Journal of Organometallic Chemistry, 270 (1984) 53–64
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ANTIFERROMAGNETIC COMPLEXES WITH A METAL–METAL BOND

XII *. SYNTHESIS, MOLECULAR STRUCTURES, AND MAGNETIC PROPERTIES OF THE CLUSTERS $(MeC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ AND $(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Mn(CO)_3$ WITH TRIANGULAR Cr_2M METAL FRAMES

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(Received February 28th, 1984)

Summary

The triangular cluster $(MeC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ (V) was obtained by reaction of the binuclear complex $(MeC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)$ (IV) with $Co_2(CO)_8$ in heptane. The structure of V was solved by an X-ray structural study. Crystals of V are monoclinic, space group $P2_1$, a 9.437(1), b 15.9460(8), c 7.2540(8) Å, β 109.399(9), V 1029.6 Å^3, $Z = 4$, $R = 0.047$, $R_w = 0.052$. The main geometric parameters of V are close to those of its previously described cyclopentadienyl analogue $(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ (III), however, the Cr–Cr bonds in V are somewhat shorter (by 0.02–0.04 Å) and the methylcyclopentadienyl rings are in a staggered conformation in contrast to the eclipsed conformation of the C_5H_5 ligands in III. A photochemical reaction of $(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)$ (I) with $Mn_2(CO)_{10}$ with a reagent ratio of 2/1 in boiling benzene (3 h) yielded the heteronuclear cluster $(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Mn(CO)_3$ (VI), characterized by an X-ray study (space group $C2$, a 18.709(7), b 9.883(4), c 11.470(5) Å, β 109.65(2)°, V 1997.3 Å^3, $Z = 4$). VI has a triangular metal frame Cr_2Mn (Cr–Cr 2.646(2), Cr–Mn 2.828(2) and 2.716(2) Å). The electronic and steric factors governing the formation of III, V and VI are discussed. I, III–VI exhibit antiferromagnetic

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* For part XI see ref. 13.

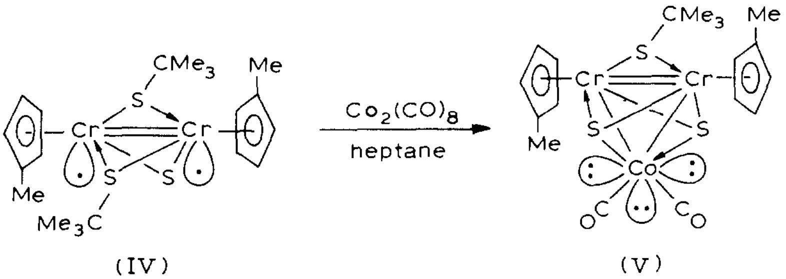
properties with the exchange parameter ($-2J$) increasing on introduction of a methyl group into the cyclopentadienyl ligand, as well as with the formation of metal cycle Cr_2M ($-2J$(Cr–Cr) 430, 530, 478, 556, 654 cm^{-1}, respectively).

Introduction

Previous papers of this series have shown that the binuclear antiferromagnetic ($-2J$ 430 cm^{-1}) complex $(CpCrSCMe_3)_2S$ (I) is capable of coordination with metal-carbonyl Lewis acids by a lone electron pair of the sulphide bridge [1]. If the metal coordination number (MCN) is equal to 6, stable $(CpCrSCMe_3)_2S \cdot ML$ adducts are formed (ML = $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$, $CpMn(CO)_2$, $Mn_2(CO)_9$ [2]), and if MCN = 5 ($Fe(CO)_5$, $(CO)_4Co$–$Co(CO)_4$), the loss of the t-butyl group occurs and the M atom is bonded to two sulphide bridges in molecules of the antiferromagnetic clusters $(Cp_2Cr_2SCMe_3)\cdot(\mu_3\text{-}S)_2Fe(CO)_3$ (II) [3] and $(Cp_2Cr_2SCMe_3)(\mu_3\text{-}S)_2 \cdot Co(CO)_2$ (III) [2]. In the latter case, formation of the metal cycle Cr_2Co is accompanied with a shortening of the Cr–Cr bond (from 2.689 to 2.617 Å) and an increase in antiferromagnetic exchange interactions (the $-2J$ value increases to 530 cm^{-1}). It appeared interesting to study the above-mentioned trends in more detail and, first of all, to obtain an analogue of complex III with one electron-donating methyl group in each cyclopentadienyl ligand. Secondly, we converted the adduct $(CpCrSCMe_3)_2S \cdot Mn_2(CO)_9$ into a cluster under UV irradiation, where the MCN decreases below 6 due to partial decarbonylation.

Results and discussion

The reaction of $Cp'_2Cr_2(\mu\text{-}SCMe_3)_2S$ (IV) ($Cp' = CH_3C_5H_4$) [4] with $Co_2(CO)_8$ in heptane leads as in the previously described reaction of complex I, to the formation of the metal cyclic cluster $(Cp_2Cr_2SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ (V):



(IV) (V)

Dark-green prisms of V (from heptane) are moderately sensitive to oxygen and air moisture, and are easily soluble even in aliphatic hydrocarbons. The IR spectrum contains two strong bands of equal intensity at 1898 and 1940 cm^{-1} (corresponding to the stretching modes of the terminal carbonyl groups), bands at 1130, 2800 and 2890 cm^{-1} (characteristic of the $SCMe_3$ group), as well as bands characteristic of methylcyclopentadienyl ligands at 789, 1012, 1420 and 3078 cm^{-1}. V is antiferromagnetic; its effective magnetic moment decreases from 1.01 μ_B to 0.63 μ_B on lowering the temperature from 291 to 79 K. The μ_{eff}/T dependence is described by a dimeric HDVV model [5] for the interaction of two Cr^{III} ions with spins of 3/2 and an exchange parameter of 556 cm^{-1} (taking into account a 3% paramagnetic monomer admixture, the mean square-error is 3%). This $-2J$ value is considerably higher than that found (530 cm^{-1}) for the analogous cluster III, and the $-2J$ value for IV (478 cm^{-1}) is higher than that for I (430 cm^{-1}).

