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## Antiferromagnetic complexes with metal–metal bonds

### XXIII \*. Synthesis, magnetic properties and structure of the heterometallospirane cluster $[\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2]_2\text{Fe}^+\text{FeI}_4^-$ and the cluster $[\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2\text{Fe}]_2(\mu\text{-Se})_2$ with “kayak-paddle” framework

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#### Abstract

Oxidative decarbonylation of the triangular cluster  $\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2\text{Fe}(\text{CO})_3$  (I) in THF has been studied. Under the action of iodine cationic antiferromagnetic heterometallospirane  $\{[(\text{Cp}_2\text{Cr}_2\text{SCMe}_3)(\mu_3\text{-S})_2]_2\text{Fe}\}^+\text{FeI}_4^-$  (II) cluster is formed, presumably as a result of disproportionation of an intermediate  $(\text{Cp}_2\text{Cr}_2\text{SCMe}_3)(\mu_3\text{-S})_2\text{FeI}_2$ . According to the X-ray structural data the core of the cationic cluster contains ordinary Cr–Cr (2.631(3) Å) and Cr–Fe (mean 2.765(3) Å) bonds with the angle between the planes  $\text{Cr}_2\text{Fe}$  92°. Prolonged treatment of I in THF with a 20-fold excess of selenium powder yields the antiferromagnetic cluster  $\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2\text{Fe}(\mu\text{-Se})_2\text{Fe}(\mu_3\text{-S})_2(\mu\text{-SCMe}_3)\text{Cr}_2\text{Cp}_2$  (III) ( $\mu_{\text{eff}} = 2.72 \mu_{\text{B}}(292 \text{ K}) - 1.56 \mu_{\text{B}}(77 \text{ K})$ ). X-Ray structural analysis of the green–brown crystals  $\text{III} \cdot 2\text{CH}_2\text{Cl}_2$  ( $P2_1/c$ ,  $a = 7.9841(8)$ ,  $b = 13.9903(8)$ ,  $c = 19.7926(12)$  Å,  $\beta = 99.072(5)^\circ$ ,  $V = 2183.2 \text{ \AA}^3$ ,  $Z = 2$ ,  $R = 0.071$ ) shows that the framework of the molecule is the planar fragment  $\text{Cr}_2\text{Fe}(\mu\text{-Se})_2\text{FeCr}_2$  in which two  $\text{Cr}_2\text{Fe}$  triangles (Cr–Cr 2.679(4), Cr–Fe 2.817(3) and 2.862(3) Å) are connected by two selenium bridges (Fe–Se 2.306(3) and 2.320(3) Å). The structure has a bonding Fe–Fe distance of 2.838(3) Å, and each Fe atom has a distorted tetrahedral configuration with two sulfur and two selenium atoms in its coordination sphere (SFeS 92.1(2)°, SFeSe 112.9(1), 116.3(1)°, SeFeSe 104.3(1)°).

#### Introduction

We have previously synthesised heterometalloclusters by applying metal complexes as ligands to other metal atoms. Specifically, we have made heterometal-

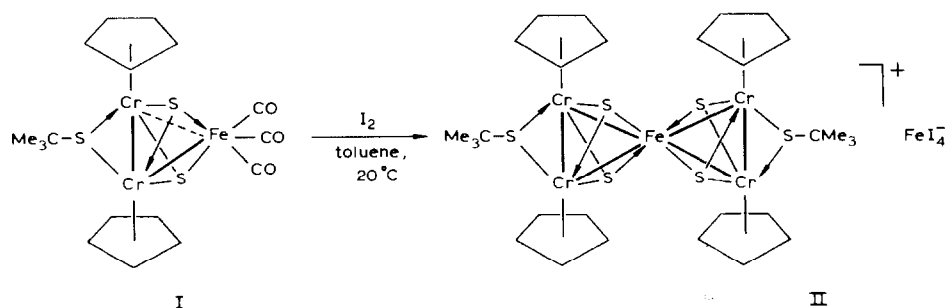
\* For Part XXII see *J. Organomet. Chem.*, 385 (1990) 277.

