

Interaction of Heteronuclear Chromium-Containing Clusters with Carboxylic Acids. Molecular Structure of the Paramagnetic Tetrahedral Cluster $\text{Cp}_3\text{Cr}_3(\mu^3\text{-S})_4\text{Fe}(\text{OCCMe}_3)$

I. L. EREMENKO, A. A. PASYNSKII*, B. ORAZSAKHATOV, O. G. ELLERT, V. M. NOVOTORTSEV, V. T. KALINNIKOV, M. A. PORAI-KOSHITS, A. S. ANTSYSHKINA, L. M. DIKAREVA, V. N. OSTRIKOVA

The N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of the U.S.S.R., Moscow V-71, Leninskii Pr. 31, U.S.S.R.

YU. T. STRUCHKOV and R. G. GERR

The A. N. Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., Moscow V-312, Vavilova St. 28, U.S.S.R.

Received January 13, 1983

The reaction of $(\text{CpCrSCMe}_3)_2\text{S}$ and the adducts $(\text{CpCrSCMe}_3)_2\text{S}\cdot\text{ML}$ ($\text{ML} = \text{Cr}(\text{CO})_5$, $\text{Mn}_2(\text{CO})_9$) and cluster $(\text{CpCrS})_2(\text{SCMe}_3)\cdot\text{Fe}(\text{CO})_3$ (I) (containing CrCrFe metal chain) with benzoic acid gives the respective antiferromagnetic μ^3 -thio-bridged carboxylates $\text{Cr}_2\text{MS}(\text{OOCPh})_6$ ($\text{M} = \text{Cr}(\text{II})$, $\text{Mn}(\text{II})$, $\text{Fe}(\text{II})$) (II–IV). On the other hand the reaction of I with the weaker trimethylacetic acid yields the tetrahedral cluster $\text{Cp}_3\text{Cr}_3(\mu^3\text{-S})_4\text{Fe}(\text{OCCMe}_3)$ (V) containing two unpaired electrons ($\mu_{\text{eff}} = 2.81 \text{ BM}$). Crystal structure of V was solved by means of X-ray analysis (sp. gr. C2/c, $a = 28.905(2)$, $b = 9.563(2)$, $c = 23.789(2) \text{ \AA}$, $\beta = 131.84(3)^\circ$, $V = 4902.8(4) \text{ \AA}^3$, $Z = 4$). In the metal tetrahedral skeleton Cr_3Fe the average bond lengths Cr–Cr and Fe–Cr are 2.838(3) and 2.759(3) \AA respectively. The μ^3 -bridged sulfur atom locates over each tetrahedron face (the average Cr–S and Fe–S distances are 2.258(4) and 2.218(4) \AA respectively). Each chromium atom is combined to $\eta^5\text{-C}_5\text{H}_5$ ligand (the average Cr–C and C–C distances are 2.224(20) and 1.391(30) \AA). The iron atom is bound to a terminal trimethylacetate group (Fe–O 1.896(10), O(1)–C(1) 1.318(13), O(2)–C(1) 1.252(21) \AA).

Introduction

In view of the study of exchange interactions in metal clusters, of specific interest are the antiferromagnetic heteronuclear complexes providing the broad variation of ion spins. Among them the μ^3 -oxocomplexes of mixed carboxylates containing the chromium and iron atoms [1] and other metals are

