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ANTIFERROMAGNETIC COMPLEXES WITH A METAL–METAL BOND

XI *. SYNTHESIS AND STRUCTURE OF THE PENTANUCLEAR CYCLOPENTADIENYL-t-BUTYLTHIOLATE-SULPHIDE CHROMIUM CLUSTER $[Cp_2Cr_2(\mu_2\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2Cr$ WITH A "BOW-TIE" FRAME

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Summary

The reaction of the binuclear complex $Cp_2Cr_2(SCMe_3)_2S$ (I) with $C_6H_6Cr(CO)_3$ in a benzene/heptane (1/2) mixture under UV irradiation yields black crystals of the cluster $[Cp_2Cr_2(SCMe_3)S_2]_2Cr$ (II), which, according to X-ray data, contains a pentanuclear "bow-tie" frame with a central Cr^{II} atom, the angle between the Cr_3 triangle planes being 90°. The bonds between the central and peripheral chromium atoms are oridinary (2.933(1) and 2.889(1) Å), while two pairs of Cr^{III} atoms are double-bonded (Cr–Cr 2.655(1) Å). Above and below each Cr_3 triangle is a μ_3-sulphide bridge (average $Cr_{(centr.)}$–S 2.333(3), average $Cr_{(periph.)}$–S 2.305(3) Å). Moreover, the peripheral Cr^{III} atoms are bonded in pairs with a μ_2-$SCMe_3$ bridge (average Cr–S 2.358(4) Å), and every Cr^{III} atom is coordinated by a π-cyclopentadienyl ligand (average Cr–C 2.26(1) Å, average C–C 1.43(2) Å).

Introduction

A series of our previous papers have shown that the binuclear complex $(CpCrSCMe_3)_2S$ (I), on coordination with metal carbonyl Lewis acids, retains its geometry when the metal coordination number (MCN) is 6 ($M(CO)_6$, where M = Cr,

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* For part X see ref. 8.

TABLE 1

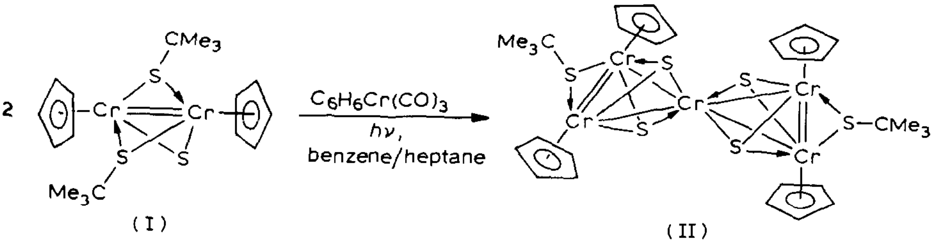
ATOMIC COORDINATES (for Cr and S, multiplied by 10^5; for the other atoms, multiplied by 10^4) AND ANISOTROPIC TEMPERATURE FACTORS IN THE FORM $T = \exp -1/4(B_{11}h^2a^{\star 2} + \ldots + 2\,B_{23}klb^{\star}c^{\star})$ FOR II