lospirane clusters with  $\text{Cr}_2\text{MCr}_2$  ( $\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ ) [1] and  $\text{Cr}_2\text{MFe}_2$  ( $\text{M} = \text{Fe}, \text{Co}, \text{Rh}$ ) [2] frameworks. In these case the carbonyl metal complexes underwent oxidative decarbonylation under the action of binuclear complexes  $\text{Cp}_2\text{Cr}_2(\text{SCMe}_3)_2\text{S}$  or  $\text{Fe}_2\text{S}_2(\text{CO})_6$ . The latter effects the rupture of the S–S bond, which is analogous to what happens with halogens. The central iron(III) ion in the  $\text{Cp}_2\text{Cr}_2\text{SCMe}_3\text{S}_2\text{FeS}_2\text{Fe}_2(\text{CO})_6$  spirane cluster is in the high-spin state and has a tetrahedral ligand surrounding which is characteristic of iron(III) ions in the ferredoxin  $2\text{Fe}_2\text{S}$  models,  $\text{X}_2\text{Fe}(\mu\text{-S})_2\text{FeX}_2^{2-}$  ( $\text{X} = \text{SR}$  or halogen) [3].

We decided it would be interesting to observe oxidative decarbonylation of the  $(\text{Cp}_2\text{Cr}_2\text{SCMe}_3)(\mu\text{-S})_2\text{Fe}(\text{CO})_3$  (I) cluster under the action of halogens or chalcogens, e.g. molecular iodine or selenium.

## Results and discussion

Reaction of I with iodine in toluene takes place almost instantly to give the ionic complex  $\{[\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2]_2\text{Fe}\}^+\text{FeI}_4^-$  (II) as dark-green antiferromagnetic crystals ( $\mu_{\text{eff}} = 5.28 \mu_{\text{B}}$  (298 K) –  $5.17 \mu_{\text{B}}$  (77 K)). II is presumably formed as a result of disproportionation of the intermediate  $(\text{Cp}_2\text{Cr}_2\text{SCMe}_3)(\mu_3\text{-S})_2\text{FeI}_2$ :



According to the X-ray structural data (Fig. 1, Tables 1–3)  $\text{Cr}_2\text{FeCr}_2$  metallospirane is the framework of the cluster cation, in which the planes of  $\text{Cr}_2\text{Fe}$  triangles are at an angle of  $92^\circ$ .

The geometry of binuclear fragments  $\text{Cp}_2\text{Cr}_2\text{SCMe}_3(\mu_3\text{-S})_2$  ( $\text{Cr}\text{--}\text{Cr}$  2.631(3) Å) in II differs only slightly from I [1]. However, formation of four strong, practically equivalent  $\text{Fe}\text{--}\text{Cr}$  bonds ( $2 \times 2.768(3)$  Å and  $2 \times 2.763(3)$  Å) is observed while in I (which has an extra electron on the antibonding orbital of the  $\text{Fe}\text{--}\text{Cr}$  bond) the

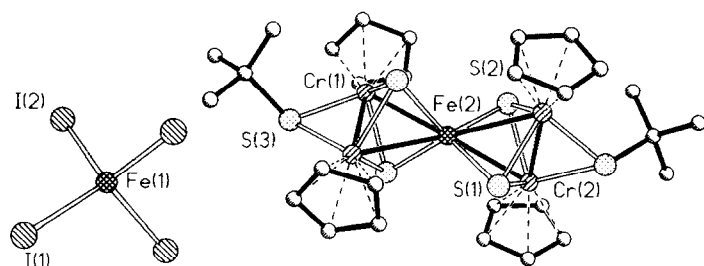


Fig. 1. The molecular structure of  $\{[\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2]_2\text{Fe}\}^+\text{FeI}_4^-$  (II).

Table 1

Atomic coordinates ( $\times 10^4$ ) (for  $I \times 10^5$ ) for the cluster  $\{[\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2]_2\text{Fe}\}^+ \text{FeI}_4^-$  (II)