In order to study the geometry changes of the cluster III on introduction of methyl groups into the cyclopentadienyl ligands, an X-ray structural analysis of complex V was carried out. The atomic coordinates are given in Table 1; anisotropic temperature factors, bond lengths and angles in Tables 2 and 3. The molecular structure of V with the main geometric parameters is shown in Fig. 1 and a projection of complex V in Fig. 2.

Similar to III, the metal frame of V is a triangle with slightly shortened Cr=Cr (2.590(2) Å) and Cr–Co bonds (av. 2.530(2) Å), which probably accounts for the stronger antiferromagnetic exchange interactions. The Cr–S and Co–S bonds supported by the μ_3-sulphide bridges are only slightly shortened (average 0.02–0.04 Å) with respect to III. The main difference lies in the conformation of the $CH_3C_5H_4$ ligands, which is staggered in V, but eclipsed in III (average Cr–C 2.25(1) Å, average $C-C_{C_5H_4}$ 1.41(2) Å). On the other hand, the unit Cp–Cr–Cr–Cp (Cp is the centroid of the Cp ligand) remains almost linear (CpCrCr 176.3°). Two carbonyl groups are situated in the metal cycle plane of Cr_2Co which is normal to the plane of three S atoms (the dihedral angle between the two planes equals 88.13°). The angle

(Continued on p. 58)

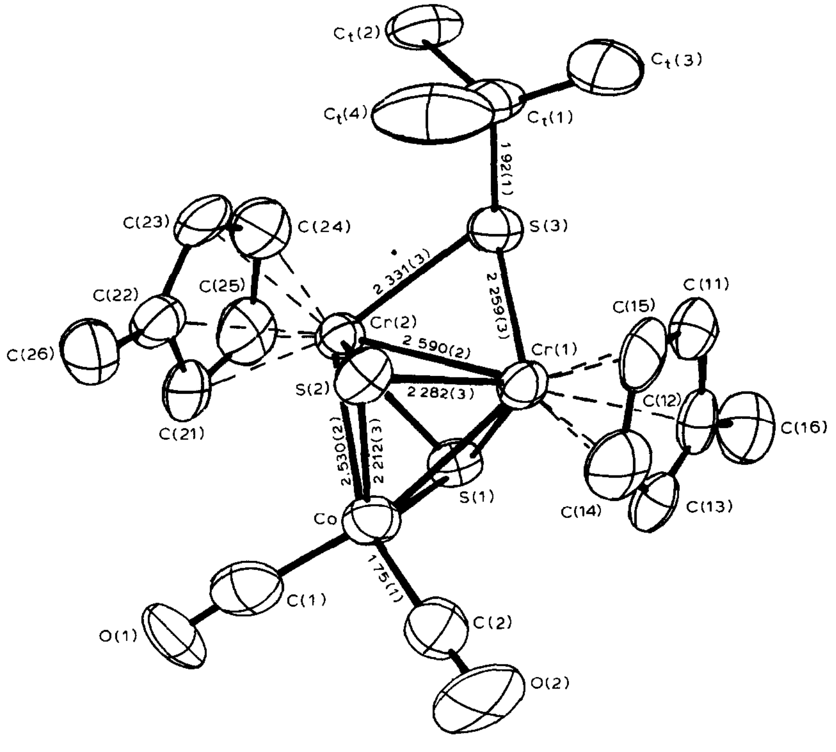


Fig. 1. Molecular structure of complex V with main bond lengths.

TABLE 1

ATOMIC COORDINATES MULTIPLIED BY 10^4, FOR $(CH_3C_5H_4)_2Cr_2(SCMe_3)S_2Co(CO)_2$ (V)

