

ANTIFERROMAGNETIC COMPLEXES WITH A METAL–METAL BOND

XV *. ANTIFERROMAGNETIC HETEROMETALLOSPIRANE CLUSTERS [(CH₃C₅H₄)₂Cr₂(μ-SCMe₃)(μ₃-S)₂]₂M (M = Mn^{II}, Fe^{II}): SYNTHESIS AND MOLECULAR STRUCTURES

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Summary

The reaction of (CH₃C₅H₄CrSCMe₃)₂S (Ia) with Cp₂Mn in boiling toluene (containing some THF) has been used to prepare a pentanuclear cluster, [(CH₃C₅H₄)₂Cr₂(SCMe₃)(μ₃-S)₂]₂Mn (II), which is antiferromagnetic and crystallizes into the monoclinic crystal system: space group *Cc*, *a* 26.540(10), *b* 9.208(3), *c* 21.595(9) Å; β 135.30(2)°, *V* = 3712.1 Å³, *Z* = 4. According to X-ray analysis, cluster II contains a metallospirane core, Cr₄Mn, which appears to be strongly distorted, compared to its earlier studied cyclopentadienyl analogue [Cp₂Cr₂SCMe₃(μ₃-S)₂]₂Mn, due to the short intramolecular contacts CH₃...S (2.9–3.1 Å). The angle between the metal triangle planes of Cr₂Mn is 109.60°. Here, the two long Cr–Mn bonds (3.019(3) and 3.104(4) Å) are combined with the shorter Cr–Cr bond (2.651(6) Å) in one triangle and, vice versa, the less extended Cr–Mn bonds (2.839(4) and 2.967(3) Å) are combined with a longer Cr–Cr bond (2.726(6) Å) in the other triangle of Cr₂Mn. By the reaction of Ia with [CpFe(CO)₂]₂ (taken in the ratio of 2/1) in boiling toluene, the antiferromagnetic cluster [(CH₃C₅H₄)₂Cr₂(SCMe₃)(μ₃-S)₂]₂Fe (III) has been synthesized in which the same distortions as in cluster II are present, as revealed by X-ray analysis. In the metallospirane core of the molecule of III, the Cr₂Fe triangles make an angle of 113.84° with each other. In

* Communication XIV see ref. 1.

this cluster, the Cr–Cr distances in the peripheral binuclear fragments $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2$ are practically equal (2.688(3) and 2.661(3) Å), whereas the Fe–Cr bond lengths are markedly different (2.749(2) and 2.827(2) Å in one triangle and 2.910(2) and 2.969(2) Å in the other). The dependence of the geometries of clusters II and III on the steric effects of the methyl substituents in the cyclopentadienyl ligands and on the electronic effect of the central metal atom (Mn^{II} or Fe^{II}) is discussed.

Introduction

In previous communications of this series [1,2] we reported the preparation of a novel class of stable antiferromagnetic $[\text{Cp}_2\text{Cr}_2\text{SCMe}_3(\mu_3\text{-S})_2]_2\text{M}$ ($\text{M} = \text{Cr}^{\text{II}}, \text{Mn}^{\text{II}}, \text{Co}^{\text{II}}$) clusters containing a heterometallospirane core, Cr_4M , with an angle of 90° between the Cr_2M triangle planes. It has been found that the geometry of the dichromium fragments $[\text{Cp}_2\text{Cr}_2\text{SCMe}_3(\mu_3\text{-S})_2]$ (Q) remains practically the same in all complexes and is similar to that observed in the metallotriangular clusters $\text{QFe}(\text{CO})_3$ [3], $\text{QMn}(\text{CO})_3$ [2] and $\text{QCo}(\text{CO})_2$ [4]. At the same time, the geometry of the environment of the central M ion shows a strong dependence upon the nature of M, in particular, upon its electronic configuration (d^4 for Cr^{II} , d^5 for Mn^{II} and d^7 for Co^{II}). In this series the looseness of the M–Cr and M–S bonds increases, which, within the framework of a simple model, can be attributed to the filling of the central M^{II} ion orbitals which are antibonding with respect to the above-mentioned bonds [1,2]. The particularly strong loosening of the Mn–Cr and Mn–S bonds could be due to the high ionic character of the bonds because Mn^{II} has a spherical d^5 -electronic configuration. It was deemed to be of interest to consider the structural variations of Q_2Mn on introduction of an electron-donating methyl substituent into each cyclopentadienyl ligand of Q. It is known that, in contrast to the high-spin, substantially ionic complex Cp_2Mn (${}^6A_{1g}$) with Mn–C bond lengths of 2.43 Å [5], an equilibrium is observed in $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Mn}$ between the high-spin and low-spin states ($S = 5/2$, Mn–C bond lengths 2.42 Å; $S = 1/2$, Mn–C bond lengths 2.14 Å) [6], whereas in $(\text{Me}_5\text{C}_5)_2\text{Mn}$ only the low-spin state occurs ($S = 1/2$, Mn–C bond lengths 2.13 Å) [7]. Besides, in view of the discovered dependence of the metallospirane Q_2M cluster structure upon the nature of the central metal ion, we believed it to be important to try to prepare and investigate the cluster with Fe^{II} as the central ion (electronic configuration d^6).

Results and discussion

The cluster $[(\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{SCMe}_3)(\mu_3\text{-S})_2]_2\text{Mn}$ had been obtained previously via a photochemical reaction of $(\text{C}_5\text{H}_5\text{CrSCMe}_3)_2\text{S}$ (I) with $\text{CpMn}(\text{CO})_3$ in boiling toluene [1]. In order to synthesize a methylcyclopentadienyl cluster containing the metallospirane core Cr_4Mn , we resorted to the ability of manganocene to break the strongly ionic Mn– C_5H_5 bond easily [5]. Indeed, the reaction of $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Cr}_2(\mu\text{-SCMe}_3)_2\text{S}$ (Ia) with Cp_2Mn in boiling toluene rapidly yields, even without promotion by UV radiation, the cluster $[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2]_2\text{Mn}$ (II) (see formula).

