ANTIFERROMAGNETIC COMPLEXES INVOLVING METAL—METAL BONDS

V *. SYNTHESIS, MOLECULAR STRUCTURES AND MAGNETIC PROPERTIES OF AN ADDUCT, (CpCrSCMe₃)₂S · Mn₂(CO)₉, AND A CLUSTER, (CpCr)₂(μ^2-SCMe₃)(μ^3-S)₂Co(CO)₂, CONTAINING THE CrCrCo METALLOCYCLE

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Summary

The photochemical reaction of the antiferromagnetic binuclear complex (CpCrSCMe₃)₂S (I, Cp = cyclopentadienyl) with Mn₂(CO)₁₀ in THF yields the adduct (CpCrSCMe₃)₂S · Mn₂(CO)₉ (IV). According to X-ray diffraction data, the fragments in IV are linked through an Mn—S bond (2.448(2) Å), and the geometry of I changes only insignificantly upon the addition of Mn₂(CO)₉: the Cr—Cr bond distance changes from 2.689(8) Å in I to 2.740(8) Å in IV, the Cr—S$_{(sulphide)}$ bond length increases from 2.24(1) Å (I) to 2.31(1) Å (IV), whereas the Cr—S (thiolate) bond and CrSCr angles (72.7(3) and 71.4(3)°) remain almost unaffected. Accordingly, formation of the adduct has little affect on the magnetic properties of I (the exchange parameter, −2J, value is equal to 440 cm⁻¹ for IV and 430 cm⁻¹ for I). Compound I reacts with Co₂(CO)₈ in THF at 20°C without UV irradiation to give the trinuclear cluster, (Cp₂Cr₂SCMe₃)-(μ^3-S)₂Co(CO)₂ (V). Compound V is antiferromagnetic (−2J 530 cm⁻¹, the Co atom is diamagnetic) and, according to the X-ray structural data, contains the CrCrCo metallacycle (the bond lengths are: Cr—Cr, 2.617(1); Cr—Co, 2.579(1) and 2.592(1) Å) and sulphide bridges above and below the metallacycle plane. The effect of the coordination number of M on the transformations of the adducts of the type (CpCrSCMe₃)₂S · M₂(CO)$_n$ is discussed.

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* For part IV see ref. 1.

Introduction

It has been shown in the previous communications of this series [1,2] that the unusual binuclear antiferromagnetic complex $(CpCrSCMe_3)_2S$ (I) (exchange parameter, $-2J$, equal to 430 cm^{-1}) which has a direct Cr—Cr bond 2.689(8) Å long [3,4] may act as an unusual antiferromagnetic ligand in complexes with metal carbonyls. The composition and geometry of I as well as its magnetic properties remain almost unchanged in the complexes $(CpCrSCMe_3)_2S \cdot M(CO)_5$ (II) (M = Cr, Mo, W) (Cr—Cr 2.73(1) Å; $-2J$ 410, 440, 440 cm^{-1}, respectively [2]). The reaction of I with $Fe(CO)_5$ is, however, accompanied by elimination of the tert.-butyl and carbonyl groups and yields the complex $(Cp_2Cr_2SCMe_3)(\mu^3\text{-}S)_2 \cdot Fe(CO)_3$ (III). Apart from the Cr—Cr bond (2.707(2) Å) assisted by the thiolate bridge, this complex contains a direct Fe—Cr bond (2.726(2) Å). The other Cr atom only interacts with Fe through two μ^3-sulphide bridges (Fe$\cdots$Cr 3.110 Å). The difference between the reactions of I with $M(CO)_6$ and $Fe(CO)_5$ was explained, first, by the smaller covalent radius of Fe (1.34 Å) compared with that of M (1.46, 1.58 and 1.58 Å, for M = Cr, Mo, W, respectively) [5] and, second, by the smaller coordination number of Fe (five) compared with M(six). Both factors favour the formation of an additional thiolate bridge between I and the species $Fe(CO)_4$ which is already bound to I via the sulphide bridge.

To check the mechanism suggested and to extend the applications of I as an antiferromagnetic ligand we have studied reactions of I with binuclear metal carbonyls, $Mn_2(CO)_{10}$ and $Co_2(CO)_8$, which differ from each other both in metal radii (r Mn 1.38 Å, r Co 1.29 Å [5]) and coordination numbers (six for Mn [6] and five for Co, as in solutions, $Co_2(CO)_8$ is present in a non-bridged form [7]).

Results

(a) Synthesis

The photochemical reaction of equimolar quantities of I and $Mn_2(CO)_{10}$ in THF gave $(CpCrSCMe_3)_2S \cdot Mn_2(CO)_9$ (IV), the product of the replacement of one of the equatorial CO groups with the sulphide bridge lone pair:
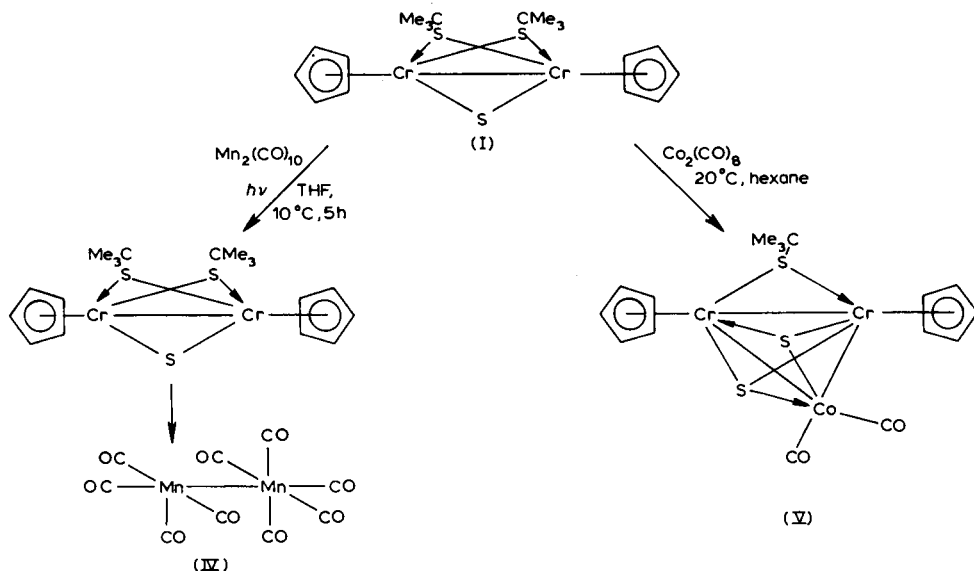
Complex IV was isolated as brownish black prisms, m.p. 165°C (decomp.), well soluble in common organic solvents apart from alkanes. The IR spectrum of IV contained CO stretching bands at 1920, 1953, 1988, 2020 and 2088 cm^{-1}, and also the bands of the π-cyclopentadienyl ligands (834, 1028, 1365, 1460 and 3100 cm^{-1}) and tert.-butyl groups (1160, 2850-2975 cm^{-1}).