Atom	x	y	z
I(1)	-8624(7)	16932(6)	29012(10)
I(2)	-11044(12)	32169(9)	7946(15)
Fe(1)	0	2479(2)	$\frac{1}{4}$
Fe(2)	$\frac{1}{2}$	3851(1)	$\frac{1}{4}$
Cr(1)	3372(1)	4334(1)	665(2)
Cr(2)	6568(1)	3373(1)	3011(2)
S(1)	6051(2)	3221(2)	4056(3)
S(2)	5975(2)	4484(2)	2439(3)
S(3)	2137(2)	3757(2)	283(3)
C(1)	1324(9)	4303(8)	335(12)
C(2)	612(10)	4535(10)	-889(13)
C(3)	1777(10)	4941(9)	1131(13)
C(4)	929(12)	3813(10)	751(17)
C(11)	2517(10)	4988(10)	-906(14)
C(12)	3069(13)	5445(8)	25(16)
C(13)	3965(11)	5287(8)	479(12)
C(14)	3923(11)	4743(8)	-210(13)
C(15)	3053(11)	4550(8)	-1037(12)
C(21)	7358(12)	2626(11)	2783(16)
C(22)	6744(15)	2252(8)	2805(14)
C(23)	5877(12)	2448(10)	1851(16)
C(24)	5970(15)	2973(11)	1263(14)
C(25)	6880(17)	3084(10)	1829(19)

Fe–Cr distances are 2.707 and 3.11 Å [4]. The shortening of the Fe–Cr bond in II is probably due to the low spin state of the central iron(III) ion ( $S = 1/2$ ), while in the analogous neutral metallocporphyrin cluster the presence of the isoelectronic manganese(II) ion in its high-spin state ( $S = 5/2$ ) leads to drastic loosening of the Cr–Mn bonds ( $2 \times 2.947(3)$  Å and  $2 \times 2.936(3)$  Å) [1].

It is noteworthy that II is the first reported example of a cationic heterometallosporphyrin cluster. At the same time the ease of formation of the II, stable in the oxidative state corresponds to the analogy between the heterometallosporphyrin clusters  $[\text{Cp}_2\text{Cr}_2\text{SCMe}_3(\mu_3\text{-S})_2]_2\text{M}$  ( $\text{Q}_2\text{M}$ ) and the sandwich complexes  $\text{Cp}_2\text{M}$  which has already been discussed [1]; formation of a stable ferricinium cation  $\text{Cp}_2\text{Fe}^+$  from  $\text{Cp}_2\text{Fe}$  at a potential of +0.5 eV is well known [5].

From this point of view it is interesting to study the product which we have obtained in the course of oxidative decarbonylation of I under the action of

Table 2

Bond lengths (Å) for the cluster  $\{[\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2]_2\text{Fe}\}^+ \text{FeI}_4^-$  (II)

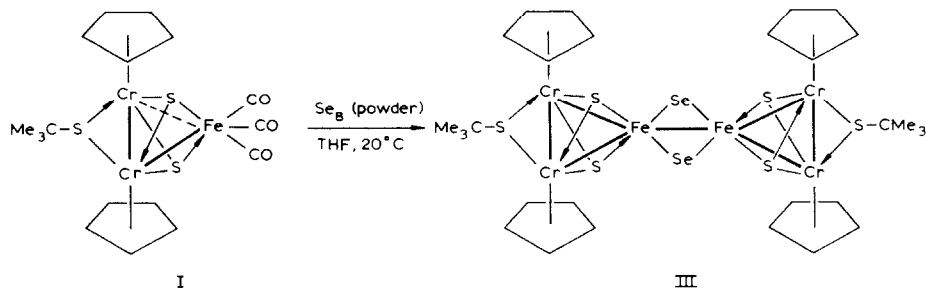
I(1)–Fe(1)	2.548(2)	I(2)–Fe(1)	2.518(2)
Fe(2)–Cr(1)	2.768(3)	Fe(2)–Cr(2)	2.763(3)
Fe(2)–Cr(2)	2.763(3)	Fe(2)–S(1)	2.274(4)
Fe(2)–S(2)	2.266(5)	Cr(1)–Cr(2)	2.631(3)
Cr(1)–S(1)	2.298(4)	Cr(1)–S(2)	2.303(4)
Cr(1)–S(3)	2.340(6)	Cr(2)–S(1)	2.309(5)
Cr(2)–S(2)	2.296(4)	Cr(2)–S(3)	2.338(5)

Table 3

Bond angles ( $^{\circ}$ ) for the cluster  $\{[\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2]\text{Fe}\}^+ \text{FeI}_4^-$  (II)