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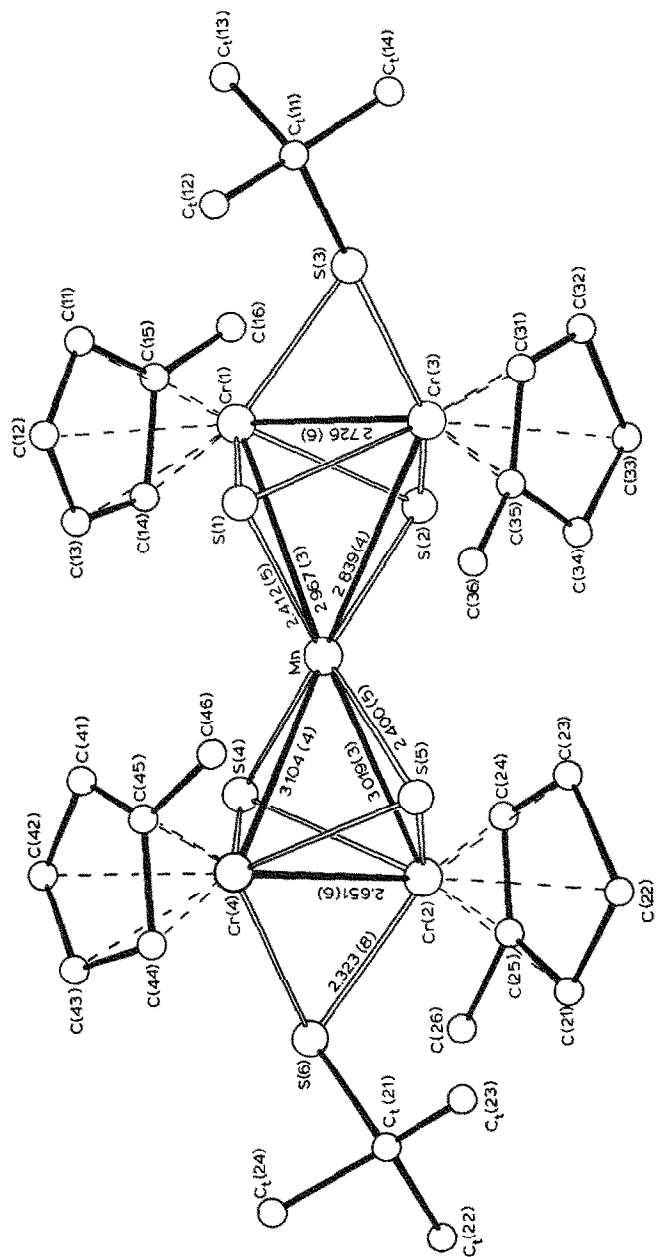


Fig. 1. Molecular structure of $[(\text{MeC}_3\text{H}_4)_2\text{Cr}_2(\mu_3\text{-S})_2]_2\text{Mn}(\text{II})$.

TABLE I
 ATOMIC COORDINATES ($\times 10^3$) FOR $[(\text{MeC}_5\text{H}_4)_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu\text{-S})_2\text{Mn}(\text{II})]$ (for $\text{Mn} \times 10^4$; for $\text{Cr} \times 10^4$; for $\text{S} \times 10^4$)

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	1328	1120(3)	6094	2.52(9)	3.0(1)	2.40(9)	-0.1(3)	1.94(9)	-0.2(3)
Cr(1)	114(1)	212(3)	4236(2)	2.0(1)	2.1(1)	3.2(1)	-0.6(1)	2.0(1)	-0.6(1)
Cr(2)	2501(2)	260(2)	8008(2)	2.4(1)	3.0(1)	3.4(2)	0.4(1)	2.2(1)	0.2(1)
Cr(3)	1169(1)	1946(3)	4696(2)	1.9(1)	2.4(1)	2.4(1)	-0.3(1)	1.6(1)	-0.4(1)
Cr(4)	1486(1)	1890(3)	7624(2)	2.0(1)	2.3(1)	2.5(1)	0.3(1)	1.7(1)	0.2(1)
S(1)	399(2)	2592(5)	4825(3)	2.6(2)	2.2(2)	3.0(2)	-0.1(2)	2.2(2)	-0.2(2)
S(2)	1319(3)	-375(5)	5221(3)	2.6(2)	2.4(2)	3.8(2)	0.5(2)	2.3(2)	0.5(2)
S(3)	248(2)	798(5)	3279(3)	2.2(2)	2.7(2)	2.9(2)	-0.2(2)	1.8(2)	-0.5(2)
S(4)	1258(3)	-380(5)	7021(3)	2.6(2)	3.0(2)	2.8(2)	0.0(2)	2.0(2)	0.0(2)
S(5)	2211(2)	2497(5)	7420(3)	2.2(2)	2.9(2)	2.9(2)	-0.3(2)	1.9(2)	-0.2(2)
S(6)	2370(2)	716(5)	8946(3)	2.3(2)	2.6(2)	2.6(2)	-0.2(2)	1.7(2)	0.0(2)
C ₁ (11)	-50(1)	206(2)	231(1)	3.2(9)	7(1)	3.1(9)	2.2(9)	2.0(9)	3.2(9)
C ₁ (12)	-76(1)	305(2)	249(1)	4.1(9)	5(1)	4(1)	0.0(8)	3.0(9)	-1.2(8)
C ₁ (13)	-107(1)	107(2)	151(1)	4(1)	6(1)	5(1)	-2.0(9)	3(1)	-3(1)
C ₁ (14)	-8(1)	267(3)	207(2)	7(1)	6(1)	7(1)	1(1)	6(1)	3(1)
C ₁ (21)	302(1)	194(2)	991(1)	0.6(6)	2.8(8)	1.6(8)	-1.3(6)	0.3(6)	0.3(7)
C ₁ (22)	366(1)	92(2)	1065(1)	2.7(8)	5(1)	1.3(8)	-1.8(8)	-1.1(7)	0.0(9)
C ₁ (23)	328(1)	321(2)	967(1)	6(1)	5(1)	5(1)	-4(1)	4(1)	-2(1)
C ₁ (24)	271(1)	271(1)	1019(1)	5(1)	7(1)	4(1)	0(1)	3(1)	-1(1)