In contrast, the reaction of I with $Co_2(CO)_8$ took place in hexane when stirred at room temperature for several minutes. After cooling the reaction mixture, $(Cp_2Cr_2SCMe_3)(\mu^3\text{-}S)_2Co(CO)_2(V)$ precipitated as dark brown prisms. The reaction thus involved not only cleavage of the Co—Co bond but also the elimination of one tert.-butyl and two carbonyl groups. Complex V has good solubility in aromatic solvents and THF but is only sparingly soluble in saturated hydrocarbonds. In the air it decomposes slowly. The IR spectrum of V contains the bands of the C_5H_5 ring stretches (818, 1023, 1448 and 3060 cm^{-1}), and the bands of the CMe_3 (1160, 2870, 2990 cm^{-1}) and CO (1948 and 2000 cm^{-1}) groups. Under the conditions of mass-spectrometry (130°C/10^{-7} torr), V decomposes to produce $[CpCrS]_4$ ions (m/e 596).
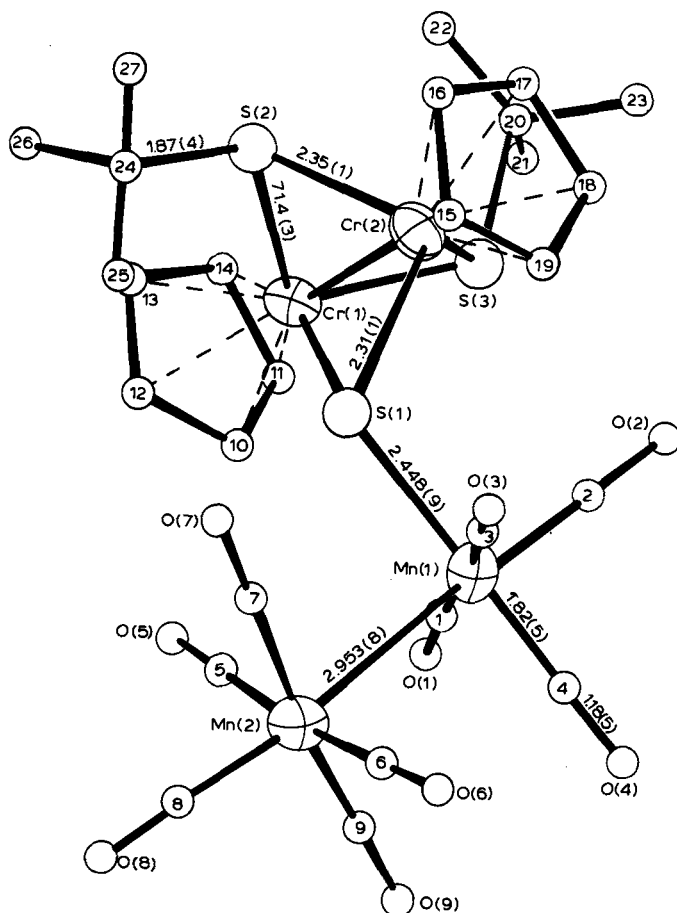

Fig. 1. The molecular structure of IV with main bond lengths and angles.

(b) Structures of complexes IV and V

A complete X-ray structural analysis of IV and V has been carried out to obtain reliable structural data.

The molecule of IV (Figs. 1 and 2, Tables 1—3) contains the binuclear fragments $(CpCrSCMe_3)_2S$ and $Mn_2(CO)_9$ linked through a μ^2-sulphide bridge (Mn—S 2.448(9) Å, angle CrSMn 125.4(5)°). The structure of I undergoes only insignificant changes on coordination of $Mn_2(CO)_9$: the Cr—Cr bond length only increases from 2.689(8) to 2.740(8) Å; the Cr—$S_{(sulphide)}$ bond length increases from 2.24(1) to 2.31(1) Å (average). The Cr—$S_{(thiolate)}$ bond length remains almost unaffected by the complex formation (2.35(1) against 2.38(1) Å in I). The same is true of the Cr—$C(C_5H_5)$ bonds (2.24(4) and 2.23(4) Å, respectively). The Cr$S_{(sulphide)}$ Cr angle narrows from 74.1(4) to 72.7(3)° on going from I to IV, whereas the Cr$S_{(thiolate)}$ Cr angles increase on average from 68.8(4) to 71.4(3)°.

The μ^3-sulphide bridge in IV replaces one of the equatorial carbonyl groups of $Mn_2(CO)_{10}$ without producing a significant elongation of the Mn—Mn bond (2.953(8) Å in IV against 2.923 Å in $Mn_2(CO)_{10}$). Both Mn atoms remain octahedral (bond lengths: Mn(1)—C(CO) (average) 1.62 and Mn(2)—C(CO) (average) 1.76(4) Å; bond angles MnCO (average) 177(4)°; bond lengths C—O (average) 1.18(5) Å).

Compound V (Figs. 3 and 4, Tables 4—7) comprises the C_5H_5Cr fragments (Cr—$C_{(aver.)}$ 2.24(1) Å) linked by a direct Cr—Cr bond (2.617(1) Å). The cyclopentadienyl ligands are planar: their centra and the chromium—chromium bond are almost on the same straight line (the CpCr(1) Cr(2) angle is equal to 177.9°).
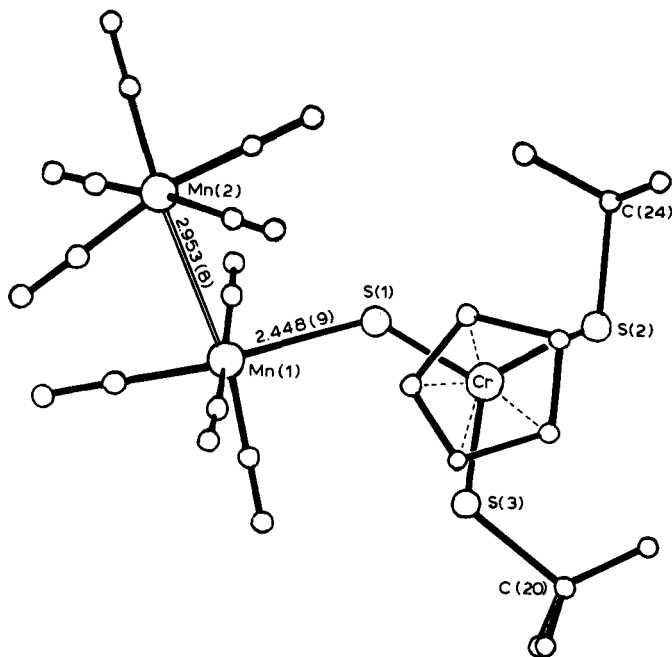

Fig. 2. Projection of IV onto plane S(1) S(2) S(3).