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr(1)	9335(2)	2292	644(2)	2.89(6)	3.09(7)	2.45(6)	-0.07(6)	0.15(5)	-0.32(6)
Cr(2)	7364(2)	1252(1)	-1499(2)	2.85(6)	2.20(5)	2.81(6)	-0.04(6)	0.23(5)	-0.20(6)
Co	8798(2)	889(1)	2024(2)	3.92(6)	3.96(6)	2.33(5)	0.05(6)	0.50(5)	0.21(5)
S(1)	9872(3)	974(2)	-151(4)	3.13(9)	3.4(1)	2.96(9)	0.53(9)	0.75(8)	0.09(9)
S(2)	7139(3)	1918(2)	1095(4)	3.5(1)	4.3(1)	3.2(1)	0.0(1)	1.04(9)	-0.08(9)
S(3)	9185(3)	2468(2)	-2604(4)	3.4(1)	2.9(1)	2.90(9)	0.32(9)	0.67(9)	0.12(9)
O(1)	7694(11)	-732(6)	2706(14)	9.9(6)	4.3(4)	5.6(5)	-1.4(4)	3.1(5)	1.0(4)
O(2)	10963(10)	997(8)	5845(11)	7.5(5)	12.5(9)	2.7(3)	0.2(6)	-0.8(3)	0.2(5)
C(1)	8077(13)	-112(8)	2368(15)	5.2(6)	6.3(7)	2.5(4)	0.6(5)	0.9(4)	0.6(5)
C(2)	10090(13)	980(9)	4392(16)	5.5(6)	6.5(7)	4.1(5)	-0.2(6)	1.9(5)	0.5(6)
C(11)	10611(12)	3500(8)	722(16)	4.3(5)	3.9(5)	4.5(5)	-1.6(4)	0.1(4)	-0.9(5)
C(12)	11682(12)	2837(7)	1216(17)	3.7(5)	3.8(5)	4.8(6)	-1.8(4)	-0.3(4)	-0.9(5)
C(13)	11572(12)	2508(8)	2921(17)	4.0(5)	4.8(6)	4.3(5)	-1.9(5)	-1.1(4)	-0.1(5)
C(14)	10442(14)	2924(9)	3491(18)	5.8(6)	5.6(7)	4.0(5)	-1.1(5)	0.2(5)	-1.9(5)
C(15)	9844(13)	3558(8)	2101(19)	4.4(5)	4.8(6)	5.7(7)	-1.6(5)	0.6(5)	-1.9(6)
C(16)	12715(13)	2577(8)	199(20)	3.9(5)	5.6(7)	6.6(7)	-0.8(5)	1.8(5)	-0.5(6)
C(21)	6426(12)	-55(6)	-2055(16)	4.5(5)	2.7(4)	3.7(5)	-1.5(4)	-0.4(4)	-1.2(4)
C(22)	5199(11)	474(7)	-2048(15)	3.1(4)	3.6(5)	3.8(5)	-0.2(4)	-0.2(4)	-0.3(4)
C(23)	4994(11)	1071(7)	-3516(15)	4.0(5)	4.6(6)	3.6(5)	-0.8(4)	-1.1(4)	0.0(4)
C(24)	6098(13)	887(8)	-4487(15)	6.1(6)	4.6(6)	3.0(4)	-1.6(5)	-0.3(4)	-0.9(5)
C(25)	6927(13)	182(7)	-3586(16)	5.6(6)	4.6(6)	3.4(5)	-1.3(5)	0.9(4)	-1.8(5)
C(26)	4288(13)	415(8)	-736(19)	4.6(5)	4.9(6)	6.0(7)	-0.5(5)	2.0(5)	0.4(5)
$C_t(1)$	6797(12)	3377(7)	-3413(16)	4.3(5)	3.4(5)	4.3(5)	1.2(4)	-0.1(4)	0.5(4)
$C_t(2)$	5722(16)	3123(9)	-5411(20)	8.0(8)	4.8(7)	4.8(8)	1.7(6)	-1.8(6)	-0.3(6)
$C_t(3)$	5794(19)	3475(12)	-2171(22)	11(1)	11(1)	6.3(8)	8.1(9)	4.3(8)	2.6(9)
$C_t(4)$	7658(18)	4170(10)	-3358(30)	7.6(9)	5.1(8)	14(1)	0.3(7)	-2.1(9)	4.6(9)

TABLE 2

BOND LENGTHS FOR V

Bond	d (Å)	Bond	d (Å)
Cr(1)–Cr(2)	2.590(2)	Co–C(1)	1.79(1)
Cr(1)–Co	2.569(2)	Co–C(2)	1.75(1)
Cr(1)–S(1)	2.280(3)	S(3)–C$_t$(1)	1.92(1)
Cr(1)–S(2)	2.282(3)	O(1)–C(1)	1.11(2)
Cr(1)–S(3)	2.259(3)	O(2)–C(2)	1.10(1)
Cr(1)–C(11)	2.26(1)	C(11)–C(12)	1.42(2)
Cr(1)–C(12)	2.29(1)	C(11)–C(15)	1.42(2)
Cr(1)–C(13)	2.23(1)	C(12)–C(13)	1.38(2)
Cr(1)–C(14)	2.22(1)	C(12)–C(16)	1.46(2)
Cr(1)–C(15)	2.26(1)	C(13)–C(14)	1.43(2)
Cr(2)–Co	2.530(2)	C(14)–C(15)	1.41(2)
Cr(2)–S(1)	2.284(3)	C(21)–C(22)	1.43(2)
Cr(2)–S(2)	2.232(3)	C(21)–C(25)	1.40(2)
Cr(2)–S(3)	2.331(3)	C(22)–C(23)	1.39(2)
Cr(2)–C(21)	2.25(1)	C(22)–C(26)	1.48(2)
Cr(2)–C(22)	2.31(1)	C(23)–C(24)	1.43(2)
Cr(2)–C(23)	2.25(1)	C(24)–C(25)	1.40(2)
Cr(2)–C(24)	2.18(1)	C$_t$(1)–C$_t$(2)	1.52(2)
Cr(2)–C(25)	2.23(1)	C$_t$(1)–C$_t$(3)	1.51(2)
Co–S(1)	2.144(3)	C$_t$(1)–C$_t$(4)	1.50(2)
Co–S(2)	2.212(3)		