C(11)	-100(1)	-88(2)	309(2)	5(1)	5(1)	9(1)	-4.3(9)	6(1)	-4(1)
C(12)	-99(1)	9(2)	370(2)	1.2(6)	5(1)	9(2)	0.0(7)	2.6(9)	2(1)
C(13)	-36(1)	-73(2)	469(1)	6(1)	7(1)	7(1)	-6(1)	5(1)	-2(1)
C(14)	-13(1)	-185(2)	452(1)	3.1(9)	4.0(9)	8(1)	-1.5(8)	4(1)	-0.1(9)
C(15)	-52(1)	-194(2)	364(2)	7(1)	2.8(1)	12(2)	-3.2(9)	8(1)	-3(1)
C(16)	-55(1)	-288(2)	304(1)	7(1)	6(1)	14(1)	-4(1)	9(2)	-6(1)
C(21)	360(1)	-64(2)	897(1)	2.6(9)	4.3(9)	1.2(7)	2.3(7)	1.1(7)	1.5(7)
C(22)	351(1)	2(2)	835(1)	3.5(9)	3.6(9)	7(1)	1.6(8)	4(1)	1.5(9)
C(23)	307(1)	-45(2)	765(1)	5(1)	4(1)	8(1)	0.9(9)	6(1)	1(1)
C(24)	276(1)	-169(2)	764(1)	6(1)	5(1)	8(2)	2(1)	5(1)	1(1)
C(25)	305(1)	-185(2)	853(1)	3.8(9)	3.9(9)	5(1)	3.1(9)	4(1)	2.4(9)
C(26)	281(1)	-315(2)	875(1)	5(1)	3.0(9)	10(2)	2.7(9)	6(1)	4(1)
C(31)	139(1)	396(2)	433(1)	5(1)	5(1)	5(1)	-3.7(10)	4(1)	-2.5(9)
C(32)	173(1)	238(2)	432(1)	3.0(8)	2.4(9)	4(1)	-0.9(7)	3.2(8)	-0.7(8)
C(33)	216(1)	206(2)	504(1)	3.3(9)	4(1)	8(1)	-2.9(8)	4.7(9)	-3.4(9)
C(34)	222(1)	296(2)	571(1)	1.8(7)	5(1)	4(1)	-1.8(9)	1.7(9)	-1.8(8)
C(35)	181(1)	395(2)	527(1)	4(1)	2.1(9)	9(1)	-1.8(8)	5(1)	-1.8(9)
C(36)	164(1)	530(1)	561(1)	5(1)	3.4(9)	6(1)	-1.9(9)	3(1)	-2.7(9)
C(41)	31(1)	270(2)	648(1)	2.7(7)	4.3(9)	1.8(7)	0.6(6)	2.4(8)	0.3(7)
C(42)	35(1)	200(2)	706(1)	1.3(7)	5(1)	2.4(9)	1.5(8)	0.8(7)	0.5(8)
C(43)	95(1)	291(2)	798(1)	5(1)	6(1)	6(1)	1.6(9)	4(1)	-1(1)
C(44)	115(1)	397(2)	781(1)	3.5(9)	2.6(8)	3.7(9)	-0.6(8)	3.9(0)	-1.1(8)
C(45)	83(1)	412(2)	695(1)	3.1(9)	3.5(9)	3.1(9)	0.7(7)	2.5(8)	-0.9(7)
C(46)	80(1)	519(2)	646(1)	6(1)	2.1(8)	7(1)	-0.2(8)	6(1)	-0.3(9)

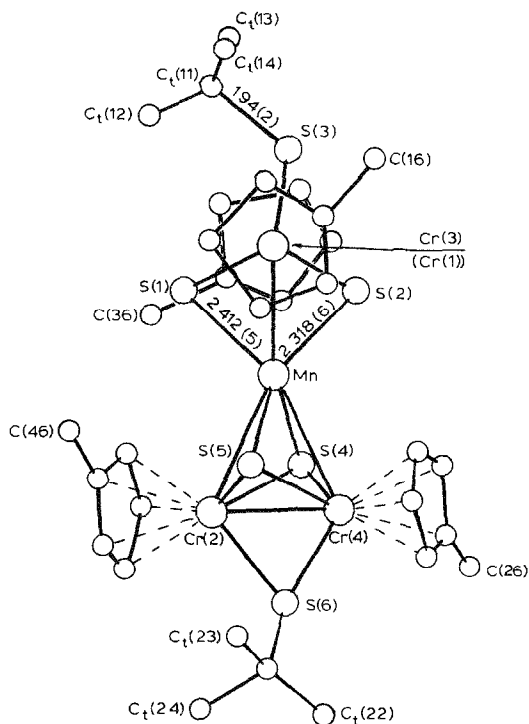
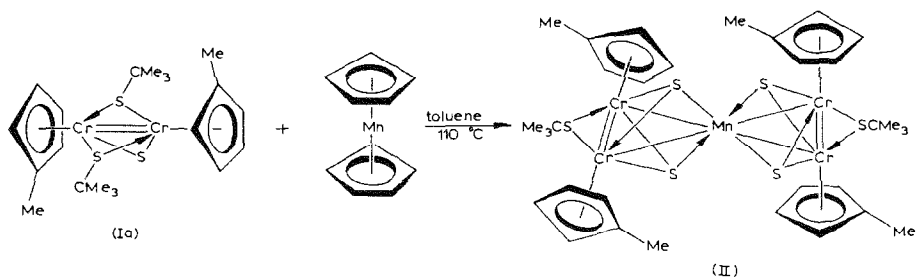


Fig. 2. Projection of $[(\text{MeC}_5\text{H}_4)_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2]_2\text{Mn}$ (II) onto the plane S(1)S(2)S(3)



II was obtained as dark-green crystals by recrystallization from toluene. The complex was found to be antiferromagnetic*; its IR spectrum showed, apart from the vibration bands of the $\pi\text{-C}_5\text{H}_4\text{R}$ rings (799, 1012, 1435 and 3060 cm^{-1}) and the CMe_3 groups (1145 and 2890 cm^{-1}), the presence of vibration bands of the CH_3 group in the cyclopentadienyl ligand (1348 cm^{-1}).

The structure of II was identified by X-ray diffraction analysis (Figs. 1 and 2). Table 1 lists the atomic coordinates; for bond lengths and valence angles see Tables 2 and 3, respectively. The structure of II is strongly distorted in comparison with its cyclopentadienyl analogue $[\text{Cp}_2\text{Cr}_2\text{SCMe}_3(\mu_3\text{-S})_2]_2\text{Mn}$ (III). For example, the angle

* The magneto-chemical experiments were carried out by Dr. V.M. Novotortsev and Dr. O.G. Ellert and will be published elsewhere.

TABLE 2
BOND LENGTHS FOR $[(\text{MeC}_5\text{H}_4)_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2]_2\text{Mn}$ (II)