I(1)Fe(1)I(1)'	108.42(8)	I(1)Fe(1)I(2)	107.03(8)
I(1)Fe(1)I(2)'	110.93(9)	I(2)Fe(1)I(2)'	112.46(9)
Cr(1)Fe(2)Cr(1)'	141.38(9)	Cr(1)Fe(2)Cr(2)	139.82(9)
Cr(1)Fe(2)Cr(2)'	56.82(8)	Cr(1)Fe(2)S(1)	161.3(1)
Cr(1)Fe(2)S(1)'	53.1(1)	Cr(1)Fe(2)S(2)	104.3(1)
Cr(1)Fe(2)S(2)'	53.3(1)	Cr(2)Fe(2)Cr(2)'	141.74(9)
Cr(2)Fe(2)S(1)'	53.5(1)	Cr(2)Fe(2)S(1)	104.5(1)
Cr(2)Fe(2)S(2)'	53.2(1)	Cr(2)Fe(2)S(2)	161.1(1)
S(1)Fe(2)S(1)'	116.6(2)	S(1)Fe(2)S(2)'	94.4(2)
S(1)Fe(2)S(2)	118.6(2)	S(2)Fe(2)S(2)'	116.1(2)
Fe(2)Cr(1)Cr(2)	61.49(8)	Fe(2)Cr(1)S(1)	52.3(1)
Fe(2)Cr(1)S(2)	52.1(1)	Fe(2)Cr(1)S(3)	116.8(1)
Cr(2)Cr(1)S(1)	55.4(1)	Cr(2)Cr(1)S(2)	55.0(1)
Cr(2)Cr(1)S(3)	55.7(1)	S(1)Cr(1)S(2)	92.8(2)
S(1)Cr(1)S(3)	85.3(2)	S(2)Cr(1)S(3)	94.1(2)
Fe(2)Cr(2)Cr(1)	61.69(8)	Fe(2)Cr(2)S(1)	52.3(1)
Fe(2)Cr(2)S(2)	52.2(1)	Fe(2)Cr(2)S(3)	117.1(1)
Cr(1)Cr(2)S(1)	55.0(1)	Cr(1)Cr(2)S(2)	55.2(1)
Cr(1)Cr(2)S(3)	55.8(1)	S(1)Cr(2)S(2)	92.7(2)
S(1)Cr(2)S(3)	85.1(2)	S(2)Cr(2)S(3)	94.4(2)
Fe(2)S(1)Cr(1)	74.5(1)	Fe(2)S(1)Cr(2)	74.1(1)
Cr(1)S(1)Cr(2)'	69.6(1)	Fe(2)S(2)Cr(1)	74.6(1)
Fe(2)S(2)Cr(2)	74.5(1)	Cr(1)S(2)Cr(2)	69.8(1)
Cr(1)S(3)Cr(2)	68.5(1)	Cr(1)S(3)C(1)	117.7(6)
Cr(2)S(3)C(1)	118.6(6)		

selenium powder in THF (reaction with tellurium occurs in an analogous way):



Green-brown needles are formed of the hexanuclear antiferromagnetic cluster  $[\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2\text{Fe}]_2(\mu\text{-Se})_2$  (III) ( $\mu_{\text{eff}}$  for the molecule as whole is  $2.72 \mu_{\text{B}}$ (202 K)  $-1.50 \mu_{\text{B}}$ (77 K)). Single crystals for the X-ray structural investigations were obtained by crystallization from the  $\text{CH}_2\text{Cl}_2$ -heptane mixture and contained two  $\text{CH}_2\text{Cl}_2$  molecules per III molecule. According to X-ray structural analysis (Fig. 2, Tables 4–6) the core of the molecule consists of the planar fragment  $\text{Cr}_2\text{FeSe}_2\text{FeCr}_2$  with the two triangles  $\text{Cr}_2\text{Fe}$  ( $\text{Cr-Cr}$  2.679(4),  $\text{Cr-Fe}$  2.817(3), and 2.862(3) Å) bonded via two bridged selenium atoms ( $\text{Fe-Se}$  2.306(3) and 2.320(3) Å) and a  $\text{Fe-Fe}$  bond (2.838(3) Å). Analogous to what is seen in I, both dichromic fragments form the framework of the molecule located in the crystallographic centre of inversion. In assumption of analogy between  $\text{Cp}_2\text{Cr}_2\text{SCMe}_3(\mu_3\text{-S})_2$  (Q) and Cp