TABLE 3

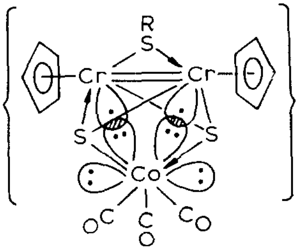
BOND ANGLES FOR V

Angle	ω (°)	Angle	ω (°)	Angle	ω (°)
Cr(2)Cr(1)Co	58.74(6)	Cr(1)CoS(2)	56.42(9)	CoC(1)O(1)	175(1)
Cr(2)Cr(1)S(1)	55.50(8)	Cr(1)CoC(1)	165.2(4)	CoC(2)O(2)	175(1)
Cr(2)Cr(1)S(2)	54.08(9)	Cr(1)CoC(2)	98.5(5)	C(12)C(11)C(15)	111(1)
Cr(2)Cr(1)S(3)	56.96(8)	Cr(2)CoS(1)	57.79(9)	C(11)C(12)C(13)	104(1)
CoCr(1)S(1)	52.08(8)	Cr(2)CoS(2)	55.66(9)	C(11)C(12)C(16)	128(1)
CoCr(1)S(2)	53.88(8)	Cr(2)CoC(1)	104.2(4)	C(13)C(12)C(16)	127(1)
CoCr(1)S(3)	115.30(9)	Cr(2)CoC(2)	159.5(4)	C(12)C(13)C(14)	112(1)
S(1)Cr(1)S(2)	94.8(1)	S(1)CoS(2)	100.9(1)	C(13)C(14)C(15)	107(1)
S(1)Cr(1)S(3)	85.4(1)	S(1)CoC(1)	117.0(4)	C(11)C(15)C(14)	106(1)
S(2)Cr(1)S(3)	92.4(1)	S(1)CoC(2)	111.8(4)	C(22)C(21)C(25)	109.4(9)
Cr(1)Cr(2)Co	60.22(6)	S(2)CoC(1)	116.2(4)	C(21)C(22)C(23)	107.8(9)
Cr(1)Cr(2)S(1)	55.35(8)	S(2)CoC(2)	115.4(4)	C(21)C(22)C(26)	127(1)
Cr(1)Cr(2)S(2)	55.90(9)	C(1)CoC(2)	96.3(6)	C(23)C(22)C(26)	125(1)
Cr(1)Cr(2)S(3)	54.35(8)	Cr(1)S(1)Cr(2)	69.15(9)	C(22)C(23)C(24)	106.8(9)
CoCr(2)S(1)	52.60(8)	Cr(1)S(1)Co	70.91(9)	C(23)C(24)C(25)	108(1)
CoCr(2)S(2)	54.94(9)	Cr(2)S(1)Co	69.61(9)	C(21)C(25)C(24)	108(1)
CoCr(2)S(3)	114.16(9)	Cr(1)S(2)Cr(2)	70.01(9)	S(3)C$_t$(1)C$_t$(2)	105.2(8)
S(1)Cr(2)S(2)	96.1(1)	Cr(1)S(2)Co	69.70(9)	S(3)C$_t$(1)C$_t$(3)	113.5(9)
S(1)Cr(2)S(3)	83.7(1)	Cr(2)S(2)Co	69.4(1)	S(3)C$_t$(1)C$_t$(4)	108.4(9)
S(2)Cr(2)S(3)	91.8(1)	Cr(1)S(3)Cr(2)	68.67(9)	C$_t$(2)C$_t$(1)C$_t$(3)	104(1)
Cr(1)CoCr(2)	61.05(9)	Cr(1)S(3)C$_t$(1)	117.0(4)	C$_t$(2)C$_t$(1)C$_t$(4)	116(1)
Cr(1)CoS(1)	57.01(9)	Cr(2)S(3)C$_t$(1)	117.3(4)	C$_t$(3)C$_t$(1)C$_t$(4)	110(1)

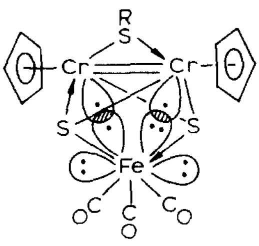
(O)C–Co–C(O) is 96.3(6)°, which corresponds to the equal intensities of the ν(CO) bands in the IR spectrum of V.

The Cr–Cr bond length in both V and III is intermediate between the values 2.950 Å for the ordinary Cr–Cr bond in the complex $[CpCr(NO)SPh]_2$ [6] and 2.30 Å for the triple Cr≡Cr bond in the dimer $[CpCr(CO)_2]_2$ [7]. If we assume that V and III have a double Cr=Cr bond, then the Cr–Co bonds can be, at the most, ordinary, and the Co^I atom is electron-saturated.

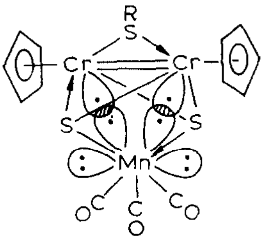
As discussed in [2], the formation of cluster III from I and $Co_2(CO)_8$ proceeds through the supposed intermediates I · $Co_2(CO)_7$ and $(Cp_2Cr_2SCMe_3)(\mu_3\text{-}S)_2Co(CO)_3$ (**A**). It is interesting to compare a probable structure of intermediate **A**, obtained by adding one carbonyl group to structure III, with the geometry of the previously studied analogous cluster II, wherein a Co^I atom is substituted for the Fe^I atom [3], as well as with the probable geometry of the hypothetical Mn-containing analogue $(Cp_2CrSCMe_3)(\mu_3\text{-}S)_2Mn(CO)_3$ (VI):



(**A**) d^8



(II) d^7



(VI) d^6

It can be seen that the complexes $(Cp_2Cr_2SCMe_3)(\mu_3\text{-}S)_2M(CO)_3$ while identical in composition, differ in the number of *d*-electrons of the M^1 atom (d^8, d^7 and d^6 for M = Co, Fe and Mn, respectively), which occupy four vacant orbitals of M. As a result, the conditions of their bonding with Cr^{III} atoms, each of which has one half-occupied orbital, are different. In the case of cluster **A**, in the antibonding orbitals of the Cr_2M frame there are two electrons, in cluster II only one electron, and in cluster VI no electrons. The geometry of cluster II [3] shows that predominantly only one Cr–Fe bond (3.11 Å) is weakened to a state of one-electron bonding, while the second Cr–Fe bond (2.726 Å) is an ordinary two-electron bond (the short Cr=Cr distance, 2.707 Å, indicates considerable double-bonding of these atoms). It may be supposed that in intermediate **A** only one ordinary Cr–Co bond is formed *. Finally, considerable Cr=Cr double-bonding may be supposed in cluster VI with the formation of two two-electron Mn–Cr bonds, which should have approximately the same length (ca. 2.75 Å) as the ordinary Fe–Cr bond in II.

To test these assumptions, we carried out a photochemical reaction of I with $Mn_2(CO)_{10}$. In contrast to the previously found conditions of I · $Mn_2(CO)_9$ adduct (VII) formation (reagent ratio 1/1, THF, 20°C, UV irradiation until cleavage of 1 mmol of CO [2]), in the present case the reagent ratio was 2/1, and UV irradiation

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* In fact, treatment of **A** with trimethylacetic acid yielded the $[Cp_3Cr_3S_3O]Co(CO)_3 \cdot HOOCCMe_3$ cluster, whose $Co(CO)_3$ fragment, according to an X-ray structural study, is weakly bonded to the trichromium cyclic frame. (These results will be published in the next paper of this series.)