Bond	d (Å)	Bond	d (Å)	Bond	d (Å)
Mn–Cr(1)	2.967(3)	Cr(1)–C(15)	2.31(2)	Cr(3)–C(34)	2.18(2)
Mn–Cr(2)	3.019(3)	Cr(2)–Cr(4)	2.651(6)	Cr(3)–C(35)	2.19(2)
Mn–Cr(3)	2.839(4)	Cr(2)–S(4)	2.352(8)	Cr(4)–S(4)	2.316(6)
Mn–Cr(4)	3.104(4)	Cr(2)–S(5)	2.250(6)	Cr(4)–S(5)	2.329(9)
Mn–S(1)	2.412(5)	Cr(2)–S(6)	2.323(8)	Cr(4)–S(6)	2.302(6)
Mn–S(2)	2.318(6)	Cr(2)–C(21)	2.21(2)	Cr(4)–C(41)	2.33(2)
Mn–S(4)	2.502(6)	Cr(2)–C(22)	2.21(2)	Cr(4)–C(42)	2.32(3)
Mn–S(5)	2.400(5)	Cr(2)–C(23)	2.24(4)	Cr(4)–C(43)	2.25(3)
Cr(1)–Cr(3)	2.726(6)	Cr(2)–C(24)	2.25(3)	Cr(4)–C(44)	2.27(2)
Cr(1)–S(1)	2.372(5)	Cr(2)–C(25)	2.20(2)	Cr(4)–C(45)	2.40(2)
Cr(1)–S(2)	2.318(8)	Cr(3)–S(1)	2.327(9)	S(3)–C _i (11)	1.94(2)
Cr(1)–S(3)	2.395(8)	Cr(3)–S(2)	2.316(6)	S(6)–C _i (21)	1.87(2)
Cr(1)–C(11)	2.34(3)	Cr(3)–S(3)	2.414(5)	C _i –C _{U(av)}	1.54(3)
Cr(1)–C(12)	2.27(3)	Cr(3)–C(31)	2.25(3)	C–C(C ₅ H ₄) _(av)	1.43(3)
Cr(1)–C(13)	2.24(3)	Cr(3)–C(32)	2.23(3)	C(C ₅ H ₄)–C(Me) _(av)	1.56(4)
Cr(1)–C(14)	2.24(2)	Cr(3)–C(33)	2.18(3)		

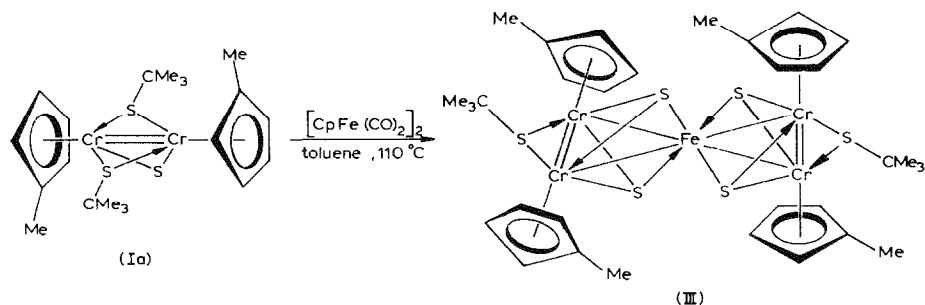
TABLE 3
BOND ANGLES (°) FOR $[(\text{MeC}_5\text{H}_4)_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2]_2\text{Mn}$ (II)

Angle	Angle	Angle	Angle
Cr(1)MnCr(2)	148.2(1)	MnCr(1)S(2)	50.2(2)
Cr(1)MnCr(3)	56.0(1)	MnCr(1)S(3)	114.7(2)
Cr(1)MnCr(4)	134.3(1)	Cr(3)Cr(1)S(1)	53.8(2)
Cr(1)MnS(1)	51.1(2)	Cr(3)Cr(1)S(2)	53.9(2)
Cr(1)MnS(2)	50.2(2)	Cr(3)Cr(1)S(3)	55.8(2)
Cr(1)MnS(4)	107.6(2)	S(1)Cr(1)S(2)	90.9(2)
Cr(1)MnS(5)	164.5(2)	S(1)Cr(1)S(3)	93.9(2)
Cr(2)MnCr(3)	139.1(1)	MnCr(2)Cr(4)	66.0(1)
Cr(2)MnCr(4)	51.3(1)	MnCr(2)S(4)	53.8(2)
Cr(2)MnS(1)	158.4(2)	MnCr(2)S(5)	51.7(2)
Cr(2)MnS(2)	111.2(2)	MnCr(2)S(6)	119.9(2)
Cr(2)MnS(4)	49.3(2)	Cr(4)Cr(2)S(4)	54.8(2)
Cr(2)MnS(5)	47.4(2)	Cr(4)Cr(2)S(5)	56.0(2)
Cr(3)MnCr(4)	151.3(1)	Cr(4)Cr(2)S(6)	54.7(2)
Cr(3)MnS(1)	51.8(2)	S(4)Cr(2)S(5)	91.1(3)
Cr(3)MnS(2)	52.2(2)	S(4)Cr(2)S(6)	82.9(2)
Cr(3)MnS(4)	160.5(2)	S(5)Cr(2)S(6)	97.1(3)
Cr(3)MnS(5)	114.1(2)	MnCr(3)Cr(1)	64.4(1)
Cr(4)MnS(1)	109.7(2)	MnCr(3)S(1)	54.6(2)
Cr(4)MnS(2)	156.4(2)	MnCr(3)S(2)	52.3(2)
Cr(4)MnS(4)	47.3(2)	MnCr(3)S(3)	118.8(2)
Cr(4)MnS(5)	48.0(2)	Cr(1)Cr(3)S(1)	55.3(2)
S(1)MnS(2)	89.9(2)	Cr(1)Cr(3)S(2)	54.0(2)
S(1)MnS(4)	128.9(2)	Cr(1)Cr(3)S(3)	55.1(2)
S(1)MnS(5)	113.7(2)	S(1)Cr(3)S(2)	92.1(2)
S(2)MnS(4)	110.0(2)	S(1)Cr(3)S(3)	94.5(2)
S(2)MnS(5)	136.1(2)	S(2)Cr(3)S(3)	83.3(2)
S(4)MnS(5)	84.2(2)	MnCr(4)Cr(2)	62.7(1)
MnCr(1)Cr(3)	59.6(1)	MnCr(4)S(4)	52.6(2)
MnCr(1)S(1)	52.3(2)	MnCr(4)S(5)	50.0(2)
		MnCr(4)S(6)	117.4(2)
		Cr(2)Cr(4)S(4)	56.0(2)
		Cr(2)Cr(4)S(5)	53.2(2)
		Cr(2)Cr(4)S(6)	55.4(2)
		S(4)Cr(4)S(5)	90.0(2)
		S(4)Cr(4)S(6)	84.1(2)
		S(5)Cr(4)S(6)	95.5(2)
		MnS(1)Cr(1)	76.7(2)
		MnS(1)Cr(3)	73.6(2)
		Cr(1)S(1)Cr(3)	70.9(2)
		MnS(2)Cr(1)	79.6(2)
		MnS(2)Cr(3)	75.6(2)
		Cr(1)S(2)Cr(3)	72.1(2)
		Cr(1)S(3)Cr(3)	69.1(2)
		Cr(1)S(3)C _i (11)	113.6(8)
		Cr(3)S(3)C _i (11)	116.4(8)
		MnS(4)Cr(2)	76.9(2)
		MnS(4)Cr(4)	80.1(2)
		Cr(2)S(4)Cr(4)	69.2(2)
		MnS(5)Cr(2)	80.9(2)
		MnS(5)Cr(4)	82.0(2)
		Cr(2)S(5)Cr(4)	70.8(2)
		Cr(2)S(6)Cr(4)	69.9(2)
		Cr(2)S(6)C _i (21)	119.5(7)
		Cr(4)S(6)C _i (21)	114.9(7)
		SC _i C _{U(av)}	108(2)
		C _i C _i C _{U(av)}	111(2)
		CCC(–C ₅ H ₄) _(av)	108(2)
		CC(–C ₅ H ₄)C(Me) _(av)	125(2)