TABLE 1

ATOMIC COORDINATES ($\times 10^4$ for Mn, Cr, S and $\times 10^3$ for O and C) AND TEMPERATURE FACTORS
FOR STRUCTURE IV

Atom	Molecule 1				Molecule 2			
	X	Y	Z	B	X	Y	Z	B
Mn(1)	3702(2)	−1301(5)	8719(2)	—	8760(2)	−1162(6)	8785(4)	—
Mn(2)	4101(2)	−773(5)	10288(3)	—	8379(2)	−528(5)	10164(3)	—
Cr(1)	3280(2)	1869(5)	7786(3)	—	9217(2)	1821(5)	7937(3)	—
Cr(2)	3815(2)	857(5)	6951(3)	—	8527(2)	1095(5)	6999(3)	—
S(1)	3766(3)	564(8)	8244(5)	—	8699(3)	719(8)	8292(5)	—
S(2)	3751(3)	2758(8)	7090(5)	—	8738(3)	2931(8)	7177(5)	—
S(3)	3101(3)	605(9)	6790(6)	—	9280(3)	600(8)	6885(5)	—
O(1)	337(1)	−225(2)	724(2)	5.7(7)	911(1)	−211(3)	744(2)	8.2(9)
O(2)	367(1)	−356(3)	929(2)	7.0(8)	876(1)	−336(3)	944(2)	8.3(9)
O(3)	289(1)	−80(3)	926(2)	7.2(8)	958(1)	−73(3)	968(2)	9.6(9)
O(4)	456(1)	−177(3)	839(2)	8.8(9)	789(1)	−177(3)	810(2)	7.2(8)
O(5)	346(1)	−214(3)	1089(2)	7.3(8)	803(1)	3(2)	1155(2)	5.6(7)
O(6)	464(1)	−267(3)	1024(2)	6.7(8)	787(1)	−252(3)	994(2)	8.6(9)
O(7)	451(1)	−20(3)	1180(2)	8.0(9)	907(1)	−172(3)	1106(2)	7.7(8)
O(8)	466(1)	59(3)	945(2)	5.9(2)	778(1)	60(3)	906(2)	7.9(9)
O(9)	350(1)	110(2)	1020(2)	5.6(7)	891(1)	146(3)	1019(2)	6.0(7)
C(1)	349(1)	−177(3)	783(2)	4.1(9)	899(2)	−167(4)	802(3)	7.3(9)
C(2)	368(1)	−266(3)	906(2)	5.6(9)	876(1)	−244(4)	919(2)	4.4(9)
C(3)	317(2)	−94(4)	903(3)	5.6(9)	925(2)	−71(5)	930(3)	9.0(9)
C(4)	425(2)	−151(4)	854(3)	6.4(9)	821(2)	−150(4)	835(3)	7.6(9)
C(5)	371(2)	−159(4)	1064(3)	6.6(9)	818(1)	−26(3)	1093(2)	3.9(9)
C(6)	422(1)	−192(4)	1024(2)	4.9(9)	804(1)	−166(4)	997(2)	5.5(9)
C(7)	436(2)	−33(4)	1120(3)	6.4(9)	880(1)	−125(3)	1073(2)	3.8(8)
C(8)	445(1)	6(3)	978(2)	4.6(9)	801(1)	14(3)	951(2)	3.9(8)
C(9)	373(1)	37(3)	1019(2)	3.9(8)	871(1)	64(4)	1016(2)	4.6(9)
C(10)	290(1)	190(3)	877(2)	4.4(9)	788(1)	29(3)	693(2)	4.6(9)
C(11)	318(1)	284(3)	885(2)	4.7(9)	813(1)	−28(3)	658(3)	4.1(9)
C(12)	307(1)	354(4)	818(3)	5.9(9)	824(1)	23(4)	590(3)	6.2(9)
C(13)	273(1)	299(4)	778(3)	6.2(9)	810(1)	128(4)	585(2)	4.5(9)
C(14)	265(2)	201(4)	816(3)	6.6(9)	788(1)	141(3)	652(2)	4.7(9)
C(15)	390(2)	−46(4)	610(3)	6.8(9)	986(1)	145(4)	853(3)	5.6(9)
C(16)	398(2)	59(5)	575(5)	7.4(10)	985(2)	252(4)	805(3)	6.8(9)
C(17)	430(1)	107(4)	616(3)	4.8(9)	961(2)	335(4)	835(3)	6.0(9)
C(18)	443(2)	29(4)	680(3)	6.5(9)	946(1)	288(3)	899(2)	4.8(9)
C(19)	417(1)	−62(4)	673(3)	5.7(9)	960(1)	176(3)	911(2)	3.4(8)
C(20)	420(1)	349(3)	769(2)	3.2(8)	819(2)	330(5)	827(3)	8.6(10)
C(21)	439(2)	286(4)	837(3)	7.0(10)	808(2)	446(4)	705(3)	7.3(10)
C(22)	451(2)	372(4)	715(3)	7.5(9)	867(2)	478(5)	808(4)	9.8(10)
C(23)	404(2)	460(5)	790(3)	9.2(10)	527(1)	84(2)	528(1)	4.2(6)
C(24)	279(1)	119(4)	568(2)	5.3(9)	943(1)	96(3)	604(2)	3.3(8)
C(25)	234(5)	120(4)	600(2)	5.3(9)	921(1)	41(4)	536(3)	6.1(9)
C(26)	295(1)	223(4)	560(3)	5.7(9)	942(1)	227(3)	589(2)	4.6(9)
C(27)	282(2)	23(5)	529(3)	8.2(10)	990(1)	68(4)	617(2)	5.3(9)
O$_W$	841(1)	385(4)	768(3)	6.3(9)				

The Cr—Cr bond is assisted by one tert.-butylthiolate (Cr—S 1.331(1) Å) and
two μ^3-sulphide bridges (Cr—S 2.287(1) and 2.299(1) Å). The latter two groups
are linked with a Co(Co—S 2.200(1) Å) bearing two terminal carbonyl groups to
form a chelate structure. The geometrical parameters of the Co(CO)$_2$ moiety are:
Co—C(CO), 1.792(2); C—O 1.145(5) Å; angle CoCO, 176°. The Co atom is also
bonded to both Cr atoms (Co—Cr, 2.579(1) and 2.592(1) Å). The angle values,

TABLE 2

ANISOTROPIC TEMPERATURE FACTOR PARAMETERS (for Mn, Cr, S) FOR STRUCTURE IV [a]

Atom	Molecule 1						Molecule 2					
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn(1)	2.0(3)	3.6(3)	4.7(3)	0.6(2)	−0.1(2)	−0.2(3)	3.5(3)	4.9(4)	3.7(3)	−0.6(3)	−0.2(2)	0.4(3)
Mn(2)	2.9(3)	4.7(4)	4.3(3)	−0.2(3)	−0.2(2)	0.2(3)	4.1(3)	4.2(3)	3.8(3)	−1.5(3)	0.3(3)	0.2(3)
Cr(1)	2.3(3)	4.1(3)	3.3(3)	0.5(3)	0.8(3)	−0.8(3)	2.1(2)	4.8(4)	3.0(3)	−1.2(3)	−0.2(2)	−0.1(3)
Cr(2)	2.9(3)	4.5(4)	2.7(3)	0.5(3)	0.5(2)	−0.4(2)	1.7(3)	3.6(3)	3.1(3)	0.0(2)	−0.2(2)	−0.2(2)
S(1)	2.2(4)	3.8(5)	2.6(4)	0 0.4(4)	0.4(4)	0.1(4)	2.3(4)	4.4(5)	2.6(4)	−1.3(4)	−1.0(3)	−0.6(4)
S(2)	2.8(5)	4.4(5)	2.2(4)	0.4(3)	−0.7(4)	−0.4(4)	2.5(4)	3.3(5)	3.2(5)	0.2(4)	0.4(4)	−0.1(4)
S(3)	2.4(5)	3.7(5)	4.3(5)	−0.7(5)	−0.6(4)	−0.2(4)	2.5(4)	2.8(5)	3.1(4)	0.5(4)	0.2(3)	−0.4(4)

[a] $T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + ... + 2B_{12}hka^*b^* + ...)]$.