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr(1)	1/2	22533(30)	1/4	1.09(9)	0.46(9)	0.96(9)	0	0.67(8)	0
Cr(2)	41329(6)	29493(21)	27599(10)	1.19(7)	0.44(6)	0.62(6)	0 (5)	0.67(6)	−0.04(5)
Cr(3)	39072(6)	12327(22)	12651(10)	1.04(7)	0.60(6)	0.56(6)	−0.12(6)	0.49(6)	−0.13(5)
S(1)	42642(10)	41702(33)	16896(16)	1.4(1)	0.66(9)	0.87(9)	0.02(8)	0.72(9)	0.19(8)
S(2)	44856(10)	1780(34)	27027(16)	1.2(1)	0.61(9)	0.86(9)	0.03(8)	0.63(9)	0.04(8)
S(3)	32680(10)	23454(34)	15248(16)	1.0(1)	0.96(9)	0.88(9)	0.17(8)	0.54(8)	0.13(8)
C(1)	2892(4)	528(14)	1705(7)	1.1(4)	1.2(4)	1.4(4)	0.1(3)	0.7(3)	0.4(3)
C(2)	2647(4)	1478(15)	2172(7)	1.2(5)	2.0(5)	1.9(5)	0.5(4)	1.1(4)	0.2(4)
C(3)	3249(4)	−1057(15)	2288(7)	1.8(5)	1.1(4)	2.2(5)	0.3(4)	1.3(4)	0.8(4)
C(4)	2461(4)	−190(16)	782(7)	1.2(5)	2.2(5)	1.4(4)	−0.6(4)	0.4(4)	−0.5(4)
C(5)	4769(4)	4305(14)	4024(6)	2.1(5)	1.3(4)	0.5(4)	−0.4(4)	0.7(4)	−0.6(3)
C(6)	4562(4)	2824(14)	4263(6)	1.8(5)	1.5(4)	0.8(4)	−0.1(4)	0.9(4)	−0.6(3)
C(7)	4009(4)	3150(14)	3899(6)	3.0(5)	1.3(4)	0.8(4)	0.3(4)	1.4(4)	−0.2(3)
C(8)	3869(5)	4879(15)	3437(7)	3.8(6)	1.1(4)	1.2(4)	0.3(4)	1.8(4)	−0.2(3)
C(9)	4347(4)	5586(14)	3532(7)	3.3(6)	0.8(4)	1.2(4)	0 (4)	1.4(4)	−0.6(3)
C(10)	3577(4)	−1321(15)	409(6)	1.6(5)	1.3(4)	1.1(4)	−0.5(4)	0.5(4)	−0.9(4)
C(11)	4128(4)	−1113(15)	706(6)	3.3(6)	1.4(4)	1.1(4)	0 (4)	1.7(4)	−0.8(4)
C(12)	4177(4)	562(14)	344(7)	2.9(5)	1.5(4)	1.1(4)	−0.4(4)	1.7(4)	−0.8(4)
C(13)	3653(4)	1379(15)	−188(6)	1.3(4)	2.2(5)	0.4(4)	−0.3(4)	0.4(4)	−0.5(3)
C(14)	3293(4)	206(15)	−134(6)	2.1(5)	1.8(5)	0.7(4)	−0.2(4)	0.7(4)	−0.7(4)

Mo, W; $Mn_2(CO)_{10}$, $CpMn(CO)_3$), but easily loses one or two CMe_3 groups with the formation of direct Cr–M bonds when the MCN = 5 ($Fe(CO)_5$, non-bridged form of $Co_2(CO)_8$, $[CpNi(CO)]_2$) [1]. It appeared interesting to study the reaction of I with the complex $C_6H_6Cr(CO)_3$. Its MCN is 6, but cleavage of the photosensitive C_6H_6–Cr bond [2] should lead to a smaller MCN and, therefore, to the formation of new Cr–M bonds (Cr–Cr in this case).

Results

It has been proved that the reaction of $Cp_2Cr_2(SCMe_3)_2S$ (I) with $C_6H_6Cr(CO)_3$ in a benzene/heptane (1/2) mixture under UV irradiation leads to skeletal transformation of I with the formation of the pentanuclear complex $Cp_4Cr_5(SCMe_3)_2(S)_4$ (II):



The black prisms of II are gradually hydrolysed in air, easily soluble in THF and benzene, and moderately soluble in heptane.

The structure of complex II was solved by an X-ray analysis. Crystals of II are monoclinic, $C2/c$ space group; a 30.123(30), b 7.279(6), c 17.749(20) Å; β 122.94(7)°, V 3266.1 Å^3, $Z = 4$. The atomic coordinates and temperature factors are given in Table 1, and bond lengths and angles in Tables 2 and 3. The frame of molecule II