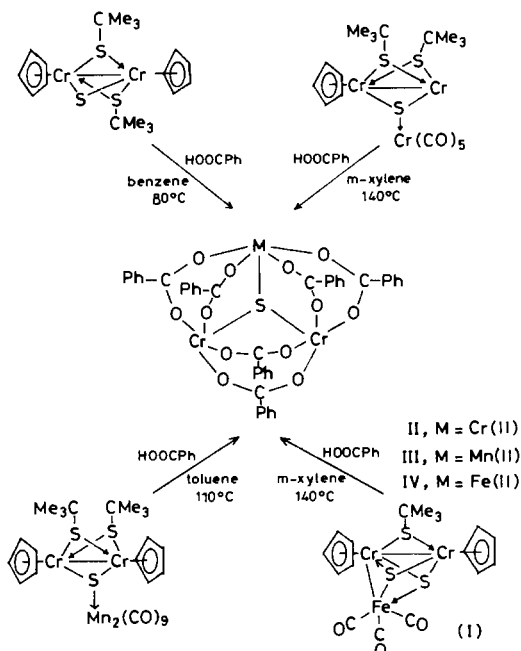
known [2, 3]. These complexes have been prepared by reactions of the mixtures of metal salts (nitrates or halides) with carboxylic acid salts. The complex composition variation was attained by changing the ratio of metal ions. Principally such methods may produce mixtures of homo- and heteronuclear complexes. Thus we made an attempt of producing analogous systems from the preliminary synthesized and reliably identified heteronuclear complexes, including the metal–metal bonds. The present paper is concerned with reactions of the complexes $(\text{CpCrSCMe}_3)_2\text{S}\cdot\text{Mn}_2(\text{CO})_9$ [4] and $(\text{CpCrS})_2(\text{SCMe}_3)\cdot\text{Fe}(\text{CO})_3$ [5] with carboxylic acids. A possibility of preparing μ^3 -thio-carboxylate complexes instead of μ^3 -oxo-carboxylates was of specific interest. Thus we also studied the reaction of homonuclear chromium complexes, $(\text{CpCrSCMe}_3)_2\text{S}$ [6] and $(\text{CpCrSCMe}_3)_2\text{S}\cdot\text{Cr}(\text{CO})_5$ [7] with benzoic acid.

Results and Discussion

The study of reactions of $(\text{CpCrSCMe}_3)_2\text{S}$ and $(\text{CpCrSCMe}_3)_2\text{S}\cdot\text{Cr}(\text{CO})_5$ with HOOCPh in refluxing aromatic solvents demonstrated that both cases produce the same μ^3 -thio-carboxylate complex $\text{Cr}_3\text{S}(\text{OOCPh})_6$ (II) (Scheme 1).

Complex II, isolated in the form of black-green needle-like crystals, shows the bands of stretching modes of only bridged groups OCO in its IR spectrum ($\nu_{\text{asym}}^{\text{OCO}} = 1632$, $\nu_{\text{sym}}^{\text{OCO}} = 1425$, $\Delta\nu = 207 \text{ cm}^{-1}$). Moreover, its relatively good solubility in nonpolar solvents (e.g. benzene) may be a manifestation of a neutral complex structure unlike the known ionic systems $[\text{Cr}_3\text{O}(\text{OOCR})_6]^+$ [3]. II is antiferromagnetic, its μ_{eff} decreases from 2.60 to 1.92 BM at 298–80 K.

*Author to whom correspondence should be addressed.



Scheme 1: Formation of μ^3 -thio-carboxylate $\text{Cr}_2\text{M}(\text{S})(\text{OOCPh})_6$ complexes.

Similar complexes, $\text{Cr}_2\text{MnS}(\text{OOCPh})_6$ (III) and $\text{Cr}_2\text{FeS}(\text{OOCPh})_6$ (IV) are produced in reactions of the heteronuclear $(\text{CpCrSCMe}_3)_2\text{S}\cdot\text{Mn}_2(\text{CO})_9$ and $(\text{CpCrS})_2(\text{SCMe}_3)\cdot\text{Fe}(\text{CO})_3$ complexes respectively with HOOCPh upon refluxing in toluene or *m*-xylene (Scheme 1). The IR spectra of the green plate crystals of III and the dark-green crystals of IV are generally similar to the IR spectrum of II, and show the stretching modes of only bridged carboxylate groups (III: $\nu_{\text{OCO}}^{\text{sym}} = 1635$, $\nu_{\text{OCO}}^{\text{asym}} = 1430$, $\Delta\nu = 205 \text{ cm}^{-1}$; IV: $\nu_{\text{OCO}}^{\text{sym}} = 1630$, $\nu_{\text{OCO}}^{\text{asym}} = 1425$, $\Delta\nu = 205 \text{ cm}^{-1}$) and phenyl rings (III, 725, 1035, 3080 cm^{-1} ; IV, 723, 1030, 3080 cm^{-1}). The compounds III and IV are antiferromagnetic with effective magnetic moment decreasing from 3.63 and 3.71 BM to 2.97 and 3.43 BM of temperatures from 290 to 112 K and 298 to 119 K respectively, analogous to the homonuclear μ^3 -thio-carboxylate complex II.