TABLE 3

BOND LENGTHS d(Å) AND BOND ANGLES ω(°) IN STRUCTURE IV

Bond	d	Angle	ω
Mn(1)—Mn(2)	2.953(8)	MnCO	177(4)
Cr(1)—Cr(2)	2.739(8)	CrS(1)Mn	125.4(5)
Mn(1)—S(1)	2.448(9)	Cr(1)S(1)Cr(2)	72.7(3)
Mn(1)—C(CO)	1.82(5)	Cr(1)S(SR)Cr(2)	71.4(3)
Mn(2)—C(CO)	1.76(4)	S(1)CrS(2)	91.6(4)
Cr—S(1)	2.31(1)	S(1)CrS(3)	84.4(4)
Cr—S(SR)	2.35(1)	S(2)CrS(3)	90.7(4)
S(SR)—C(CMe$_3$)	1.87(4)	CpCr(1)Cr(2) [a]	176.2(4)
C—O(CO)	1.18(5)	C(CMe$_3$)S(SR)Cr	118(1)
C(CMe$_3$)—C(Me)	1.53(6)	S(SR)C(CMe$_3$)C(Me)	112(3)
Cr—C(C$_5$H$_5$)	2.24(4)	C(Me)C(CMe$_3$)C(Me)	108(4)
C—C(C$_5$H$_5$)	1.41(6)	CCC(C$_5$H$_5$)	109(4)

[a] Cp is centre of the cyclopentadienyl ring.
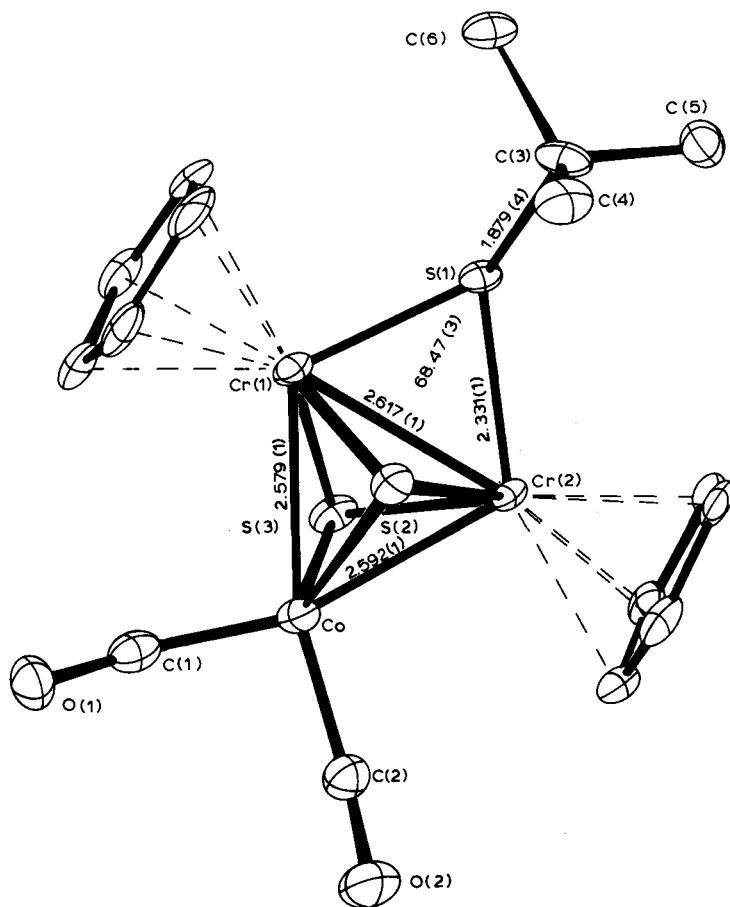
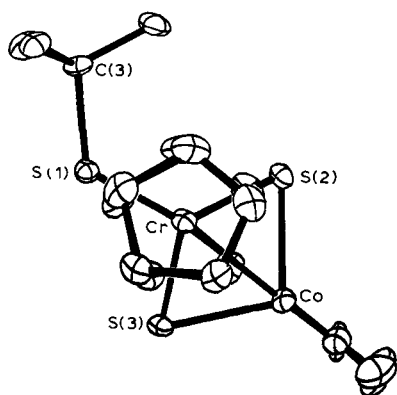Fig. 3. The molecular structure of (C$_5$H$_5$)$_2$Cr$_2$(SCMe$_3$)(μ-S)$_2$ · Co(CO)$_2$.

Fig. 4. Projection of V onto plane S(1) S(2) S(3).

Cr(1) SCr(2), 69.18°, and CrSCo, 70.24°, confirm the presence of direct bonds between the metal atoms in the Cr_2Co triangle. The sulphur atoms are located above and below the triangle plane.

(c) Magnetic properties

The temperature dependence of the magnetic susceptibilities (χ_m) of IV and

TABLE 4

ATOMIC COORDINATES ($\times 10^4$) FOR STRUCTURE V

Atom	Molecule 1			Molecule 2		
	X	Y	Z	X	Y	Z
Co	5813.7(3)	2090.2(3)	−58.5(3)	5723.5(3)	3599.4(3)	6723.8(3)
Cr(1)	5532.5(3)	2607.1(3)	1029.9(3)	6389.0(3)	3035.4(5)	5895.9(3)
Cr(2)	6946.5(3)	1999.4(5)	1193.7(3)	5831.7(3)	1259.7(5)	6423.3(3)
S(1)	6633.5(5)	2820.6(8)	2091.1(5)	6291.5(5)	934.0(9)	5551.8(5)
S(2)	5890.6(5)	699.1(9)	752.5(5)	6835.4(5)	2574.6(9)	7077.8(5)
S(3)	6281.9(5)	3760.9(8)	606.6(5)	5031.9(5)	2784.3(9)	5660.6(5)
O(1)	4302(2)	2357(3)	−1264(2)	5839(2)	6339(3)	6760(2)
O(2)	6516(2)	1369(4)	−1020(2)	5095(2)	3502(3)	7800(2)
C(1)	4875(2)	2252(4)	−777(2)	5801(3)	5269(4)	6734(2)
C(2)	6260(2)	1647(4)	−621(2)	5315(2)	3502(4)	7362(2)
C(3)	6712(2)	1719(4)	2826(2)	7216(2)	−3(4)	5826(2)
C(4)	7564(2)	1774(4)	3365(2)	6971(3)	−1383(4)	5785(3)
C(5)	6473(2)	385(4)	2570(2)	7539(2)	254(5)	5272(2)
C(6)	6185(2)	2251(4)	3161(2)	7820(2)	340(4)	6553(2)
C(7)	4780(2)	3389(4)	1541(2)	7448(2)	3883(4)	5849(3)
C(8)	4650(2)	4110(4)	934(2)	7061(2)	4841(4)	6057(2)
C(9)	4330(2)	3311(4)	338(2)	6328(3)	5019(4)	5495(3)
C(10)	4269(2)	2091(4)	576(2)	6259(3)	4199(5)	4947(2)
C(11)	4547(2)	2131(4)	1319(2)	6951(3)	3495(5)	5162(3)
C(12)	8113(2)	2566(4)	1228(2)	5811(2)	262(4)	7369(2)
C(13)	8222(2)	2083(4)	1898(2)	5053(2)	676(4)	6944(2)
C(14)	7988(2)	812(4)	1805(2)	4800(2)	68(4)	6281(2)
C(15)	7739(2)	512(4)	1085(2)	5401(2)	−727(4)	6302(2)
C(16)	7819(2)	1594(4)	727(2)	6032(2)	−602(4)	6977(2)