between the Cr_2Mn triangular fragment planes has changed from 90 to 109.60° ; this rotation is probably the reason for the greater electron density delocalization over both Cr_2Mn triangles. As a result, the long Cr-Mn bonds ($3.019(3)$ and $3.104(4)$ Å) are combined with the short Cr-Cr bond ($2.651(6)$ Å) in one Cr_2Mn triangle, whereas in the other Cr_2Mn triangle the shorter Cr-Mn bonds ($2.839(4)$ and $2.967(3)$ Å) are combined with the extended Cr-Cr bond ($2.726(6)$ Å). Analysis of the geometry of **II** has shown that such considerable distortions are due to the short-range intramolecular contacts between the methyl substituents of the cyclopentadienyl rings and the tridentate-bridge sulfur atoms (2.9 to 3.1 Å). This results in staggered ring conformation in the peripheral bichromium fragments (Fig. 2) instead of the eclipsed one in the cyclopentadienyl analogue.

Note also the non-equivalence of the Mn-S bonds, whose lengths varied from 2.318 to 2.502 Å (correspondingly, the CrSMn angles varied from 73.6 to 82.0°). The rather long Mn-S and Cr-Mn bonds in the complex, as well as in the cyclopentadienyl analogue, are apparently due to the d^5 -electronic configuration of the central Mn^{II} ion responsible for the high ionicity of the bonds formed by Mn.

To verify this assumption, an analogue of cluster **II** which contained Fe^{II} as the central atom with d^6 -electronic configuration was synthesized. The cluster $[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Cr}_2(\text{SCMe}_3)(\mu_3\text{-S})_2]_2\text{Fe}$ (**III**) was produced by boiling $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Cr}_2(\mu\text{-SCMe}_3)_2(\mu\text{-S})$ (**Ia**) with $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ in toluene. It was obtained in the form of large, blackish-brown prisms by recrystallization from CH_2Cl_2 :



Cluster **III** is antiferromagnetic; its IR spectrum contains the characteristic vibration bands of the $\text{CH}_3\text{C}_5\text{H}_4$ ring at 810 , 1020 , 1440 and 3060 cm^{-1} and the CMe_3 group at 1150 and $2860\text{--}2940$ cm^{-1} . The structure of cluster **III** was identified by a complete X-ray diffraction analysis (Fig. 3). Atomic coordinates are listed in Table 4; for bond lengths and valence angles see Tables 5 and 6, respectively. Cluster **III** was found to be isomorphous with its manganese analogue $[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2]_2\text{Mn}$ (**II**), but there are substantial differences as regards the molecular geometry of the cluster. For example, in **III** the angle between the triangular Cr_2Fe fragments (113.84°) is somewhat larger than the 109.40° angle in **II** and is substantially larger than the 90° angle in cyclopentadienyl metallospirane clusters with Cr_4Cr , Cr_4Co and Cr_4Mn cores. Likewise in the case of **II**, such a strong distortion of the spirane core in **III** is probably due to the intramolecular non-valence interactions between the methyl group of the cyclopentadienyl ligand and the $\mu_3\text{-S}$ bridges ($\text{CH}_3\cdots\text{S}$, $2.9\text{--}3.1$ Å). The same reason is responsible again for the staggered conformation of the $\text{CH}_3\text{C}_5\text{H}_4$ rings with respect to the Cr-Cr axis. On the other hand, the inter-ligand interactions have no effect on

(Continued on p. 360)

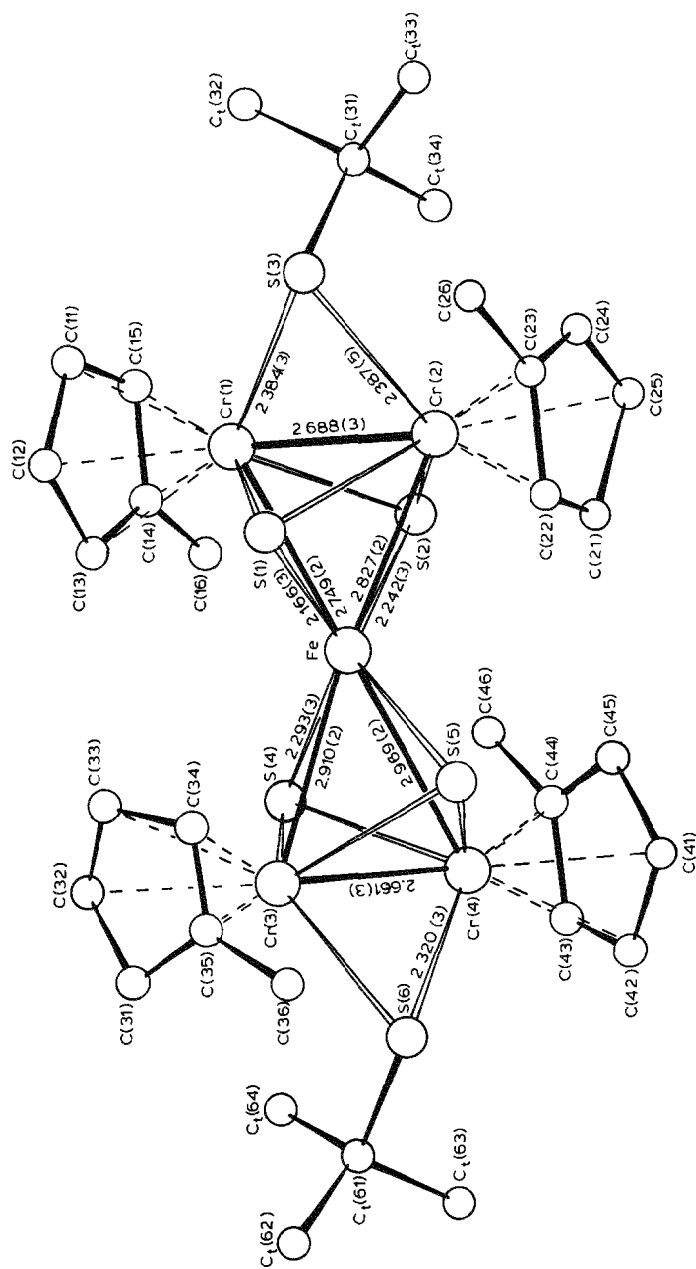


Fig. 3. Molecular structure of $[(\text{MeC}_5\text{H}_4)_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2]_2\text{Fe}$ (III).