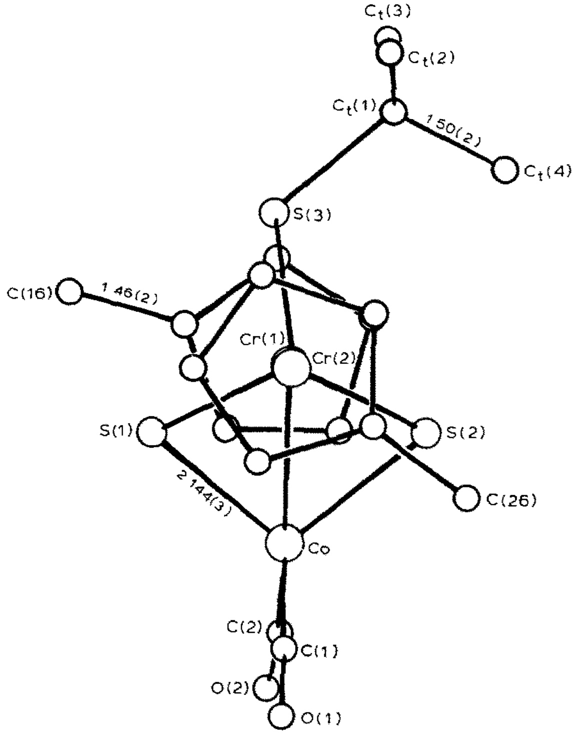
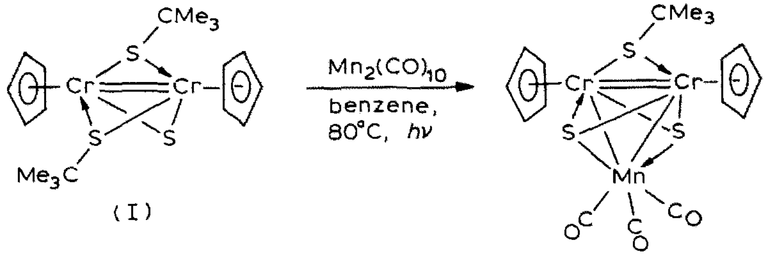


Fig. 2. Projection of the molecule of complex V along the Cr–Cr axis.

of the boiling mixture in benzene was continued until gas elimination had completely ceased and the ν(CO) bands of the intermediate complex VII (1920, 1953, 1988, 2020 and 2088 cm^{-1}) had disappeared:



(I)

(VI)

VI was isolated in the form of black prisms; it was easily soluble in organic solvents and moderately sensitive to oxygen and air moisture. In the IR spectrum of VI in KBr pellets, there are three strong bands of terminal carbonyl group stretching modes at 1895, 1915 and 1975 cm^{-1} with an intensity ratio characteristic of the local C_{3v} symmetry (in heptane the ν(CO) bands are shifted to 1915, 1933, 1990 cm^{-1}). As for the rest, the spectrum of VI closely resembles the spectra of II and III. VI is antiferromagnetic; the decrease of $\mu_{eff.}$ from 0.76 to 0.37 μ_B in the 297–79 K

TABLE 4

ATOMIC COORDINATES ($\times 10^4$, FOR Mn, Cr AND S$\times 10^5$) AND ANISOTROPIC TEMPERATURE FACTORS FOR $(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Mn(CO)_3$ (VI) IN THE FORM $T = \exp[-1/4(B_{11}h^2a^{\star 2} + \ldots + 2B_{12}hka^{\star}b^{\star} + \ldots)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	32987(6)	11581	27982(10)	1.61(4)	0.95(3)	1.45(4)	−0.05(9)	0.64(3)	−0.0(1)
Cr(1)	19040(8)	25652(13)	21693(12)	2.10(5)	0.47(4)	1.65(5)	0.14(4)	1.05(4)	0.09(4)
Cr(2)	19356(7)	−1116(13)	22051(11)	1.34(4)	0.41(4)	1.16(4)	0.01(4)	0.64(4)	0.04(4)
S(1)	23424(8)	12053(66)	9449(14)	1.75(6)	1.11(5)	1.25(6)	−0.1(2)	0.85(5)	−0.1(2)
S(2)	24603(9)	12108(69)	38711(14)	2.13(6)	1.28(6)	1.20(6)	−0.2(2)	0.77(5)	−0.1(2)
S(3)	8330(9)	12191(65)	14350(14)	1.60(6)	1.04(5)	1.63(6)	−0.0(2)	0.88(5)	−0.0(2)
O(1)	4152(4)	3502(8)	4364(7)	4.5(4)	2.8(3)	3.2(3)	−0.7(3)	1.2(3)	−0.9(3)
O(2)	4413(3)	1209(22)	1473(5)	2.5(2)	3.3(3)	3.3(2)	0.1(9)	1.8(2)	−0.2(9)
O(3)	4160(4)	−880(8)	4474(7)	3.1(3)	4.8(4)	4.8(4)	2.8(3)	1.9(3)	3.2(4)
C(1)	3802(5)	2619(11)	3787(9)	1.6(3)	3.0(4)	3.3(4)	0.4(3)	1.4(3)	−0.2(4)
C(2)	3966(4)	1151(27)	1966(7)	2.0(3)	1.3(3)	2.0(3)	−0.0(7)	0.4(2)	0.2(7)
C(3)	3852(5)	−72(10)	3758(8)	2.1(3)	2.4(4)	2.1(4)	0.6(3)	0.8(3)	0.7(3)
$C_t(1)$	184(4)	1246(29)	2369(7)	1.7(3)	2.2(3)	2.6(3)	−0.4(7)	1.5(2)	−0.0(9)
$C_t(2)$	597(5)	1281(32)	3738(7)	3.1(3)	3.1(5)	2.7(3)	−0.3(8)	2.1(3)	−0.4(8)
$C_t(3)$	−322(5)	74(10)	1960(10)	1.9(3)	2.8(4)	4.3(5)	0.7(3)	1.9(4)	1.3(4)
$C_t(4)$	−274(5)	2580(10)	2019(9)	2.4(4)	2.0(4)	3.7(5)	1.4(3)	2.0(3)	0.3(4)
Cp(11)	1736(6)	4439(9)	1079(9)	5.4(6)	0.9(3)	2.1(4)	0.2(4)	−0.0(4)	0.5(3)
Cp(12)	2499(5)	4508(9)	2174(10)	2.3(4)	1.1(3)	4.5(5)	−0.5(3)	1.4(4)	−0.3(3)
Cp(13)	2266(7)	4499(9)	3144(9)	7.8(7)	0.7(3)	1.6(4)	0.3(4)	0.8(4)	−0.7(3)
Cp(14)	1443(6)	4448(10)	2698(12)	4.7(6)	1.1(4)	8.0(8)	0.8(4)	4.1(6)	0.2(4)
Cp(15)	1117(6)	4363(10)	1521(10)	6.0(6)	1.3(4)	4.3(5)	1.1(4)	3.5(5)	1.0(4)
Cp(21)	1251(4)	−1995(7)	1519(8)	0.4(2)	0.6(3)	2.7(4)	−0.3(2)	0.7(2)	−0.4(3)
Cp(22)	1839(5)	−1999(8)	1038(8)	2.3(3)	0.7(3)	3.6(4)	−0.4(3)	2.9(3)	−0.8(3)
Cp(23)	2516(5)	−2055(7)	2009(8)	3.9(4)	0.2(3)	2.4(4)	0.2(3)	2.1(3)	−0.0(3)
Cp(24)	2348(5)	−2088(8)	3196(9)	1.8(4)	0.6(3)	4.2(5)	0.8(3)	1.3(4)	0.4(3)
Cp(25)	1553(4)	−2022(7)	2885(7)	2.2(3)	0.4(3)	1.1(3)	−0.1(2)	0.5(3)	0.5(2)

