated from the solution by decantation, washed with cold (−20 °C) heptane and dried at 60 °C/0.1 torr. Yield 0.1 g (14%).

The fine brown-black crystalline, insoluble (C₅H₅)₄Cr₄Se₄, which remained after the extraction with hexane, was washed with hexane and dried at 60 °C/0.1 torr. Yield 0.17 g (32%).

IR spectrum (ν , cm^{−1}): 800 s., 900 w.br., 1000 m.br., 1420 w.br. Mass spectrum *: (Cp₄Cr₄Se₄)⁺ (m/z 784), (Cp₃Cr₄Se₄)⁺ (m/z 719), (Cp₂Cr₄Se₄)⁺ (m/z 654), (CpCr₄Se₄)⁺ (m/z 589), (Cr₄Se₄)⁺ (m/z 524).

Thermolysis of (C₅H₅)₂Cr₂(μ-OCMe₃)₂(μ-Te) (IVa)

The reaction of Cp₂Cr₂(μ-OCMe₃)₂ with the tellurium metal was performed as described for Se, and yielded 0.05 g (6.9%) of Cp₂Cr(μ-OCMe₃)₂(OCMe₃)₂ [3] and 0.23 g (35%) of Cp₄Cr₄Te₄ respectively.

IR spectrum of Cp₄Cr₄Te₄ (ν , cm^{−1}): 795 s., 995 m., 1410 w.br. Mass spectrum of Cp₄Cr₄Te₄: (Cp₄Cr₄Te₄)⁺ (m/z 980), (Cp₃Cr₄Te₄)⁺ (m/z 915), (Cp₂Cr₄Te₄)⁺ (m/z 850), (CpCr₄Te₄)⁺ (m/z 785), (Cr₄Te₄)⁺ (m/z 720).

References

- 1 M.H. Chisholm, F.A. Cotton, M.W. Extine, D.C. Rideout, Inorg. Chem., 18 (1979) 120.
- 2 S.E. Nefedov, A.A. Pasynskii, I.L. Eremenko, B. Orazsakhatov, O.G. Ellert, V.M. Novotortsev, S.B. Katser, A.S. Antsyshkina, M.A. Porai-Koshits, J. Organomet. Chem., 345 (1988) 97.
- 3 S.E. Nefedov, A.A. Pasynskii, I.L. Eremenko, B. Orazsakhatov, V.M. Novotortsev, O.G. Ellert, A.F. Shestakov, A.I. Yanovskii, Yu.T. Struchkov, J. Organomet. Chem., 384 (1989) 279.

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- 4 I.L. Eremenko, A.A. Pasynskii, Yu.V. Rakitin, O.G. Ellert, V.M. Novotortsev, V.T. Kalinnikov, V.E. Shklover, Yu.T. Struchkov, *J. Organomet. Chem.*, 256 (1983) 291.
- 5 A.A. Pasynskii, I.L. Eremenko, Yu.V. Rakitin, V.M. Novotortsev, V.T. Kalinnikov, G.G. Aleksandrov, Yu.T. Struchkov, *J. Organomet. Chem.*, 165 (1979) 57.
- 6 I.L. Eremenko, S.E. Nefedov, A.A. Pasynskii, B. Orazsakhmatov, O.G. Ellert, Yu.T. Struchkov, A.I. Yanovsky, D.V. Zagorevskii, *J. Organomet. Chem.*, 368 (1989) 185.
- 7 R.B. King, "Organometallic synthesis. 1. Transition metal compounds", Academic Press, New York—London, 1965.
- 8 V.M. Novotortsev, Ph.D. Thesis, Moscow, 1974.