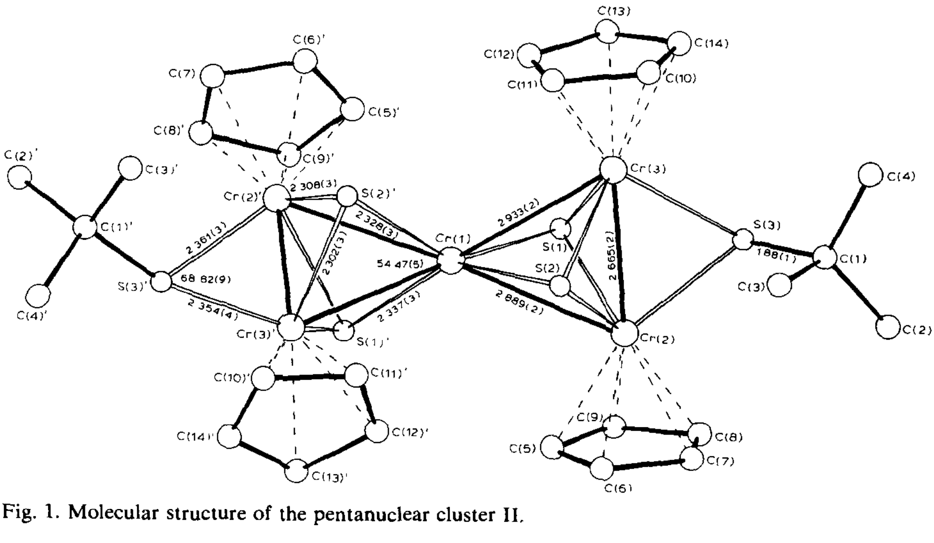


Fig. 1. Molecular structure of the pentanuclear cluster II.

TABLE 2

BOND LENGTHS FOR II

Bond	d (A)	Bond	d (Å)	Bond	d (Å)
Cr(1)–Cr(2)	2.933(2)	Cr(2)–C(9)	2.24(1)	C(1)–C(4)	1.53(1)
Cr(1)–Cr(3)	2.889(2)	Cr(3)–S(1)	2.327(3)	C(5)–C(6)	1.42(2)
Cr(1)–S(1)	2.337(3)	Cr(3)–S(2)	2.302(3)	C(5)–C(9)	1.43(2)
Cr(1)–S(2)	2.328(3)	Cr(3)–S(3)	2.354(4)	C(6)–C(7)	1.44(2)
Cr(2)–Cr(3)	2.665(2)	Cr(3)–C(10)	2.26(1)	C(7)–C(8)	1.43(2)
Cr(2)–S(1)	2.318(3)	Cr(3)–C(11)	2.25(1)	C(8)–C(9)	1.45(2)
Cr(2)–S(2)	2.308(3)	Cr(3)–C(12)	2.24(1)	C(10)–C(11)	1.45(2)
Cr(2)–S(3)	2.361(3)	Cr(3)–C(13)	2.259(9)	C(10)–C(14)	1.41(2)
Cr(2)–C(5)	2.24(1)	Cr(3)–C(14)	2.27(1)	C(11)–C(12)	1.42(2)
Cr(2)–C(6)	2.247(9)	S(3)–C(1)	1.88(1)	C(12)–C(13)	1.46(2)
Cr(2)–C(7)	2.25(1)	C(1)–C(2)	1.54(2)	C(13)–C(14)	1.42(2)
Cr(2)–C(8)	2.26(1)	C(1)–C(3)	1.53(2)		

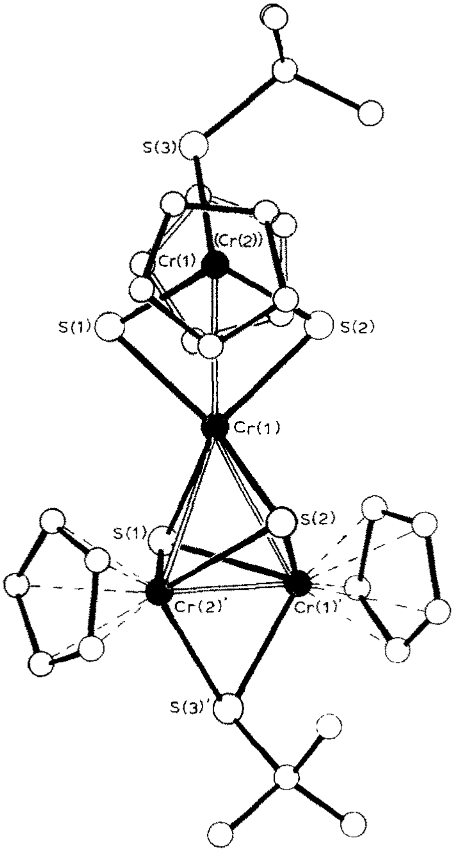


Fig 2 Projection of the molecule of the pentanuclear cluster II along the Cr–Cr axis