TABLE 5

TEMPERATURE FACTOR PARAMETERS (×10) FOR STRUCTURE V [a]

Atom	Molecule 1						Molecule 2					
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	14.4(3)	16.1(3)	14.9(3)	0.0(2)	8.1(2)	−0.7(2)	15.5(3)	13.2(3)	21.9(3)	0.3(2)	9.1(2)	−2.5(2)
Cr(1)	12.4(3)	12.3(3)	16.3(3)	0.5(2)	9.1(3)	0.7(3)	13.8(3)	15.8(3)	17.4(3)	−1.5(3)	8.2(3)	3.9(3)
Cr(2)	12.2(3)	11.7(3)	14.7(3)	0.0(2)	8.7(2)	−0.1(3)	11.9(3)	11.9(3)	13.2(3)	−1.1(2)	7.9(3)	0.4(3)
S(1)	14.7(5)	12.1(5)	14.4(5)	−1.8(4)	9.4(4)	−0.4(4)	13.0(5)	18.6(5)	12.2(5)	0.0(4)	7.5(4)	−0.6(4)
S(2)	14.3(5)	11.9(5)	19.1(5)	−1.4(4)	8.8(4)	−0.9(4)	12.4(5)	13.8(5)	14.7(5)	−1.8(4)	5.6(4)	−1.1(4)
S(3)	16.5(5)	12.0(5)	17.5(5)	0.0(4)	10.5(5)	2.1(4)	12.0(5)	17.5(5)	18.1(5)	1.2(4)	5.5(4)	2.5(4)
O(1)	18(2)	61(3)	41(2)	22(2)	4(2)	6(2)	61(3)	15(2)	56(3)	3(2)	15(2)	1(2)
O(2)	27(3)	61(3)	26(2)	4(2)	13(2)	−13(2)	36(3)	47(3)	41(2)	−10(2)	27(2)	−19(2)
C(1)	23(2)	20(2)	22(2)	−1(2)	15(2)	1(2)	28(3)	21(3)	33(3)	5(2)	9(2)	0(2)
C(2)	18(2)	22(2)	21(2)	2(2)	8(2)	−4(2)	18(2)	24(2)	31(3)	−4(2)	13(2)	−8(2)
C(3)	23(2)	20(2)	15(2)	−2(2)	−11(2)	4(2)	14(2)	23(2)	19(2)	4(2)	10(2)	−2(2)
C(4)	19(2)	35(3)	21(2)	7(2)	5(2)	5(2)	32(3)	18(2)	42(3)	5(2)	23(2)	−5(2)
C(5)	31(3)	15(2)	28(3)	−3(2)	18(2)	−5(2)	23(2)	46(3)	27(3)	1(2)	18(2)	−5(2)
C(6)	25(2)	26(2)	20(2)	−1(2)	16(2)	1(2)	17(2)	32(3)	19(2)	6(2)	4(2)	−2(2)
C(7)	18(2)	31(3)	25(2)	9(2)	15(2)	0(2)	22(2)	28(3)	42(3)	−2(2)	20(2)	12(2)
C(8)	17(2)	19(2)	32(3)	7(2)	15(2)	1(2)	26(2)	15(3)	42(3)	−5(2)	18(2)	8(2)
C(9)	16(2)	28(2)	24(3)	10(2)	11(2)	3(2)	29(3)	22(2)	42(3)	1(2)	20(2)	17(2)
C(10)	8(2)	27(2)	35(3)	−1(2)	10(2)	23(2)	30(3)	43(3)	29(3)	−6(3)	10(2)	23(2)
C(11)	14(2)	29(3)	36(3)	4(2)	19(2)	9(2)	44(3)	32(3)	35(3)	−8(2)	29(3)	8(2)
C(12)	10(2)	25(2)	22(2)	−1(2)	7(2)	3(2)	29(3)	20(2)	14(2)	−9(2)	13(2)	2(2)
C(13)	8(2)	27(2)	16(2)	2(2)	4(2)	1(2)	26(2)	20(2)	27(2)	−7(2)	22(2)	−2(2)
C(14)	13(2)	22(2)	26(2)	9(2)	11(2)	7(2)	18(2)	21(2)	26(2)	−9(2)	13(2)	−1(2)
C(15)	17(2)	18(2)	36(3)	5(2)	16(2)	−2(2)	29(2)	14(2)	25(2)	−9(2)	18(2)	−1(2)
C(16)	14(2)	31(2)	20(2)	4(2)	11(2)	−1(2)	24(2)	15(2)	22(2)	−3(2)	12(2)	7(2)

[a] $T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + ... + 2B_{12}hka^*b^* + ...)]$.

TABLE 6

BOND LENGTHS $d(Å)$ IN STRUCTURE V

Bond	Molec. 1 d	Molec. 2 d	Bond	Molec. 1 d	Molec. 2 d
Co—Cr(1)	2.579(1)	2.579(1)	Cr(1)—C(5)	2.251(4)	2.253(5)
Co—Cr(2)	2.592(1)	2.593(1)	Cr(1)—C(10)	2.238(4)	2.247(5)
Cr(1)—Cr(2)	2.625(1)	2.609(1)	Cr(1)—C(11)	2.232(4)	2.235(6)
Co—S(2)	2.196(1)	2.202(1)	Cr(2)—C(12)	2.253(4)	2.242(4)
Co—S(3)	2.197(1)	2.202(1)	Cr(2)—C(13)	2.241(4)	2.239(5)
Co—C(1)	1.789(5)	1.781(5)	Cr(2)—C(14)	2.236(4)	2.236(4)
Co—C(2)	1.795(5)	1.787(5)	Cr(2)—C(15)	2.250(4)	2.240(4)
Cr(1)—S(1)	2.328(1)	2.329(1)	Cr(2)—C(16)	2.286(4)	2.241(4)
Cr(2)—S(1)	2.339(1)	2.328(1)	C(1)—O(1)	1.139(6)	1.140(6)
Cr(1)—S(2)	2.285(1)	2.288(1)	C(2)—O(2)	1.155(6)	1.142(6)
Cr(2)—S(2)	2.282(1)	2.292(1)	S(1)—C(3)	1.878(4)	1.880(4)
Cr(1)—S(3)	2.300(1)	2.303(1)	C(3)—C(4)	1.533(6)	1.530(6)
Cr(2)—S(3)	2.301(1)	2.292(1)	C(3)—C(5)	1.517(6)	1.511(6)
Cr(1)—C(7)	2.251(5)	2.229(5)	C(3)—C(6)	1.535(6)	1.527(6)
Cr(1)—C(8)	2.257(4)	2.248(4)	Cp(1)—Cr(1) [a]	1.895(1)	1.896(1)
			Cp(2)—Cr(2) [a]	1.907(1)	1.892(1)

[a] Cp is centre of the cyclopentadienyl ring.