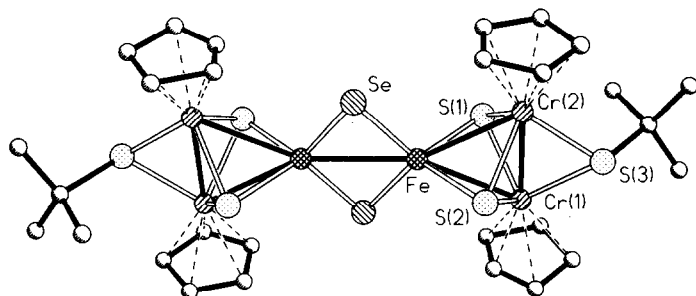


Fig. 2. The molecular structure of  $[\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2\text{Fe}(\mu\text{-Se})]_2$  (III).

Table 4

Atomic coordinates ( $\times 10^3$ ) (for Se, Fe, Cr, S  $\times 10^4$ ) for the cluster  $[\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2\text{Fe}(\mu\text{-Se})]_2 \cdot 2\text{CH}_2\text{Cl}_2$  (III)

Atom	x	y	z
Se	6189(3)	949(1)	4654(1)
Fe	4283(3)	688(2)	5397(1)
Cr(1)	2147(3)	1201(2)	6343(1)
Cr(2)	4087(3)	2579(2)	5931(1)
Cl(1)	1046(1)	25(1)	907(0)
Cl(2)	787(1)	162(1)	866(0)
S(1)	5077(5)	1212(3)	6496(2)
S(2)	1992(5)	1725(3)	5220(2)
S(3)	1995(6)	2824(3)	6623(2)
C(1)	274(3)	3149(1)	757(1)
C(2)	124(3)	291(1)	794(1)
C(3)	440(3)	2629(1)	784(1)
C(4)	311(3)	424(1)	756(1)
C(11)	935(2)	15(1)	387(1)
C(12)	-47(2)	60(1)	627(1)
C(13)	4(2)	91(1)	695(1)
C(14)	158(3)	35(1)	723(1)
C(15)	192(2)	-32(1)	672(1)
C(21)	484(3)	415(1)	602(1)
C(22)	633(3)	355(2)	624(1)
C(23)	663(3)	299(1)	569(1)
C(24)	539(4)	324(2)	512(1)
C(25)	424(3)	392(2)	531(1)
CX	947(3)	128(2)	931(1)

Table 5

Bond lengths ( $\text{\AA}$ ) for the cluster  $[\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2\text{Fe}(\mu\text{-Se})]_2 \cdot 2\text{CH}_2\text{Cl}_2$  (III)

Se-Fe	2.306(3)	Se-Fe	2.320(3)
Fe-Fe	2.838(3)	Fe-Cr(1)	2.817(3)
Fe-Cr(2)	2.862(3)	Fe-S(1)	2.288(4)
Fe-S(2)	2.318(5)	Cr(1)-Cr(2)	2.679(4)
Cr(1)-S(1)	2.311(5)	Cr(1)-S(2)	2.325(4)
Cr(1)-S(3)	2.345(5)	Cr(2)-S(1)	2.291(4)
Cr(2)-S(2)	2.338(5)	Cr(2)-S(3)	2.346(5)

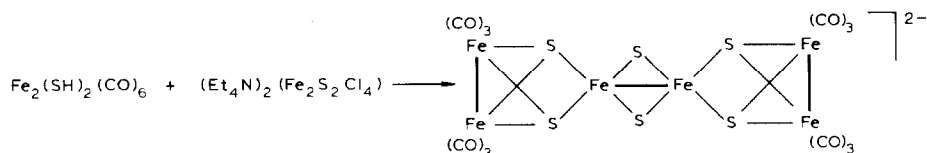
Table 6

Bond angles ( $^{\circ}$ ) for the cluster  $[\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2\text{-Fe}(\mu\text{-Se})]_2 \cdot 2\text{CH}_2\text{Cl}_2$  (III)