(Fig. 1) is a pentanuclear metal spirane containing $[Cr^{III}]_2 \cdot Cr^{II} \cdot [Cr^{III}]_2$ ions. The central Cr(1) atom is situated on the two-fold axis $2[1/2, y, 1/4]$ and thus the planes of the two Cr_3 triangles are normal to each other. Each metal triangle has two long Cr–Cr bonds (Cr(1)–Cr(2) 2.938(1) and Cr(1)–Cr(3) 2.889(1) Å) and one short Cr–Cr bond (Cr(2)–Cr(3) 2.665(1) Å). This difference in the distances between chromium is accompanied with corresponding changes of the CrSCr angles in the μ_3-sulphide bridges situated above and below the Cr_3 triangles (Fig. 2). Thus, the longer Cr(1)–Cr(2) and Cr(1)–Cr(3) bonds correspond to the larger CrSCr angles in the range 76.5(1)–78.5(1)°, while the shorter Cr(2)–Cr(3) bond corresponds to the smaller CrSCr angles (70.02(9)–70.62(9)°). The Cr(1)S(1)S(2) plane is, in fact, normal to the Cr(1)Cr(2)Cr(3) triangle and the Cr(1)S(1)′S(2)′ plane. Thus, the Cr(1) atom with a d^4 electronic configuration is surrounded by a tetrahedron of sulphur and chromium atoms Cr(2) and Cr(3). Each of the latter is additionally coordinated by one η^5-C_5H_5 ligand (Cr–C 2.24(1)–2.27(1), average C–C 1.43(2) Å), two μ_3-bridging sulphur atoms and a μ_2-bridging ligand $SCMe_3$ (Cr–S 2.361(3) and 2.354(4), S–C 1.88(1) Å, CrSCr 68.82(9)°).

Discussion

Photochemical synthesis of the pentanuclear cluster II from I and $C_6H_6Cr(CO)_3$ probably occurs through intermediate formation of the adduct $(CpCrSCMe_3)_2S \cdot Cr(CO)_2C_6H_6$. The elimination of the C_6H_6 tridentate ligand from the latter under UV irradiation obviously not only leads to the conversion of coordinated I with the loss of one CMe_3 group, but also allows coordination of the second molecule of I with the final formation of II. On the other hand, formation of the intermediate $(Cp_2Cr_2SCMe_3)(\mu_3\text{-}S)_2Cr(CO)_2$ cannot be ruled out. This intermediate is analogous to the recently described cyclic metal cluster $(Cp_2Cr_2SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ (III) [1], but being electron-deficient, it is disproportionated into II and the $Cr(CO)_4$ fragment.

The metal spirane structure of cluster II is especially interesting due to fact that the bond lengths between the peripheral Cr^{III} atoms remain virtually unchanged (2.665(1) Å), compared to the original molecule of I (2.689 Å), despite the formation of ordinary bonds of ca. 2.9 Å between each peripheral Cr^{III} atom and the central Cr^{II} atom. The lengths of these bonds are close to the ordinary Cr–Cr bond length (2.906 Å) in the complex $Cp_2Cr_2(NO)_2(\mu\text{-}SCMe_3)(\mu\text{-}SSCMe_3)$ [3]. The same situation was observed on formation of cluster III with a cyclic metal frame Cr_2Co, where, in spite of the formation of two oridinary Co–Cr bonds (2.579 and 2.529 Å), the Cr–Cr multiple bond was preserved and even shortened to 2.625(1) and 2.609(1) Å in two independent molecules. A recent discussion of this problem [4] has shown that on the assumption of a double Cr=Cr bond in I and in the $(Cp_2Cr_2SCMe_3)(\mu_3\text{-}S)_2$ fragment (Q), each chromium atom still has one half-occupied orbital capable of accepting one electron from the added metal-containing group. In the process oridinary Cr–M bonds are formed, but without affecting the oribitals of the double Cr=Cr bond, which therefore remains unchanged. For instance, in complex II the central Cr^{II} atom requires only 4 electrons to fill the four half-occupied orbitals of the four Cr^{III} atoms in the two (Q) fragments. This explains the formation of four oridinary $Cr_{(centr.)}$–$Cr_{(periph)}$ bonds, as well as the high symmetry of structure II.