TABLE I. Magnetic Properties of $\text{Cr}_2\text{MS}(\text{OOCPh})_6$ Complexes.

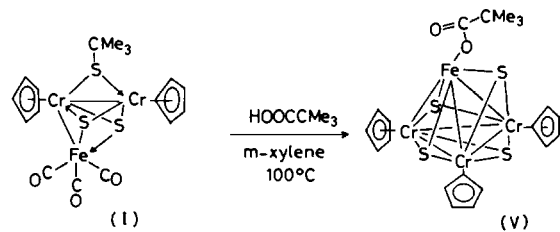
No.	Compound	T (K)	μ_{eff} BM			$-J_{\text{Cr(III)-Cr(III)}}$ cm^{-1}	$-J_{\text{Cr(III)-M(II)}}$ cm^{-1}	Mean sq. err. %	Monom. impur. %
II	$\text{Cr}_3\text{S}(\text{OOCPh})_6$	298	192	80	43	18	2.5	0	
			2.60	2.45	1.92				
III	$\text{MnCr}_2\text{S}(\text{OOCPh})_6$	290	170	112	30	14	2.3	0	
			3.63	3.25	2.97				
IV	$\text{FeCr}_2\text{S}(\text{OOCPh})_6$	298	191	119	27	3	3.5	0	
			3.71	3.52	3.43				

The parameters of the best agreement between theoretical and experimental magnetic susceptibilities for II–IV (Table I) were obtained in terms of isotropic HDVV model [8] which for C_{2v} symmetry of the complexes, and taking account for the outer magnetic field, has the form:

$$H = -2J_1\hat{S}_2\hat{S}_3 - 2J_2(\hat{S}_3\hat{S}_1 + \hat{S}_1\hat{S}_2) + \beta H(G_1\hat{S}_1 + G_2(\hat{S}_2 + \hat{S}_3))$$

An increase of the exchange parameter $-J_{\text{Cr-Cr}}$ in II–IV with respect to $-J_{\text{Cr-Cr}}$ in $[\text{Cr}_3\text{O}(\text{OOCR})_6]^+$ ($-J_{\text{Cr-Cr}} = 10\text{--}15 \text{ cm}^{-1}$) [3] may be explained by enhanced electron-releasing properties of the tridentate sulfur atom with respect to the oxygen atom, as well as by the changed Cr_2MS main fragment geometry owing to an S atom removed out of the Cr_2M plane. These two factors ensure the most efficient exchange for II–IV via an overlap of d_{xz} Cr(III) orbitals and the central sulfur atom π -orbitals (a similar analysis of the molecular orbital overlap has been performed for analogous μ^3 -oxo-carboxylates [9]).

Investigating the reactions of chromium-containing clusters with carboxylic acids, we carried out the reaction of I with weaker trimethylacetic acid by heating the reagents at 100 °C in *m*-xylene. This reaction led to the heteronuclear cluster $\text{Cp}_3\text{Cr}_3(\mu^3\text{-S})_4\text{Fe}(\text{OOCMe}_3)$ (V):



The IR spectrum of V, isolated in the form of black prisms, shows the bands of stretching modes of C_5H_5 rings (820, 1020, 1435 and 3120 cm^{-1}) and weak bands of OCO stretching modes ($\nu_{\text{OCO}}^{\text{asym}} = 1635$, $\nu_{\text{OCO}}^{\text{sym}} = 1320$, $\Delta\nu = 315 \text{ cm}^{-1}$). The structure of I was

TABLE II. Atomic Coordinates (for Fe and Cr $\times 10^5$, for O, S, C and H* $\times 10^4$) in the structure of $Cp_3Cr_3(\mu^3-S)_4Fe(O_2CCMe_3)$.