FeSeFe'	75.67(9)	SeFeSe'	104.3(1)
SeFeFe'	52.40(8)	SeFeCr(1)	155.9(1)
SeFeCr(2)	99.7(1)	SeFeS(1)	116.3(1)
SeFeS(2)	112.9(1)	Se'FeFe'	51.93(8)
SeFeCr(1)	99.8(1)	SeFeCr(2)	155.6(1)
SeFeS(1)	112.1(1)	SeFeS(2)	119.5(1)
Fe'FeCr(1)	151.7(1)	Fe'FeCr(2)	151.8(1)
Fe'FeS(1)	132.0(1)	Fe'FeS(2)	135.9(1)
Cr(1)FeCr(2)	56.28(8)	Cr(1)FeS(1)	52.6(1)
Cr(1)FeS(2)	52.8(1)	Cr(2)FeS(1)	51.4(1)
Cr(2)FeS(2)	52.4(1)	S(1)FeS(2)	92.1(2)
FeCr(1)Cr(2)	62.72(9)	FeCr(1)S(1)	51.9(1)
FeCr(1)S(2)	52.5(1)	FeCr(1)S(3)	117.6(1)
S(1)Cr(1)S(2)	91.4(2)	S(1)Cr(1)S(3)	93.0(2)
S(2)Cr(1)S(3)	85.6(2)	FeCr(2)Cr(1)	60.99(9)
FeCr(2)S(1)	51.3(1)	FeCr(2)S(2)	51.7(1)
FeCr(2)S(3)	115.9(1)	Cr(1)Cr(2)S(1)	54.7(1)
Cr(1)Cr(2)S(2)	54.7(1)	Cr(1)Cr(2)S(3)	55.2(1)
S(1)Cr(2)S(2)	91.5(2)	S(1)Cr(2)S(2)	91.5(2)
S(2)Cr(2)S(3)	85.3(2)	FeS(1)Cr(1)	75.5(1)
FeS(1)Cr(2)	77.4(1)	Cr(1)S(1)Cr(2)	71.2(1)
FeS(2)Cr(1)	74.7(1)	FeS(2)Cr(2)	75.9(1)
Cr(1)S(2)Cr(2)	70.1(1)	Cr(1)S(3)Cr(2)	69.6(1)

fragments III may be represented as an analogue of the fragment  $\text{Cp}_2\text{Fe}_2\text{S}_2$  which is known to dimerize into tetrahedral  $\text{Cp}_4\text{Fe}_4\text{S}_4$  cluster with only two Fe–Fe bonds [6]. Dimerization of the cluster III into the corresponding cluster  $\text{Q}_4\text{Fe}_4\text{Se}_4$  is not likely because the bulky Q fragments cannot deviate from the Fe–Fe axis, which would be necessary for formation of  $\text{Cp}_4\text{Fe}_4\text{S}_4$ . The geometry of the central fragment  $\text{S}_2\text{FeSe}_2\text{FeS}_2$  resembles the structure of the above-mentioned 2Fe2S ferredoxin models  $(\text{RS})_2\text{Fe}(\text{S})_2\text{Fe}(\text{SR})_2^{2-}$  (Fe–Fe 2.691 Å at R = *para*-tolyl) [3], in which antiferromagnetic exchange interactions between the high spin iron(III) ions ( $S = 5/2$ ;  $-2J = 300 \text{ cm}^{-1}$ ) [7] can occur.

It is also interesting to compare the geometry of the metal framework in III with that of the analogous homonuclear cluster  $\text{Fe}_6\text{S}_6(\text{CO})_{12}^{2-}$  synthesized by Averill and coworkers [8] in accordance with the following reaction:



As in III there are peripheral M–M bonds (Fe–Fe 2.499(1) Å). The bond between the internal iron atoms is shortened to 2.693(1) Å in comparison with 2.838(3) Å in III probably because of differences in the nature of the chalcogenide bridges. However in this cluster there are no bonds between the peripheral and the central iron atoms. It is therefore no surprise that magnetic data of this cluster ( $\mu_{\text{eff}} = 1.96 \mu_{\text{B}}$  at 25°C,  $-2J = 312 \text{ cm}^{-1}$ ) are very close to the values found for the complexes

Table 7

Crystal data for the clusters  $[\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu_3\text{-S})_2]_2\text{Fe}^+\text{FeI}_4^-$  (II),  $[\text{Cp}_2\text{Cr}_2(\mu\text{-SCMe}_3)(\mu\text{-S})_2\text{Fe}]_2(\mu\text{-Se})_2$  (III)