temperature interval is in agreement with the HDVV model [5] for the interaction of two Cr^{III} ions with spins of 3/2 and an exchange parameter $-2J$ 654 cm^{-1} (taking into account a monomer admixture of 1% and an error of 3%).

To establish the structure of VI unequivocally, its X-ray study was carried out. The molecular structure is shown in Fig. 3; atomic coordinates, anisotropic temperature factors, bond lengths and angles are given in Tables 4–6.

In accordance with our assumption, the molecule VI contains the metal cyclic Cr_2Mn frame with a short, evidently partially double Cr=Cr bond (2.646(2) Å) and ordinary Cr–Mn bonds (2.716(2) and 2.828(2) Å). Above and below the Cr_2Mn plane are the μ_3-bridging S atoms with mean distances of 2.270(4) Å (Cr–S) and of 2.285(2) Å (Mn–S). The chromium atoms are additionally linked by a $SCMe_3$ bridge (average Cr–S 2.334(4) Å), and coordinated by planar π-cyclopentadienyl ligands (average Cr–$C_{C_5H_5}$ 2.23(1) Å). Three terminal CO groups are, in turn, coordinated by the Mn atom. Their asymmetric arrangement relative to the metal frame, which is

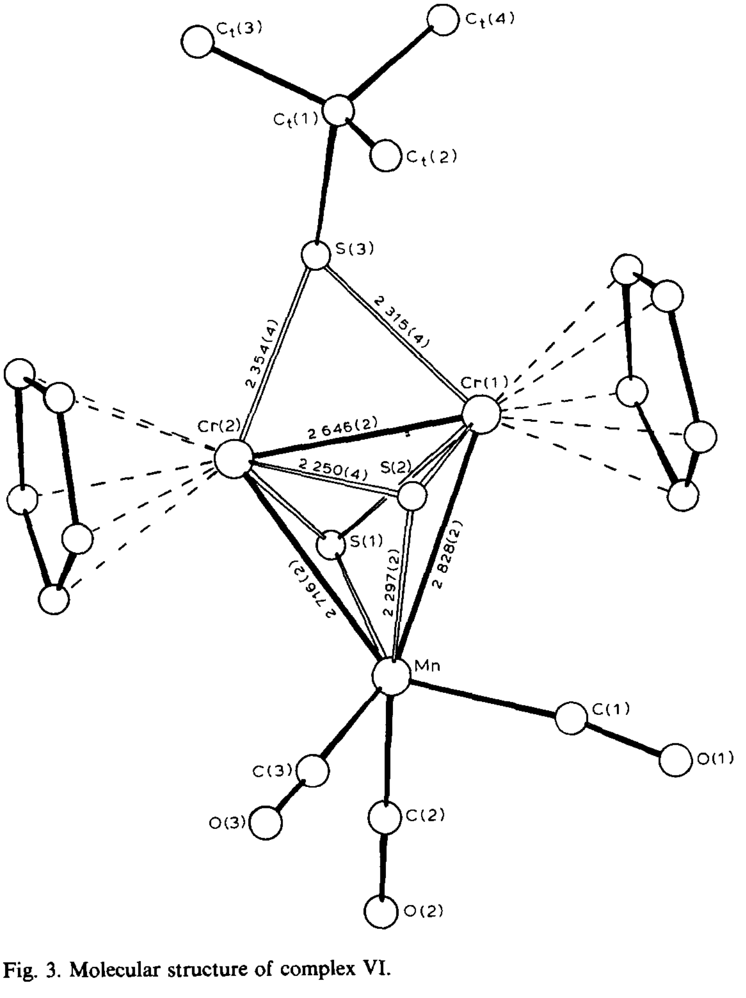


Fig. 3. Molecular structure of complex VI.