Atom	X	Y	Z	Atom	X	Y	Z
Fe	36247(9)	-18087(20)	35439(9)	C(32)	3203(9)	-3338(19)	1242(11)
Cr(1)	37374(9)	2782(20)	28354(10)	C(42)	3133(13)	-4385(30)	1575(10)
Cr(2)	45766(10)	-20070(22)	35677(11)	C(52)	2626(15)	-4086(30)	1507(13)
Cr(3)	33309(10)	-24234(21)	21919(10)	C(13)	5460(7)	-1839(26)	3802(10)
S(1)	4402(1)	-314(3)	4062(1)	C(23)	5588(7)	-1439(19)	4449(12)
S(2)	2865(1)	-866(3)	2402(2)	C(33)	5466(7)	-2601(31)	4702(9)
S(3)	3895(2)	-3688(3)	3274(2)	C(43)	5292(7)	-3712(18)	4226(13)
S(4)	4082(2)	-1094(3)	2417(2)	C(53)	5273(7)	-3233(26)	3645(9)
O(1)	3406(4)	-2109(9)	4129(4)	H(11)	3210	1617	1432
O(2)	4349(5)	-2750(11)	5110(5)	H(12)	4461	2006	2636
C(1)	3809(7)	-2507(14)	4840(8)	H(13)	4567	2634	3806
C(2)	3587(7)	-2720(13)	5249(6)	H(14)	3464	2636	3383
C(3)	3263(6)	-4179(14)	4988(7)	H(15)	2616	2111	1897
C(4)	4186(6)	-2763(16)	6119(6)	H(21)	1986	-2372	966
C(5)	3158(6)	-1521(15)	5067(6)	H(22)	2607	-1456	618
C(11)	3427(8)	1899(14)	1993(7)	H(23)	3560	-3244	1220
C(21)	4091(6)	2095(18)	2634(9)	H(24)	3422	-5291	1844
C(31)	4140(7)	2423(12)	3246(7)	H(25)	2462	-4790	1723
C(41)	3558(7)	2437(12)	3025(7)	H(31)	5498	-1180	3470
C(51)	3109(6)	2142(13)	2239(8)	H(32)	5751	-434	4714
C(12)	2384(11)	-2883(33)	1115(13)	H(33)	5503	-2616	5180
C(22)	2708(15)	-2416(19)	938(8)	H(34)	5189	-4749	4284
				H(35)	5142	-3831	3177

*Hydrogen atoms were located in the difference Fourier map but were not refined.

established by means of its complete X-ray analysis. The crystals of complex are monoclinic (spatial group $C 2/c$) with unit cell parameters: $a = 28.905(2)$, $b = 9.563(2)$, $c = 23.789(2)$ Å, $\beta = 131.84(3)^\circ$, $V = 4902.8(4)$ Å³, $Z = 4$. The structure was solved by direct method using the MULTAN program. All non-hydrogen atoms were refined in a full-matrix anisotropic approximation. The cyclopentadienyl hydrogen atoms were localized by difference Fourier synthesis without refinement of their coordinates and temperature factors (Table II). The final values of R_1 and R_2 are 0.055 and 0.059 respectively for 1624 reflections $F^2 \geq 2\sigma$. The molecule of II has a metal tetrahedron skeleton Cr_3Fe ($Cr-Cr_{aver}$ 2.838(3), $Fe-Cr_{aver}$ 2.759(3) Å) slightly flattened along the axis of Cr_3 triangle center and Fe atom. The tridentate sulfur atom locates over each face of the tetrahedron ($Cr-S$ 2.258(4), $Fe-S$ 2.218(4) Å). The main geometry of the Cr_3FeS_4 cuban-like system is close to that of Cr_3CoS_4 skeleton in $Cp_3Cr_3(\mu^3-S)_4Co(CO)$ (VI) complex ($Cr-Cr$ 2.818(4), $Cr-S$ 2.244(6), $Co-Cr$ 2.658(4), $Co-S$ 2.163(6) Å [10]. Analogous to the Co atom in IV the Fe atom in cluster V has one monodentate ligand, and three Fe-Cr bonds and three Fe-S bonds. In this case however it is O_2CCMe_3 carboxylate group ($Fe-O$ 1.869(10), $O(1)-C(1)$ 1.318(13), $O(2)-C(1)$ 1.252(21) Å). Thus the Fe atom now has a 16-electron (instead of 18) shell, and unlike the diamagnetic cluster VI the molecule V is paramagnetic. Its effective magnetic