TABLE 4

ATOMIC COORDINATES ($\times 10^4$) for Fe, Cr and S. $\times 10^5$) AND ANISOTROPIC TEMPERATURE FACTORS IN THE FORM $T = \exp -1/4(B_{11}h^2a^{*2} + \dots + 2B_{12}hka^*b^* + \dots)$ FOR $[(\text{MeC}_5\text{H}_4)_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2\text{Fe}(\text{III})]$

Atom	x	y	z	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	13319	11200(12)	60902	1.65(4)	2.50(4)	-0.02(11)	2.02(4)	0.01(11)
Cr(1)	12045(8)	18843(17)	47400(11)	2.59(7)	3.14(7)	-0.43(6)	2.15(6)	-0.38(6)
Cr(2)	1368(8)	2928(18)	42818(11)	2.84(6)	4.08(8)	-0.42(6)	2.68(7)	-0.25(6)
Cr(3)	24944(8)	2925(17)	79719(11)	2.35(6)	3.46(7)	0.33(5)	2.19(6)	0.14(6)
Cr(4)	14478(8)	18778(17)	75378(10)	2.41(6)	3.01(7)	0.32(5)	2.07(6)	0.24(6)
S(1)	13315(14)	-3565(28)	53019(19)	2.64(11)	4.43(13)	0.66(9)	2.78(10)	0.89(9)
S(2)	4788(14)	25574(29)	49157(18)	2.81(11)	3.61(11)	-0.02(9)	2.47(10)	-0.23(9)
S(3)	2725(13)	7508(27)	33128(17)	2.69(11)	3.52(11)	-0.23(9)	2.30(10)	-0.69(9)
S(4)	21517(13)	25552(27)	73369(16)	2.51(10)	3.12(10)	-0.07(8)	2.29(9)	0.01(8)
S(5)	12871(14)	-3726(27)	69499(18)	2.92(11)	3.71(12)	-0.01(10)	2.49(10)	-0.01(10)
S(6)	23571(13)	7394(27)	89130(17)	2.71(11)	2.99(10)	-0.07(8)	2.11(9)	0.10(8)
C ₁ (31)	-438(6)	2022(14)	2322(7)	5.6(6)	3.8(5)	2.0(5)	2.7(5)	1.6(5)
C ₁ (32)	-89(7)	2709(14)	2058(8)	6.1(7)	4.9(7)	-0.6(6)	4.0(6)	0.9(5)
C ₁ (33)	-1022(6)	1067(14)	1580(7)	7.2(7)	3.2(5)	0.8(5)	1.9(4)	-2.0(5)
C ₁ (34)	-712(5)	3051(10)	2527(6)	2.2(4)	3.0(4)	0.3(4)	2.2(4)	0.1(3)
C ₁ (61)	2994(5)	1980(10)	9878(6)	2.7(4)	2.8(4)	0.1(3)	2.1(4)	0.6(3)
C ₁ (62)	3658(6)	1024(14)	10697(7)	5.7(7)	3.0(5)	0.5(5)	1.0(4)	-0.8(5)
C ₁ (63)	2622(7)	2654(14)	10103(9)	4.8(7)	6.2(7)	-2.6(6)	5.3(7)	-2.4(5)
C ₁ (64)	3198(6)	3319(12)	9624(6)	3.6(5)	4.8(6)	-1.6(4)	3.0(5)	-0.8(5)

C(11)	1774(6)	2577(14)	4371(7)	4.0(5)	6.0(7)	4.4(5)	-1.9(5)	3.5(5)	-0.9(5)
C(12)	2268(5)	1919(13)	5217(7)	2.9(4)	5.0(6)	4.6(5)	-1.5(5)	2.8(5)	-1.4(5)
C(13)	2285(5)	2848(11)	5783(6)	1.9(3)	4.1(5)	2.9(4)	-1.4(3)	1.5(4)	-1.0(4)
C(14)	1822(5)	4044(11)	5294(7)	4.0(5)	2.8(4)	5.4(6)	-1.4(4)	3.6(5)	-0.3(4)
C(15)	1456(5)	3861(10)	4405(6)	4.7(5)	3.5(4)	4.1(5)	-2.0(4)	3.4(4)	-1.7(5)
C(16)	1682(8)	5333(12)	5598(9)	9.8(9)	2.9(5)	6.9(7)	-1.7(5)	6.9(8)	-1.7(5)
C(21)	-372(5)	-609(10)	4692(7)	3.2(4)	3.1(4)	4.2(5)	-0.9(3)	2.7(4)	-0.2(4)
C(22)	-155(5)	-1595(10)	4597(7)	3.4(4)	2.9(4)	4.8(5)	-1.3(3)	2.7(4)	0.5(4)
C(23)	-511(5)	-1747(8)	3667(7)	4.4(4)	0.6(3)	6.9(6)	-1.9(3)	4.4(5)	2.1(3)
C(24)	-937(5)	-856(11)	3197(7)	3.9(5)	4.4(5)	3.5(4)	-2.6(4)	3.0(4)	-0.9(3)
C(25)	-1000(6)	153(14)	3655(11)	3.5(5)	5.2(7)	8.6(10)	-0.6(5)	5.8(7)	0.9(7)
C(26)	-445(8)	-2867(14)	3172(11)	8.4(9)	4.1(7)	12.4(11)	-1.9(6)	8.6(9)	-2.8(7)
C(31)	3625(6)	-482(13)	9024(8)	3.3(5)	5.1(6)	6.1(7)	1.2(4)	3.5(5)	0.5(5)
C(32)	3531(5)	188(12)	8384(7)	3.4(4)	3.9(5)	5.0(6)	0.1(4)	3.3(4)	0.2(4)
C(33)	3143(6)	-232(11)	7702(9)	5.9(6)	3.0(5)	8.7(8)	0.7(5)	6.2(6)	0.0(5)
C(34)	2776(6)	-1772(14)	7683(10)	4.7(6)	5.3(7)	9.5(9)	0.5(5)	5.4(7)	-1.8(7)
C(35)	3060(7)	-1968(15)	8492(9)	4.8(6)	6.3(7)	7.4(8)	1.3(6)	4.9(7)	0.1(6)
C(36)	2854(7)	-3160(15)	8740(10)	6.9(8)	5.4(8)	9.0(9)	2.0(6)	6.2(8)	3.2(7)
C(41)	385(6)	1988(12)	7059(9)	4.1(5)	3.8(5)	9.1(8)	0.7(4)	5.5(6)	1.6(5)
C(42)	870(6)	2635(14)	7858(8)	4.8(6)	6.6(7)	5.6(7)	2.3(5)	4.3(6)	2.4(6)
C(43)	1086(6)	3872(13)	7757(7)	4.1(5)	5.3(6)	4.6(5)	1.1(4)	3.4(5)	0.2(5)
C(44)	755(5)	3954(11)	6868(6)	3.4(4)	4.1(5)	3.7(4)	1.1(5)	2.8(4)	0.7(4)
C(45)	279(5)	2705(11)	6388(8)	3.5(5)	3.5(5)	5.6(6)	0.3(3)	3.5(5)	-0.2(4)
C(46)	818(5)	5189(11)	6450(7)	4.0(5)	2.4(4)	4.4(5)	0.1(4)	3.0(4)	-0.5(4)