V were determined by the Faraday technique. The effective magnetic moments were calculated by the formula

$$\mu_{eff.} = \sqrt{8\chi_m T}$$

The $\mu_{eff.}$ vs. T plots for IV and V are given in Figs. 5 and 6, respectively. These

TABLE 7

BOND ANGLES $\omega(°)$ IN STRUCTURE V

| Angle	Mol. 1 ω	Mol. 2 ω	Angle	Mol. 1 ω	Mol. 2 ω
CoCr(1)Cr(2)	59.73(2)	59.96(2)	Cp(1)Cr(1)Co	121.91(3)	121.72(3)
CoCr(2)Cr(1)	59.24(2)	59.43(2)	Cp(1)Cr(1)Cr(2)	177.78(3)	178.30(3)
Cr(1)CoCr(2)	61.03(2)	60.61(2)	Cp(2)Cr(2)Co	122.63(3)	122.45(3)
CoS(2)Cr(1)	70.21(4)	70.07(4)	Cp(2)Cr(2)Cr(1)	177.43(3)	177.82(3)
CoS(2)Cr(2)	70.69(4)	70.43(4)	Cr(1)S(1)C(3)	116.5(1)	118.0(1)
CoS(3)Cr(1)	69.93(4)	69.79(4)	Cr(2)S(1)C(3)	116.7(1)	116.2(1)
CoS(3)Cr(2)	70.32(4)	70.46(4)	S(1)C(3)C(4)	105.9(3)	105.7(3)
CoCr(1)S(1)	114.87(4)	115.34(4)	S(1)C(3)C(5)	112.8(3)	113.3(3)
CoCr(1)S(2)	53.30(4)	53.41(4)	S(1)C(3)C(6)	106.7(3)	106.6(3)
CoCr(2)S(1)	114.00(4)	114.84(4)	C(5)C(3)C(4)	111.1(4)	111.8(4)
CoCr(2)S(2)	53.13(4)	53.16(3)	C(5)C(3)C(6)	110.5(4)	109.6(4)
CoCr(1)S(3)	53.15(3)	53.26(3)	C(4)C(3)C(6)	109.7(3)	109.5(4)
CoCr(2)S(3)	52.95(3)	53.17(3)	C(8)C(7)C(11)	107.9(4)	107.9(4)
Cr(1)S(1)Cr(2)	68.47(3)	68.15(3)	C(9)C(8)C(7)	107.9(4)	107.4(4)
Cr(1)S(2)Cr(2)	70.19(3)	69.46(3)	C(10)C(9)C(8)	108.4(4)	108.6(4)
Cr(1)S(3)Cr(2)	69.57(3)	69.32(3)	C(11)C(10)C(9)	107.9(4)	108.2(4)
Cr(1)CoC(1)	102.5(2)	100.3(2)	C(7)C(11)C(10)	108.4(4)	107.9(4)
Cr(1)CoC(2)	164.3(1)	162.8(2)	C(13)C(12)C(16)	108.2(4)	108.2(4)
Cr(2)CoC(1)	163.5(2)	160.9(2)	C(14)C(13)C(12)	107.7(4)	108.3(4)
Cr(2)CoC(2)	103.3(2)	102.9(2)	C(15)C(14)C(13)	108.2(4)	107.7(4)
CoC(1)C(1)	175.5(4)	177.3(5)	C(16)C(15)C(14)	108.2(4)	108.1(4)
CoC(2)O(2)	176.4(4)	174.9(4)	C(12)C(16)C(15)	107.9(4)	107.7(4)
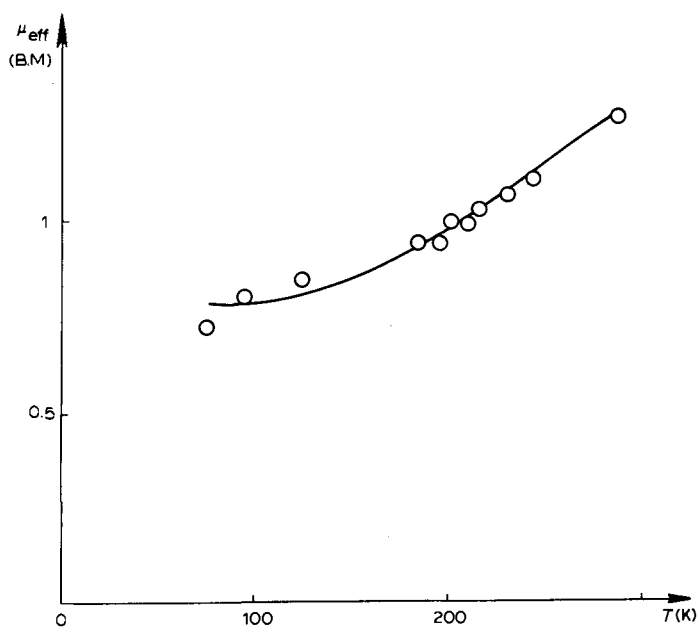
Fig. 5. Temperature dependence of the effective magnetic moment of IV.

plots fit the Heisenberg-Dirac-Van Vleck model (HDVV) well for two exchange-coupled ions (the addend metal atoms, Mn and Co, are diamagnetic) in the absence of orbital degeneracy of the complexes in the ground states. The spin
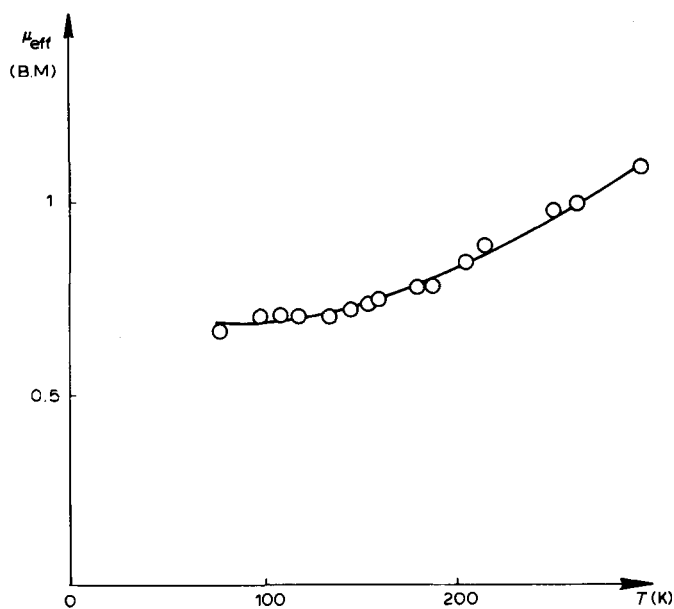

Fig. 6. Temperature dependence of the effective magnetic moment of V.