moment is 2.81 BM and it is temperature independent at 298–77 K, which corresponds to the presence of two unpaired electrons per Cr_3Fe skeleton.

Experimental

All operations were carried out under pure argon atmosphere in dried solvents. The compounds $(Cp_2Cr_2(SCMe_3)_2)_2S$, $(CpCrSCMe_3)_2S \cdot ML$ and I were synthesized by literature methods [4–7]. Trimethylacetic acid was purified by fractional distillation under argon. Benzoic acid was purified by subliming under vacuum. The IR spectra were taken on a UR-20 instrument in KBr pellets. The magnetic measurements were carried out (using Faraday's method) at the Inst. Gen. Inorg. Chem. Acad. Sci. USSR [11]. Experimental data for investigating the structure of crystals were obtained on an autodiffractometer Syntex P2₁ ($\lambda Mo-K_\alpha$). 2402 non-zero independent reflections were measured by $\theta-2\theta$ scan for $2^\circ \leq 2\theta \leq 52^\circ$ of which 1624 reflections $\geq 2\sigma$ were used in the refinement.

$Cr_3S(OOCPh)_6$ (II)

A solution of 0.7 g of $Cp_2Cr_2(SCMe_3)_2S$ in 25 ml of benzene was mixed with a solution of 0.4 g of $HOOCPh$ in 10 ml of benzene. The obtained violet solution was refluxed for 6 hours until appearance of

TABLE III. Bond Lengths in the Structure of $Cp_3Cr_3(\mu^3-S)_4Fe(OOCCMe_3)$.

Bond	d(Å)	Bond	d(Å)	Bond	d(Å)
Fe–Cr(1)	2.768(3)	Cr(2)–S(4)	2.253(4)	Cr(3)–C(23)	2.230(13)
Fe–Cr(2)	2.721(4)	Cr(3)–S(2)	2.277(5)	Cr(3)–C(33)	2.212(22)
Fe–Cr(3)	2.787(3)	Cr(3)–S(3)	2.270(4)	Cr(3)–C(43)	2.210(19)
Cr(1)–Cr(2)	2.838(3)	Cr(3)–S(4)	2.251(5)	Cr(3)–C(53)	2.215(29)
Cr(1)–Cr(3)	2.828(3)	Cr(1)–C(11)	2.197(12)	O(1)–C(1)	1.318(13)
Cr(2)–Cr(3)	2.848(3)	Cr(1)–C(21)	2.224(15)	O(2)–C(1)	1.252(21)
Fe–S(1)	2.217(4)	Cr(1)–C(31)	2.236(13)	C(1)–C(2)	1.492(17)
Fe–S(2)	2.249(3)	Cr(1)–C(41)	2.246(13)	C(2)–C(3)	1.561(19)
Fe–S(3)	2.219(4)	Cr(1)–C(51)	2.247(14)	C(2)–C(4)	1.532(15)
Cr(1)–S(1)	2.247(3)	Cr(2)–C(12)	2.227(24)	C(2)–C(5)	1.525(21)
Cr(1)–S(2)	2.249(5)	Cr(2)–C(22)	2.250(29)	C(11)–C(21)	1.463(22)
Cr(1)–S(4)	2.242(5)	Cr(2)–C(32)	2.227(17)	C(21)–C(31)	1.400(22)
Cr(2)–S(1)	2.247(4)	Cr(2)–C(42)	2.251(21)	C(31)–C(41)	1.388(28)
Cr(2)–S(3)	2.262(5)	Cr(2)–C(52)	2.230(23)	C(41)–C(51)	1.423(17)
Fe–O(1)	1.896(10)	Cr(3)–C(13)	2.212(23)	C(51)–C(11)	1.399(27)

TABLE IV. Bond Angles in the Structure of $Cp_3Cr_3(\mu^3-S)_4Fe(OOCCMe_3)$.