the strong Cr–Cr bonds in the peripheral bichromium fragments $[(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2]$ (Q) (Cr–Cr = 2.688(3) and 2.661(3) Å), the lengths of the Cr–Cr bonds being practically equal and typical of any other Q-containing complex. As regards the Fe–Cr bonds, they are, as in cluster II, different in different triangles, and only in one of them is it close to the ordinary Fe–Cr bond length in $\text{QFe}(\text{CO})_3$ (2.749(2) Å). In the second FeCr_2 triangle, the Fe–Cr bonds are much weaker (2.910(2) and 2.969(2) Å). A probable reason for the general increase of the Fe–Cr bond length may be the presence of two extra electrons in the metal-core Cr_4Fe compared to the Cr_4Cr core of the metallocspirane $[(\text{C}_5\text{H}_5)_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2]_2\text{Cr}$ with ordinary two-electron $\text{Cr}_{\text{centr}}\text{--Cr}_{\text{periph}}$ bonds (2.933 and 2.889 Å). In III these two electrons probably populate the orbital which is antibonding with respect to the Cr–Fe bonds. Simultaneously, the Cr–Fe bond lengths in III are about 0.1 Å shorter than the Cr–Mn lengths in II, which would be expected in view of the different electronic configurations of the central ion (d^5 for Mn^{II} and d^6 for Fe^{II}).

Thus the geometry of the metallocspirane cluster is determined both by the electronic configuration of the central ion and the steric influence of the substituents in the cyclopentadienyl ligands.

Experimental

All operations were conducted in a stream of pure argon. The hydrocarbon solvents were purified by distillation over dispersed Na in an argon stream. CH_2Cl_2

TABLE 5
BOND LENGTHS FOR $[(\text{MeC}_5\text{H}_4)_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2]_2\text{Fe}$ (III)

Bond	d (Å)	Bond	d (Å)
Fe–Cr(1)	2.749(2)	Cr(2)–C(25)	2.28(2)
Fe–Cr(2)	2.827(2)	Cr(3)–Cr(4)	2.661(3)
Fe–Cr(3)	2.910(2)	Cr(3)–S(4)	2.286(3)
Fe–Cr(4)	2.969(2)	Cr(3)–S(5)	2.329(4)
Fe–S(1)	2.166(3)	Cr(3)–S(6)	2.331(4)
Fe–S(2)	2.242(3)	Cr(3)–C(31)	2.22(1)
Fe–S(4)	2.293(3)	Cr(3)–C(32)	2.24(2)
Fe–S(5)	2.368(4)	Cr(3)–C(33)	2.24(2)
Cr(1)–Cr(2)	2.688(3)	Cr(3)–C(34)	2.29(2)
Cr(1)–S(1)	2.285(3)	Cr(3)–C(35)	2.32(2)
Cr(1)–S(2)	2.311(5)	Cr(4)–S(4)	2.298(5)
Cr(1)–S(3)	2.384(3)	Cr(4)–S(5)	2.296(3)
Cr(1)–C(11)	2.25(2)	Cr(4)–S(6)	2.320(3)
Cr(1)–C(12)	2.23(2)	Cr(4)–C(41)	2.22(2)
Cr(1)–C(13)	2.20(1)	Cr(4)–C(42)	2.21(2)
Cr(1)–C(14)	2.29(1)	Cr(4)–C(43)	2.27(2)
Cr(1)–C(15)	2.23(1)	Cr(4)–C(44)	2.31(1)
Cr(2)–S(1)	2.302(5)	Cr(4)–C(45)	2.31(1)
Cr(2)–S(2)	2.287(3)	S(3)–C ₁ (31)	1.92(1)
Cr(2)–S(3)	2.387(5)	S(6)–C ₁ (61)	1.85(1)
Cr(2)–C(21)	2.24(1)	C–C(CMe ₃) _{av.}	1.52(2)
Cr(2)–C(22)	2.20(1)	C–C(C ₅ H ₄) _{av.}	1.41(2)
Cr(2)–C(23)	2.23(1)	C(C ₅ H ₄)–C(Me) _{av.}	1.54(2)
Cr(2)–C(24)	2.27(1)		

was distilled over P_2O_5 in a stream of argon. The starting complexes Ia [8] and Cp_2Mn and $[CpFe(CO)_2]_2$ [9] were obtained as described in the references.

IR spectra of the compounds investigated were recorded with a SPECORD-IR-75 spectrometer, in KBr tablets. The set of F_{exper} for the X-ray analyses of II and III was obtained with four-circle automatic diffractometers, SYNTEX P2₁ and HILGER & WATTS, respectively (Mo- K_{α} , λ 0.71049 nm, $\theta-2\theta$ scan, $\theta \leq 52^\circ$ (for II) and 60° (for III)). The structures were solved by the direct method using a modified MULTAN program and were refined in the full-matrix anisotropic approximation for all non-hydrogen atoms to $R = 0.066$, $R_w = 0.054$ for a total of 2576 independent reflections with $I \geq 2\sigma$ for II, and to $R = 0.048$ and $R_w = 0.045$ for 3630 independent reflections with $I \geq 2\sigma$ for III.

Crystals of II are monoclinic: space group Cc , a 25.540(10), b 9.208(3), c 21.595(9) Å, β 135.30(2)°, $Z = 4$. Crystals of III are also monoclinic: space group Cc , a 26.738(5), b 9.195(1), c 21.419(3) Å, β 135.976(2)°, V 3659.6 Å³, $Z = 4$.