Hamiltonian has the form [8]:

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 + g\beta H(\hat{S}_{1z} + \hat{S}_{2z})$$

where J is the isotropic exchange parameter, g is the isotropic g-factor, and S are the spins of the exchange coupled ions (in the case under discussion, $S_1 = S_2 = 3/2$). The calculation of the theoretical χ_m and $\mu_{eff.}$ values (the solid line in Fig. 5) and least squares treatment of the data were carried out using the program described in ref. 9. The results are: IV, $g = 1.98$, $-2J = 440$ cm^{-1}, monomer admixture 4%; V, $g = 1.98$, $-2J = 530$ cm^{-1}, monomer admixture 3%.

Discussion

The study of the reactions of (CpCrSCMe$_3$)$_2$S (I) with binuclear metal carbonyls, Mn$_2$(CO)$_{10}$ and Co$_2$(CO)$_8$, has shown that the first of the carbonyls reacts with I only under forcing conditions (UV irradiation in THF, 5 h) to result in only insignificant changes of the initial complexes, limited to the replacement of one of the equatorial CO groups at one of the Mn atoms with the sulphide bridge lone pair. The product has the composition (CpCrSCMe$_3$)$_2$S · Mn$_2$(CO)$_9$ (IV). Conversely, the other reaction goes under very mild conditions (20°C in hexane, several minutes) and results in a major reorganization of both initial binuclear complexes: I looses the tert.-butyl group, and the cobalt carbonyl undergoes cleavage of the Co—Co bond and elimination of two carbonyl groups. The product is the cluster (Cp$_2$Cr$_2$SCMe$_3$)(μ^3-S)$_2$Co(CO)$_2$ (V), containing the trinuclear metallocycle, Cr$_2$Co.

The differences observed in the reactions of I with the binuclear metal carbonyls M$_2$(CO)$_n$ resemble those of reactions of I with the mononuclear metal carbonyls, M(CO)$_m$. These differences have been discussed in the Introduction, emphasizing the influence of the radii and coordination numbers of M on the transformations of the initially formed adducts (CpCrSCMe$_3$)$_2$S · M(CO)$_m$. These two factors determine the possibility of chelation by additional bonding of M with the thiolate sulphur atom.

It is reasonable to assume that the same factors are responsible for the two directions of the reactions of I with Mn$_2$(CO)$_{10}$ and Co$_2$(CO)$_8$ discussed in this work. However, the ligand environment of M is probably the dominant factor. In fact, the Mn—S (2.448 Å) bond is noticeably shorter than the M—S bonds in the adducts of the I with M(CO)$_5$ (M = Mo, W, 2.58 Å [2]). Approach of the thiolate sulphur atom to Mn is, however, hindered for the same reasons as with M = Mo, W: the presence of a closed 18-electron shell, six-coordinate octahedral environment (one coordination site is occupied by the second manganese atom) and the presence of two CO groups which hinder approach to Mn sterically (Figs. 1 and 2). This prevents the formation of the chelate structure required for structural transformations of I.

On the other hand, assuming that the first stage of the reaction of I with Co$_2$-(CO)$_8$ is similar to that with Mn$_2$(CO)$_{10}$, one would expect the formation of an intermediate adduct, (CpCrSCMe$_3$)$_2$S · Co$_2$(CO)$_7$. Because cobalt is five-coordinate and the Co—S bond in this intermediate should be short (the Co covalent radius is fairly small, 1.29 Å [5]), the formation of the Co—S$_{(thiolate)}$ bond is facilitated. After the elimination of the Co(CO)$_4$ and CMe$_3$ groups, this would

give a heteronuclear complex of the composition $(CpCrS)_2(SCMe_3)Co(CO)_3$, having a structure analogous to that of $(CpCrS)_2(SCMe_3)Fe(CO)_3$ but involving no Cr(2)Co bond because Co is saturated with electrons. The suggested reaction scheme is as follows:
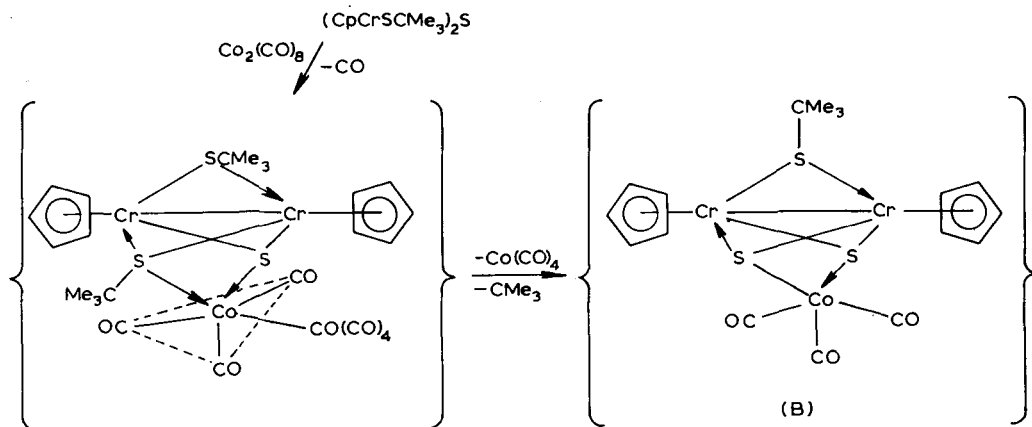
It seems likely that the reaction does in fact follow this scheme, but the product (B) looses one more CO group to form two direct Co—Cr bonds seen in the final product, complex V:
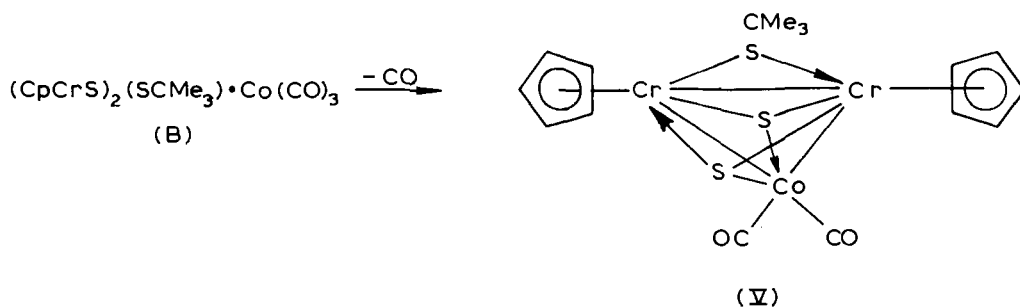
Thus it follows that mono- and binuclear metal carbonyls which act as Lewis acids towards I cause changes in the structure of I if the coordination number of M is 5 (in this case, chelates involving two M—S bonds are formed and one carbonyl and one tert.-butyl groups are eliminated). If the coordination number of M is equal to 6, I retains its structure upon the adduct formation.