TABLE 3

BOND ANGLES FOR II

Angle	ω (°)	Angle	ω (°)	Angle	ω (°)
Cr(2)Cr(1)Cr(2)′	160.11(7)	Cr(3)Cr(2)S(2)	54.59(9)	Cr(2)S(2)Cr(3)	70.62(9)
Cr(2)Cr(1)Cr(3)	54.47(5)	Cr(3)Cr(2)S(3)	55.46(9)	Cr(2)S(3)Cr(3)	68.82(9)
Cr(2)Cr(1)Cr(3)′	132.06(7)	S(1)Cr(2)S(2)	90.6(1)	Cr(2)S(3)C(1)	115.9(4)
Cr(2)Cr(1)S(1)	50.65(8)	S(1)Cr(2)S(3)	84.5(1)	Cr(3)S(3)C(1)	115.1(4)
Cr(2)Cr(1)S(1)′	115.33(9)	S(2)Cr(2)S(3)	95.6(1)	S(3)C(1)C(2)	106.6(8)
Cr(2)Cr(1)S(2)	50.45(8)	Cr(1)Cr(3)Cr(2)	63.60(6)	S(3)C(1)C(3)	112 2(8)
Cr(2)Cr(1)S(2)′	149.43(9)	Cr(1)Cr(3)S(1)	51.88(8)	S(3)C(1)C(4)	107.4(8)
Cr(3)Cr(1)S(1)	51.57(8)	Cr(1)Cr(3)S(2)	51.79(8)	C(2)C(1)C(3)	109.9(9)
Cr(3)Cr(1)S(1)′	158.22(9)	Cr(1)Cr(3)S(3)	118.61(9)	C(2)C(1)C(4)	110.8(9)
Cr(3)Cr(1)S(2)	51.00(8)	Cr(2)Cr(3)S(1)	54.83(9)	C(3)C(1)C(4)	110.0(9)
Cr(3)Cr(1)S(2)′	107.19(9)	Cr(2)Cr(3)S(2)	54.78(9)	C(6)C(5)C(9)	106.7(9)
S(1)Cr(1)S(1)′	106.7(1)	Cr(2)Cr(3)S(3)	55.72(9)	C(5)C(6)C(7)	109.2(9)
S(1)Cr(1)S(2)	89.7(1)	S(1)Cr(3)S(2)	90 5(1)	C(6)C(7)C(8)	108 (1)
S(1)Cr(1)S(2)′	141.3(1)	S(1)Cr(3)S(3)	84.5(1)	C(7)C(8)C(9)	106 (1)
S(2)Cr(1)S(2)′	99.1(1)	S(3)Cr(3)S(2)	96.0(1)	C(5)C(9)C(8)	110 (1)
Cr(1)Cr(2)Cr(3)	61.92(6)	Cr(1)S(1)Cr(2)	78.1(1)	C(11)C(10)C(14)	108 (1)
Cr(1)Cr(2)S(1)	51.24(8)	Cr(1)S(1)Cr(3)	76.5(1)	C(10)C(11)C(12)	108 (1)
Cr(1)Cr(2)S(2)	54.59(9)	Cr(2)S(1)Cr(3)	70.02(9)	C(11)C(12)C(13)	107.5(9)
Cr(1)Cr(2)S(3)	116.70(9)	Cr(1)S(2)Cr(2)	78.5(1)	C(12)C(13)C(14)	107.9(9)
Cr(3)Cr(2)S(1)	55.15(9)	Cr(1)S(2)Cr(3)	77 2(1)	C(10)C(14)C(13)	109 (1)

Experimental

All experiments were carried out in a pure argon atmosphere. Benzene and heptane were purified by distillation over Na sand in pure argon stream. Initial $(CpCrSCMe_3)_2S$ and $C_6H_6Cr(CO)_3$ were prepared by the methods of refs. 5 and 6, respectively.

IR spectra were measured with a UR-20 spectrometer in KBr pellets. Experimental data for an X-ray structural study were obtained with a Syntex $P2_1$ autodiffractometer ($\lambda = \text{Mo-}K_\alpha$, graphite monochromator, T −100 °C, $\theta/2\theta$-scan, $2\theta \leqslant 52°$). The structure was solved by the direct method using a modified MULTAN program [7], and refined in a full-matrix anisotropic approximation for all non-hydrogen atoms to $R = 0.064$ and $R_w = 0.080$ for 2696 independent reflections with $I \geqslant 2\sigma$.

$[Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2Cr$ (II)

A violet solution of 0.13 g (0.6 mmol) of $C_6H_6Cr(CO)_3$ and 0.30 g (0.6 mmol) of $(CpCrSCMe_3)_2S$ in a mixture of 15 ml of benzene and 30 ml of heptane was exposed to UV radiation (PRK-4 lamp) in a quartz Schlenk vessel equipped with a water-cooled jacket (20 °C) and a magnetic stirrer. After 4 h the colour of the mixture changed to black-violet and black crystals were precipitated. After standing for 3 d at ca. 0 °C, the crystals were separated from the mother liquor, washed with pentane and dried in vacuo. M.p. (dec.) 148–153 °C. Yield 73%.

IR spectrum (ν, cm^{-1}): 810s, 1018m, 1060w, 1168m, 2930w, 2970w, 2985w, 3090w.

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