$[(CH_3C_5H_4)_2Cr_2(\mu-SCMe_3)(\mu_3-S)_2]_2Mn$ (II)

To the violet-coloured solution of 1.70 g (3.6 mmol) of $(CH_3C_5H_4)_2Cr_2(\mu-SCMe_3)_2(\mu-S)$ (Ia) in 40 ml of toluene was added a slightly yellow solution of 0.33 g

TABLE 6

BOND ANGLES (°) FOR $[(MeC_5H_4)_2Cr_2(\mu-SCMe_3)(\mu_3-S)_2]_2Fe$ (III)

Angle	Angle	Angle	Angle	Angle	Angle
Cr(1)FeCr(2)	57.62(6)	FeCr(1)Cr(2)	62.65(7)	S(4)Cr(3)S(6)	96.2(1)
Cr(1)FeCr(3)	136.46(6)	FeCr(1)S(1)	49.93(10)	S(5)Cr(3)S(6)	83.4(1)
Cr(1)FeCr(4)	151.60(6)	FeCr(1)S(2)	51.72(9)	FeCr(4)Cr(3)	61.97(6)
Cr(1)FeS(1)	53.84(10)	FeCr(1)S(3)	117.50(11)	FeCr(4)S(4)	49.65(9)
Cr(1)FeS(2)	54.01(10)	Cr(2)Cr(1)S(1)	54.4(1)	FeCr(4)S(5)	51.54(9)
Cr(1)FeS(4)	111.69(9)	Cr(2)Cr(1)S(2)	53.8(1)	FeCr(4)S(6)	116.56(10)
Cr(1)FeS(5)	158.29(10)	Cr(2)Cr(1)S(3)	55.8(1)	Cr(3)Cr(4)S(4)	54.3(1)
Cr(2)FeCr(3)	148.93(6)	S(1)Cr(1)S(2)	88.9(1)	Cr(3)Cr(4)S(5)	55.5(1)
Cr(2)FeCr(4)	131.33(6)	S(1)Cr(1)S(3)	84.5(1)	Cr(3)Cr(4)S(6)	55.3(1)
Cr(2)FeS(1)	52.90(10)	S(2)Cr(1)S(3)	95.7(1)	S(4)Cr(4)S(5)	89.8(1)
Cr(2)FeS(2)	52.09(10)	FeCr(2)Cr(1)	59.73(6)	S(4)Cr(4)S(6)	96.2(1)
Cr(2)FeS(4)	160.47(9)	FeCr(2)S(1)	48.7(1)	S(5)Cr(4)S(6)	84.4(1)
Cr(2)FeS(5)	105.67(10)	FeCr(2)S(2)	50.7(1)	FeS(1)Cr(1)	76.2(1)
Cr(3)FeCr(4)	53.81(6)	FeCr(2)S(3)	114.5(1)	FeS(1)Cr(2)	78.5(1)
Cr(3)FeS(1)	108.49(10)	Cr(1)Cr(2)S(1)	53.8(1)	Cr(1)S(1)Cr(2)	71.8(1)
Cr(3)FeS(2)	156.92(10)	Cr(1)Cr(2)S(2)	54.64(1)	FeS(2)Cr(1)	74.3(1)
Cr(3)FeS(4)	50.44(9)	Cr(1)Cr(2)S(3)	55.7(1)	FeS(2)Cr(2)	77.3(1)
Cr(3)FeS(5)	51.12(9)	S(1)Cr(2)S(2)	89.0(1)	Cr(1)S(2)Cr(2)	71.6(1)
Cr(4)FeS(1)	154.48(10)	S(1)Cr(2)S(3)	84.0(1)	Cr(1)S(3)Cr(2)	68.6(1)
Cr(4)FeS(2)	106.94(10)	S(2)Cr(2)S(3)	96.3(1)	FeS(4)Cr(3)	78.9(1)
Cr(4)FeS(4)	49.78(9)	FeCr(3)Cr(4)	64.23(6)	FeS(4)Cr(4)	80.6(1)
Cr(4)FeS(5)	49.42(9)	FeCr(3)S(4)	50.66(9)	Cr(3)S(4)Cr(4)	71.0(1)
S(1)FeS(2)	93.7(1)	FeCr(3)S(5)	52.32(9)	FeS(5)Cr(3)	76.6(1)
S(1)FeS(4)	137.1(1)	FeCr(3)S(6)	118.4(1)	FeS(5)Cr(4)	79.1(1)
S(1)FeS(5)	105.7(1)	Cr(4)Cr(3)S(4)	54.73(1)	Cr(3)S(5)Cr(4)	70.2(1)
S(2)FeS(4)	108.5(1)	Cr(4)Cr(3)S(5)	54.3(1)	Cr(3)S(6)Cr(4)	69.8(1)
S(2)FeS(5)	129.4(1)	Cr(4)Cr(3)S(6)	54.9(1)		
S(4)FeS(5)	88.2(1)	S(4)Cr(3)S(5)	89.3(1)		

(1.8 mmol) of $(C_5H_5)_2Mn$ in 45 ml of THF. The resulting violet solution was concentrated to 40 ml and refluxed for 4 h until the solution acquired a stable dark-green colour. The solvent was then removed in vacuo and unreacted Ia was removed with heptane. The dry residue was recrystallized from heated toluene. The precipitated large, dark-green prisms were washed with pentane and dried in vacuo. Yield 0.5 g (31%). IR spectrum, ν , (cm^{-1}): 590 w, 799 s, 855 w, 920 w, 1012 m, 1060 w, 1145 s, 1348 m, 1380 w, 1435 m, 2890 b.w, 3060 w.

$[(CH_3C_5H_4)_2Cr_2(\mu-SCMe_3)(\mu_3-S)_2]_2Fe$ (III)

To the violet-coloured solution of 1.1 g (2.3 mmol) of $(CH_3C_5H_5)_2Cr_2(\mu-SCMe_3)_2(\mu-S)$ (Ia) in 30 ml of toluene was added a solution of 0.4 g (1.1 mmol) of $[CpFe(CO)_2]_2$ in 60 ml of toluene. The reaction mixture was boiled for 6 h until it acquired a stable dark-brown colour and the CO valence vibration bands disappeared in the IR spectrum of the solution. The resulting solution was chromatographed on an Al_2O_3 -packed column (5×15 cm) and the brown zone was eluted with benzene. The benzene solution was concentrated to 8–10 ml and was kept for 24 h. The precipitated small, blackish-brown crystals were washed with heptane and dried in vacuo. Crystals for the X-ray analysis were obtained by recrystallization from CH_2Cl_2 . Yield 0.4 g (41%). IR spectrum, ν (cm^{-1}): 795 s, 810 s, 850 w, 920 w, 1020 m, 1040 w, 1060 w, 1120 w, 1150 m, 1350 w, 1480 w, 2860–2940 b.w, 3060 w.

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