Comparison of the structural and magnetic characteristics of complexes IV and V is very instructive. The exchange interactions between the two paramagnetic Cr^{III} centres in IV involve a rather complex system of bonds including the direct Cr—Cr bond, the two thiolate bridges and one sulphide bridge with the $Mn_2(CO)_9$ moiety attached to it. In general, the geometry of I remains unchanged from that of the free ligand, but the formation of the adduct results numerous small variations of the Cr—Cr and Cr—S bond lengths and CrSCr valence angles. The retention of the exchange parameter value, $-2J = 440$ cm^{-1} (against 430 cm^{-1} for free I) may in principle be explained by a balancing of the variations of contributions from different exchange channels. Thus, weakening of direct

exchange across the elongated Cr—Cr bond (2.740 Å in IV against 2.689 Å in I) may be compensated for by strengthening of indirect exchange caused by variations of CrSCr angles (see above). It seems more probable, however, that the absence of a noticeable dependence of the overall exchange on the electron-withdrawing properties of the $Mn_2(CO)_9$ group attached to the sulphide bridge is indicative of a dominant contribution from direct exchange (we have already discussed this point in the works on $(CpCrSCMe_3)_2S \cdot M(CO)_5$ (M = Cr, Mo, W) (II) [2] and $(Cp_2Cr_2SCMe_3)(\mu^3\text{-}S)_2Fe(CO)_3$ (III) [3]).

The same is probably true of the complex $(Cp_2Cr_2SCMe_3)(\mu^3\text{-}S)_2 \cdot Co(CO)_2$ (V) where exchange between the two Cr^{III} centres involves the direct Cr—Cr bond, one thiolate and two sulphide bridges, and also the diamagnetic Co^I centre. The geometry of this complex closely resembles that of III, except for the presence of two short (observed for the first time) Co—Cr bonds (2.579 and 2.592 Å) (III contains only one Cr—Fe bond, the other Cr···Fe distance is non-bonded, see Introduction). As the Cr—S distances and CrSCr angles in III and V are very similar, the considerable increases of exchange interactions between the Cr atoms on going from III ($-2J = 380$ cm^{-1}) to V ($-2J = 530$ cm^{-1}) may be caused by two factors: the shortening of the Cr—Cr bond from 2.707 to 2.617 Å and the appearance of the metal bridge CrCoCr in addition to the direct Cr—Cr bond. According to the literature data [4,10] the exchange parameter across the direct M—M bond ($-2J^d$) is characterized by the exponential dependence

$$-2J^d(R) = Ae^{-\alpha R}$$

where R is the M—M bond length and $\alpha = 6.3$. The $-2J^d$ value may vary by a factor of 2 when R varies by only 0.1 Å. It therefore seems likely that the shortening of the Cr—Cr bond is responsible for the increase of the $-2J$ value on going from III to V. On the other hand, the contribution from exchange across the CrCoCr bridge (CrCoCr 61.03°) may be significant.

Though the relative contributions from the two channels discussed here can not be estimated at present, it is of importance that complex V is the first cluster studied with a metallacyclic skeleton showing antiferromagnetic behaviour.

Experimental

All operations were carried out under pure argon. The dimers $(CpCrSCMe_3)_2S$ [3], $Mn_2(CO)_{10}$ [11], and $Co_2(CO)_8$ [11] were prepared as recommended in the literature. The absolute solvents were prepared by distillation over sodium metal suspension under an argon flow.

The IR spectra were obtained with an UR-20 instrument (KBr pellets). The mass spectrum was recorded on a DS-50 mass spectrometer. The magnetic susceptibility measurements were taken by the Faraday technique in the range 298 to 78 K [12]. The experimental data for the X-ray structural analysis of IV were collected with a Hilger-Watts autodiffractometer (λ Cu), 3328 reflections ($>\sigma$). The structure was solved by the direct method. Full-matrix anisotropic refinement was performed for C and O. The unit cell parameters: a 32.823(4), b 12.184(2), c 17.453(4) Å, β 97.55°, $V = 7519.2$ Å^3, $Z = 8$ (two independent molecules), space group $P2_1/n$, R_1 8.4%, $R_w = 9.6\%$ (the unit cell contains a water molecule). The X-ray data for V were collected with a Syntex P2$_1$ auto-

diffractometer (λ Mo, $2\theta \leqslant 48°$, $T = -120°C$), 6000 reflections. 5028 reflections were included in the full-matrix anisotropic refinement. The unit cell parameters: a 18.855(8), b 10.632(5), c 20.706(10) Å; β 114.40(3)°; $V = 2781.0$ Å^3 $Z = 8$ (two independent molecules), Space group $P2_1/n$, $R_1 = 3.50\%$, $R_w = 4.11\%$.

(CpCrSCMe₃)₂S · Mn₂(CO)₉ (IV)

A violet solution of (CpCrSCMe$_3$)$_2$S (I) (0.50 g, 1.1 mmol) and Mn$_2$(CO)$_{10}$ (0.43 g, 1.1 mmol) in 25 ml THF was irradiated under argon at 10°C for 5 h with a high pressure PRK-4 mercury lamp in a quartz vessel equipped with a magnetic stirrer and jacket cooled with flowing water. The reaction mixture was chromatographed on neutral Al$_2$O$_3$ (11.5 × 2.4 cm, from heptane). A brown band was separated from a violet band of the initial complex (the latter underwent elution at a lower rate). The brown eluate was cooled to $-78°C$ to produce brownish black crystals. These were filtered, washed with pentane and dried under vacuum. The yield was 0.20 g, m.p. 165°C (decomp.). Found: C, 40.10; H, 3.54; S, 12.00. C$_{27}$H$_{28}$Cr$_2$Mn$_2$O$_9$S$_3$ calcd.: C, 40.20; H, 3.47; S, 11.91%. IR spectrum (ν, cm^{-1}): 424w, 485w, 504w, 570w, 625s, 642m, 658m, 820s, 1028w, 1075vs, 1160s, 1380w, 1440w, 1460w, 1920s, 1953s, 1988s, 2020s, 2088s, 2850—2975m, 3100w. Crystals for X-ray structure analysis were obtained by evaporating the reaction mixture to dryness (without chromatography), extraction of the residue with benzene/heptane (1/1) and concentration of the extract at 50°C/15 torr.

(Cp₂Cr₂SCMe₃)(μ³-S)₂Co(CO)₂ (V)

A filtered violet solution of (CpCrSCMe$_3$)$_2$S in 65 ml hexane was added to a dark orange solution of Co$_2$(CO)$_8$ (0.17 g, 0.5 mmol) in 7 ml hexane. The brown solution thus obtained was cooled to $-5°C$, the dark-brown precipitate was isolated from the mother liquor, washed with pentane and dried under vacuum. The yield was 0.12 g, m.p. 160—163°C (decomp.) Found: C, 38.50; H, 4.40, C$_{16}$H$_{19}$CoCr$_2$O$_2$S$_3$ calcd.: C, 38.25; H, 3.78%. IR spectrum (ν, cm^{-1}): 430w, 500w, 544w, 818s, 1023m, 1072w, 1160m, 1370w, 1448w, 1460w, 1948s, 2000s, 2780—2990m, 3060w.

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