TABLE 5

BOND LENGTHS IN THE MOLECULE OF $(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Mn(CO)_3$ (VI)

Bond	d (Å)	Bond	d (Å)	Bond	d (Å)
Mn–Cr(1)	2.828(2)	Cr(1)–Cp(14)	2.22(1)	C_t(1)–C_t(2)	1.50(1)
Mn–Cr(2)	2.716(2)	Cr(1)–Cp(15)	2.27(1)	C_t(1)–C_t(3)	1.47(2)
Mn–S(1)	2.272(2)	Cr(2)–S(1)	2.259(4)	C_t(1)–C_t(4)	1.55(3)
Mn–S(2)	2.297(2)	Cr(2)–S(2)	2.250(4)	Cp(11)–Cp(12)	1.55(1)
Mn–C(1)	1.88(1)	Cr(2)–S(3)	2.354(4)	Cp(11)–Cp(15)	1.41(2)
Mn–C(2)	1.809(8)	Cr(2)–Cp(21)	2.247(8)	Cp(12)–Cp(13)	1 32(2)
Mn–C(3)	1.731(9)	Cr(2)–Cp(22)	2.267(8)	Cp(13)–Cp(14)	1.45(2)
Cr(1)–Cr(2)	2.646(2)	Cr(2)–Cp(23)	2.254(8)	Cp(14)–Cp(15)	1.28(2)
Cr(1)–S(1)	2.286(4)	Cr(2)–Cp(24)	2.261(9)	Cp(21)–Cp(22)	1.39(1)
Cr(1)–S(2)	2.306(4)	Cr(2)–Cp(25)	2.249(8)	Cp(21)–Cp(25)	1.48(1)
Cr(1)–S(3)	2.315(4)	S(3)–C_t(1)	1.869(7)	Cp(22)–Cp(23)	1.38(1)
Cr(1)–Cp(11)	2.197(9)	O(1)–C(1)	1.16(1)	Cp(23)–Cp(24)	1.50(1)
Cr(1)–Cp(12)	2.218(9)	O(2)–C(2)	1.159(9)	Cp(24)–Cp(25)	1.41(1)
Cr(1)–Cp(13)	2.202(9)	O(3)–C(3)	1.15(1)		

different from that found in clusters III and V, evidently explains the non-equivalence of the Mn–C distances (1.73(1) and 1.88(1) Å).

Thus, in the presently discussed series of $(Cp_2Cr_2SCMe_3)(\mu_3\text{-}S)_2ML$-type complexes, where ML = $Co(CO)_2$, $Fe(CO)_3$ or $Mn(CO)_3$, the dichromium fragment

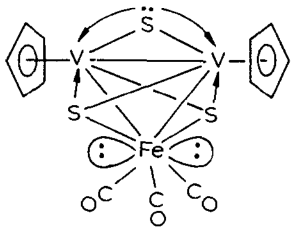
TABLE 6

BOND ANGLES IN THE MOLECULE OF $(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Mn(CO)_3$ (VI)

Angle	ω (°)	Angle	ω (°)	Angle	ω (°)
Cr(1)MnCr(2)	56.98(4)	MnCr(1)S(1)	51.4(1)	MnS(2)Cr(1)	75.8(1)
Cr(1)MnS(1)	51.9(1)	MnCr(1)S(2)	51.9(1)	MnS(2)Cr(2)	73.3(1)
Cr(1)MnS(2)	52.2(1)	MnCr(1)S(3)	114.9(1)	Cr(1)S(2)Cr(2)	71.0(1)
Cr(1)MnC(1)	90.5(3)	Cr(2)Cr(1)S(1)	53.9(1)	Cr(1)S(3)Cr(2)	69.0(1)
Cr(1)MnC(2)	127.5(5)	Cr(2)Cr(1)S(2)	53.5(1)	Cr(1)S(3)C_t(1)	115.6(6)
Cr(1)MnC(3)	144.2(3)	Cr(2)Cr(1)S(3)	56.2(1)	Cr(2)S(3)C_t(1)	116.7(6)
Cr(2)MnS(1)	52.9(1)	S(1)Cr(1)S(2)	91.5(2)	MnC(1)O(1)	175.3(9)
Cr(2)MnS(2)	52.5(1)	S(1)Cr(1)S(3)	83.3(1)	MnC(2)O(2)	176(1)
Cr(2)MnC(1)	138.0(3)	S(2)Cr(1)S(3)	93.6(2)	MnC(3)O(3)	171.8(8)
Cr(2)MnC(2)	128.5(5)	MnCr(2)Cr(1)	63.65(5)	S(3)C_t(1)C_t(2)	113(1)
Cr(2)MnC(3)	98.4(3)	MnCr(2)S(1)	53.4(1)	S(3)C_t(1)C_t(3)	106(1)
S(1)MnS(2)	92.1(1)	MnCr(2)S(2)	54.1(1)	S(3)C_t(1)C_t(4)	106(1)
S(1)MnC(1)	128.7(3)	MnCr(2)S(3)	117.8(1)	C_t(2)C_t(1)C_t(3)	114(1)
S(1)MnC(2)	88.4(5)	Cr(1)Cr(2)S(1)	54.9(1)	C_t(2)C_t(1)C_t(4)	107(1)
S(1)MnC(3)	136.4(3)	CR(1)Cr(2)S(2)	55.5(1)	C_t(3)C_t(1)C_t(4)	110(1)
S(2)MnC(1)	87.3(3)	Cr(1)Cr(2)S(3)	54.8(1)	Cp(12)Cp(11)Cp(15)	110.7(9)
S(2)MnC(2)	178.8(5)	S(1)Cr(2)S(2)	93.7(2)	Cp(12)Cp(13)Cp(14)	108.3(9)
S(2)MnC(3)	92.6(3)	S(1)Cr(2)S(3)	83.1(1)	Cp(13)Cp(14)Cp(15)	116(1)
C(1)MnC(2)	91.5(6)	S(2)Cr(2)S(3)	94.1(2)	Cp(11)Cp(15)Cp(14)	103(1)
C(1)MnC(3)	94.8(4)	MnS(1)Cr(1)	76.7(1)	Cp(22)Cp(21)Cp(25)	110.4(7)
C(2)MnC(3)	87.8(6)	MnS(1)Cr(2)	73.6(1)	Cp(21)Cp(22)Cp(23)	108.3(7)
MnCr(1)Cr(2)	59.37(4)	Cr(1)S(1)Cr(2)	71.2(1)	Cp(22)Cp(23)Cp(24)	108.6(8)
				Cp(23)Cp(24)Cp(25)	107.2(7)
				Cp(21)Cp(25)Cp(24)	105.4(7)