	II	III · 2CH <sub>2</sub> Cl <sub>2</sub>
Crystal system	Monoclinic	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , Å	19.135(4)	7.9841(8)
<i>b</i> , Å	18.964(4)	13.9913(8)
<i>c</i> , Å	14.849(4)	19.7926(12)
$\alpha$ , °	90	90
$\beta$ , °	127.37(2)	99.072(5)
$\gamma$ , °	90	90
<i>V</i>	4282.3	2183.2
<i>Z</i>	4	2
2 $\theta_{\text{max}}$	56	56
Number of reflections measured	4320	4126
Number of independent reflections with $I > 3\sigma(I)$	2039	1617
<i>R</i> <sub>1</sub>	0.048	0.071
<i>R</i> <sub>2</sub>	0.045	0.061

$(\text{SR})_4\text{Fe}_2\text{S}_2\text{L}_4^{2-}$ . As to cluster III, it is an unusual example of a planar metal framework of "kayak paddle" type. This molecule has six paramagnetic centres and is too complicated for exchange interactions to be calculated.

## Experimental

All operations connected with the synthesis of the initial and the final clusters were carried out under an argon flow in absolute solvents. IR spectra were measured with a Specord 75 IR instrument in KBr pellets. Magnetic susceptibility was measured by the Faraday method using the technique designed in the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR [9].

X-Ray structural data were obtained with Hilger & Watts and Siemens automatic diffractometers ( $\lambda(\text{Mo-K}\alpha)$ ,  $\theta$ - $2\theta$  scan, 20 °C). Crystal data are listed in Table 7. The structures were solved by the direct method and refined in block-diagonal approximation for all non-hydrogen atoms using an Eclipse S/200 computer.

### $\{[(\text{Cp}_2\text{Cr}_2(\text{SCMe}_3)\text{S}_2)]_2\text{Fe}\}^+\text{FeI}_4^-$ (II)

A raspberry-coloured solution of 0.48 g (1.9 mmol) of I<sub>2</sub> in 20 ml of toluene was added to the red-brown solution of 0.985 g (1.9 mmol) of  $\text{Cp}_2\text{Cr}_2(\text{SCMe}_3)\text{S}_2\text{Fe}(\text{CO})_3$  in 40 ml of toluene. The fine, black-green crystals precipitated immediately. After a day the crystals were removed from the mother liquor, washed with hexane and dried *in vacuo*. The yield of the crystals was 0.85 g (64%). Single crystals for X-ray structural investigations were obtained by cooling to -18 °C of the concentrated solution of II in the CH<sub>2</sub>Cl<sub>2</sub>-toluene (2:1) mixture.

IR ( $\nu$ , cm<sup>-1</sup>): 540 w., 810 m., 990 m., 1150 w., 1420 m., 1500 w.  $\mu_{\text{eff}} = 5.28 \mu_{\text{B}}$ (293 K) - 5.17  $\mu_{\text{B}}$ (77 K).

$$[Cp_2Cr_2(\mu-SCMe_3)(\mu_3-S)_2]_2Fe_2(\mu-Se)_2 \cdot 2CH_2Cl_2 \text{ (III)}$$

The red-brown solution 0.64 g (1.2 mmol) of  $Cp_2Cr_2(SCMe_3)_2Fe(CO)_3$  in 30 ml of THF was stirred by a magnetic stirrer at room temperature for 30 h in an argon flow with a 20-fold excess (1.89 g, 24 mmol) of selenium as a powder. The solution gradually changed to a brown–green colour, with simultaneous precipitation of an amorphous product. The solution was filtered, and the precipitate extracted by 50 ml of methylene chloride. The green–brown extract was concentrated at 40/0.1 Torr to 20 ml, 20 ml of hexane added and the solution concentrated to 15 ml. The resulting solution was stored at  $-18^\circ C$  for some days. The green–brown needles precipitates were isolated by decantation, washed with pentane and dried *in vacuo*. Yield 0.41 g (60%).

Single crystals for X-ray structural analysis were obtained by crystallization from  $CH_2Cl_2$  solution carefully covered by a heptane layer after 10 d storage at  $-18^\circ C$ .

IR ( $\nu$ ,  $cm^{-1}$ ): 720 s., 730 s., 800 s., 1000 w., 1040 w., 1145 m., 1460., 2900–3100 w.br.

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