Angle	ω (°)	Angle	ω (°)	Angle	ω (°)
Cr(1)FeCr(2)	62.28(8)	Cr(2)Cr(1)S(1)	50.82(11)	S(1)FeS(3)	103.11(14)
Cr(1)FeCr(3)	61.21(8)	Cr(2)Cr(1)S(2)	98.26(12)	S(2)FeS(3)	102.97(13)
Cr(2)FeCr(3)	62.38(9)	Cr(2)Cr(1)S(4)	51.01(11)	FeS(1)Cr(1)	76.63(13)
FeCr(1)Cr(2)	58.05(7)	Cr(3)Cr(1)S(1)	99.16(12)	FeS(1)Cr(2)	75.15(13)
FeCr(1)Cr(3)	59.72(7)	Cr(3)Cr(1)S(2)	51.64(11)	Cr(1)S(1)Cr(2)	78.34(13)
FeCr(2)Cr(1)	59.68(7)	Cr(3)Cr(1)S(4)	51.13(11)	FeCr(1)S(2)	75.53(13)
FeCr(2)Cr(3)	60.00(8)	Cr(1)Cr(2)S(1)	50.83(11)	FeS(2)Cr(3)	76.00(13)
Cr(1)Cr(2)Cr(3)	59.65(8)	Cr(1)Cr(2)S(3)	98.41(13)	Cr(1)S(2)Cr(3)	76.94(14)
Cr(2)Cr(1)Cr(3)	60.35(8)	Cr(1)Cr(2)S(4)	50.66(11)	FeS(3)Cr(2)	74.84(14)
FeCr(3)Cr(1)	59.06(7)	FeCr(2)S(1)	51.96(11)	FeS(3)Cr(3)	76.74(19)
FeCr(3)Cr(2)	57.72(8)	FeCr(2)S(3)	51.90(11)	Cr(2)S(3)Cr(3)	77.85(19)
Cr(1)Cr(3)Cr(2)	60.00(8)	FeCr(2)S(4)	97.72(13)	Cr(1)S(4)Cr(2)	78.30(14)
Cr(1)FeS(1)	52.17(11)	Cr(3)Cr(2)S(1)	98.58(13)	Cr(1)S(4)Cr(3)	78.00(14)
Cr(1)FeS(2)	52.58(11)	Cr(3)Cr(2)S(3)	51.17(12)	Cr(2)S(4)Cr(3)	78.44(15)
Cr(1)FeS(3)	101.58(13)	Cr(3)Cr(2)S(4)	50.74(12)	S(1)Cr(1)S(2)	101.39(15)
Cr(2)FeS(1)	52.94(11)	Cr(1)Cr(3)S(2)	51.43(11)	S(1)Cr(1)S(4)	100.37(15)
Cr(2)FeS(2)	108.28(12)	Cr(1)Cr(3)S(3)	98.51(11)	S(2)Cr(1)S(4)	101.79(15)
Cr(2)FeS(3)	53.34(12)	Cr(1)Cr(3)S(4)	50.84(11)	S(1)Cr(2)S(3)	102.65(16)
Cr(3)FeS(1)	101.14(12)	FeCr(3)S(2)	51.54(12)	S(1)Cr(2)S(4)	100.11(16)
Cr(3)FeS(2)	52.44(11)	FeCr(3)S(3)	50.81(12)	S(3)Cr(2)S(4)	100.70(16)
Cr(3)FeS(3)	52.44(12)	FeCr(3)S(4)	95.91(12)	S(3)Cr(3)S(2)	100.52(16)
FeCr(1)S(1)	50.82(11)	Cr(2)Cr(3)S(2)	97.82(13)	S(2)Cr(3)S(4)	101.34(16)
FeCr(1)S(2)	98.26(12)	Cr(2)Cr(3)S(4)	50.79(14)	S(3)Cr(3)S(4)	100.46(16)
FeCr(1)S(4)	96.65(13)	S(1)FeS(2)	102.97(15)		