$(Cp_2Cr_2SCMe_3)(\mu_3\text{-}S)_2$ (referred to as Q below) acts as a little-changing group with an essentially double Cr=Cr bond. In regard to ML, the Q fragment acts as a tetradentate five-electron-donating ligand, bonded to M by two sulphide bridges and two half occupied orbitals of the Cr^{III} atoms. The Q–ML bonding is determined by the number of electrons in the two orbitals of M which take part in Cr–M bond formation. If the number of electrons exceeds two, the Cr–M bonds are weakened, which nevertheless has little effect on the Cr=Cr double-bonding.

A similar situation should be observed in the recently described cluster $(Cp_2V_2S)(\mu_3\text{-}S)_2Fe(CO)_3$ [14], in which the Fe^{II} atom, like the Mn^I atom in VI, has a d^6 electronic configuration. The Fe–V bonds are ordinary with a length of 2.82(1) Å (unfortunately, only the mean value is given in [14]). It should be noted that the complex contains a very short V–V bond (2.51 Å), although with a d^2 electronic configuration and Fe–V bonds the V–V bond can only be ordinary. The authors [14], however, stress a strong shortening of the V–(μ_2-S) bonds (2.23(1) Å), assuming partial double-bonding due to interaction of the lone electron pairs of the sulphide bridge with the vacant orbital of each vanadium atom.



Experimental

All operations were carried out under a pure argon atmosphere. Benzene and heptane were purified by distillation over dispersed Na in a pure argon stream. Initial $Cp_2Cr_2(SCMe_3)_2S$, $(MeC_5H_4)_2Cr_2(SCMe_3)_2S$, $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ were prepared according to the methods in [8], [4], [9] and [10], respectively.

IR spectra were measured in KBr pellets with a UR-20 spectrometer. Magnetic measurements were carried out using the Faraday method in the 283–80 K temperature interval with apparatus designed by the Institute of General and Inorganic Chemistry of Academy of Sciences of the U.S.S.R. [11]. Experimental X-ray data for V were obtained with a Hilger and Watts autodiffractometer (Mo-K_α, λ 0.7041 Å, T 20 °C) and for VI with a Syntex $P2_1$ autodiffractometer (Mo-K_α, θ–2θ scan, $\theta \geqslant 52°$, T −120 °C). Crystals of V are monoclinic, space group $P2_1$, a 9.437(1), b 15.9460(8), c 7.2540(8) Å β 109.399(9)°, V 1029.6 Å^3, $Z = 4$. The structure was solved by the direct method with a modified MULTAN program [12] and refined in a full-matrix anisotropic approximation for all non-hydrogen atoms to $R = 0.047$ and $R_w = 0.052$. Crystals of VI are monoclinic, space group $C2$, a 18.709(7), b 9.883(4), c 11.470(5) Å, β 109.65(2)°, V 1997.3 Å^3, $Z = 4$. The structure was solved by the heavy-atom method and refined in a block-diagonal approximation for all non-hydrogen atoms (hydrogen atoms were located in the difference Fourier series, but their coordinates were not refined) to $R = 0.041$, $R_w = 0.044$ for 2464 independent reflections with $I \geqslant 2\sigma$.

$(MeC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2 \cdot Co(CO)_2$ (V)

To a violet solution of 1.1 g (2.33 mmol) of $(MeC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)$ in 60 ml heptane, a red solution of 0.78 g (2.28 mmol) of $Co_2(CO)_8$ in 20 ml of heptane was added. The resulting brownish-red solution was concentrated to half-volume in vacuo. Precipitated dark-brown prisms were separated from the solution, washed with cold pentane, and dried in vacuo. Yield 0.56 g (46.3%). IR spectrum (ν, cm^{-1}): 405w, 475m, 520w, 570w, 789w, 855w, 1012m, 1050w, 1130w, 1335m, 1420m, 1898vs, 1940vs, 2800br.m, 2890br.m, 3070w.

$(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2 \cdot Mn(CO)_3$ (VI)

A violet solution of 0.3 g (0.77 mmol) of $Mn_2(CO)_{10}$ and 0.68 g (1.5 mmol) of $Cp_2Cr_2(SCMe_3)_2S$ in 25 ml of benzene was irradiated by UV light (PRK-lamp) on boiling for 3 h. The resulting greenish-brown solution was concentrated to half-volume in vacuo and purified by chromatography on a 3 × 8 cm Al_2O_3 column (the dark brown zone was eluted with benzene). 20 ml of heptane was added to the obtained brown benzene solution; it was then concentrated to 10 ml at 60 °C/0.1 Torr. The obtained solution was cooled to −6 °C. The precipitated large black crystals were separated from the mother liquor, washed with 15 ml of pentane and dried. Yield 0.2 g (25%). IR spectrum (ν, cm^{-1}): 505w, 565m, 608m, 635m, 800s, 925w, 1005m, 1015m, 1055m, 1115w, 1155m, 1185w, 1350w, 1385w, 1425m, 1445w, 1520w, 1540w, 1630w, 1895s, 1915s, 1975s, 2840w, 2915w, 3075w.

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