a green colour; it was then filtered, concentrated to 15 ml, and cooled to 10 °C. The precipitated black-green crystals were washed with benzene/heptane mixture (1/2) and dried under vacuum. Yield 0.46 g. Found (calculated) %: C 56.07 (55.14), H 3.19 (3.28), S 3.28 (3.50).

A solution of 0.25 g of HOOCPh in 4 ml of m-xylene was added to a brown solution of 0.2 g of $Cp_2Cr_2(SCMe_3)_2S \cdot Cr(CO)_5$ in 7 ml of m-xylene. The

obtained solution was refluxed until appearance of stable green colour. After cooling the solution to room temperature the precipitated black-green crystals were washed with a benzene–heptane (1/2) mixture and dried under vacuum. Yield 0.2 g. Found (calculated) %: C 54.59 (55.14), H 4.06 (3.28), S 4.00 (3.50). IR spectrum, ν cm⁻¹: 512 w, 530 w, 690 w, 725 m, 805 w, 1028 w, 1078 m, 1180 w, 1425 vs, 1495 m, 1550 m, 1550 m, 1578 m, 1632 vs, 3065 w.

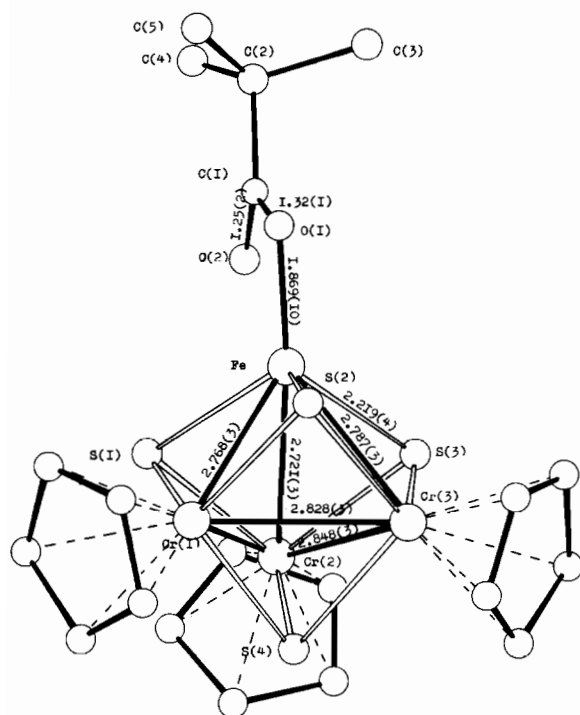


Fig. 1. Representation of the structure.

 $\text{MnCr}_2\text{S}(\text{OOCPh})_6$ (III)

A solution of 0.27 g of HOOCPh in 4 ml of toluene was added to a brown solution of 0.2 g of $\text{Cp}_2\text{Cr}_2(\text{SCMe}_3)_2\text{S}\cdot\text{Mn}_2(\text{CO})_9$ in 8 ml of toluene. The obtained solution was refluxed for 2 hours and allowed to stand overnight at room temperature. The green, plate crystals which precipitated were separated from the solution, washed with toluene and heptane, and dried under vacuum. Yield 0.23 g. Found (calculated) %: C 54.76 (54.96), H 3.28 (3.27). IR spectrum, ν cm^{-1} : 570 m, 690 m, 725 s, 1035 w, 1080 w, 1182 w, 1430 vs, 1560 w, 1580 m, 1635 vs, 3080 w.

 $\text{FeCr}_2\text{S}(\text{OOCPh})_6$ (VI)

A solution of 0.42 g of HOOCPh in 4 ml of m-xylene was added to a brown-cherry solution of 0.3 g of $\text{Cp}_2\text{Cr}_2(\text{SCMe}_3)_2\text{S}\cdot\text{Fe}(\text{CO})_3$ in 5 ml of m-xylene. The obtained solution was refluxed for 0.5 hr. The dark-green crystals which precipitated after cooling the solution to room temperature were separated, washed with xylene, and dried under vacuum. Yield

0.32 g. Found (calculated) %: C 55.40 (54.90), H 3.40 (3.26), S 3.70 (3.48). IR spectrum, ν cm^{-1} : 513 m, 610 w, 688 m, 723 s, 820 w, 1030 m, 1075 m, 1180 m, 1425 vs, 1500 w, 1630 s, 3080 w.

 $\text{Cp}_3\text{Cr}_3(\mu^3\text{-S})_4\text{Fe}(\text{OCCMe}_3)$ (V)

A brown-cherry solution of 0.20 g of $\text{Cp}_2\text{Cr}_2(\text{SCMe}_3)_2\text{S}\cdot\text{Fe}(\text{CO})_3$ and 0.5 ml of Me_3CCOOH in 10 ml of m-xylene was heated under argon with reflux condenser at 100 °C for 1 hour. After cooling the reaction mixture a black crystalline solid precipitated. The mixture was concentrated to half-volume, the precipitate separated by decanting, washed with pentane, and dried under vacuum. Yield 0.08 g. The analytically pure product was obtained by dissolving the precipitated black crystals in THF, passing the resultant solution over alumina layer and crystallizing after addition of pentane. IR spectrum, ν cm^{-1} : 630 w, 820 s, 1020 m, 1080–1130 m, br, 1210 m, 1320 m, 1370 w, 1435 m, 1490 w, 1560 m, 1635 s, br, 2980 w, br, 3120 w, br.

References

- 1 A. B. Blake and A. Yavari, *J. Chem. Soc. Chem. Commun.*, 1247 (1982).
- 2 S. Uemura, A. Spencer and G. Wilkinson, *J. Chem. Soc. Dalton Trans.*, 2565 (1973).
- 3 A. Earnshaw, B. N. Figgis and J. Lewis, *J. Chem. Soc., A*, 1656 (1966).
- 4 A. A. Pasynskii, I. L. Eremenko, B. Orazsakhmatov, Yu. V. Rakitin, V. M. Novotortsev, O. G. Ellert, V. T. Kalinnikov, G. G. Aleksandrov and Yu. T. Struchkov, *J. Organometal. Chem.*, 214, 351 (1981).
- 5 A. A. Pasynskii, I. L. Eremenko, B. Orazsakhmatov, Yu. V. Rakitin, V. M. Novotortsev, O. G. Ellert, G. G. Aleksandrov and Yu. T. Struchkov, *J. Organometal. Chem.*, 210, 385 (1981).
- 6 A. A. Pasynskii, I. L. Eremenko, Yu. V. Rakitin, V. M. Novotortsev, V. T. Kalinnikov, G. G. Aleksandrov and Yu. T. Struchkov, *J. Organometal. Chem.*, 165, 57 (1979).
- 7 A. A. Pasynskii, I. L. Eremenko, B. Orazsakhmatov, Yu. V. Rakitin, V. M. Novotortsev, O. G. Ellert, V. T. Kalinnikov, G. G. Aleksandrov and Yu. T. Struchkov, *J. Organometal. Chem.*, 210, 377 (1981).
- 8 J. H. Van Vleck, 'The Theory of Electric and Magnetic Susceptibilities', Oxford Univ. Press, London, 1932.
- 9 Yu. V. Rakitin, V. V. Volkov, T. A. Zhemtchuzhnikova, V. V. Zelentsov, Sh. H. Yablokov, *Koordinatsionnaya Khimiya*, 8, 977 (1982).
- 10 A. A. Pasynskii, I. L. Eremenko, B. Orazsakhmatov, V. T. Kalinnikov, G. G. Aleksandrov and Yu. T. Struchkov, *J. Organometal. Chem.*, 214, 367 (1981).
- 11 V. M. Novotortsev, *Ph.D. Thesis*, Moscow, 1974.