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ANTIFERROMAGNETIC COMPLEXES INVOLVING METAL—METAL BONDS

IV *. SYNTHESIS, MOLECULAR STRUCTURE AND MAGNETIC PROPERTIES OF THE HETEROTRINUCLEAR CLUSTER, $(C_5H_5Cr)_2(\mu^2\text{-}SCMe_3)(\mu^3\text{-}S)_2Fe(CO)_3$, WITH DIRECT AND INDIRECT EXCHANGE BETWEEN Cr^{III} AND Fe^{I} CENTERS

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Summary

The photochemical reaction between the antiferromagnetic complex $(C_5H_5\text{-}CrSCMe_3)_2S$ (I) (containing a Cr—Cr bond 2.689 Å long) and $Fe(CO)_5$ results in the elimination of two carbonyl groups and one tert-butyl radical to give $(C_5H_5Cr)_2(\mu^2\text{-}SCMe_3)(\mu^3\text{-}S)_2 \cdot Fe(CO)_3$ (III). As determined by X-ray diffraction, III contains a Cr—Cr bond of almost the same length as in I (2.707 Å), together with one thiolate and two sulphide bridges. The latter are also linked with the Fe atom of the $Fe(CO)_3$ moiety (average Fe—S bond length 2.300 Å). Fe also forms a direct bond, 2.726 Å long, with one of the Cr atoms, whereas its distance from the other Cr atom (3.110 Å) is characteristic for non-bonded interactions. Complex III is antiferromagnetic, the exchange parameter, $-2J$, values for Cr—Cr, Cr(1)—Fe and Cr(2)...Fe are 380, 2600 and 170 cm^{-1}, respectively. The magnetic properties of III are discussed in terms of the "exchange channel model". The contributions from indirect interactions through bridging ligands are shown to be insignificant compared with direct exchange involving metal—metal bonds. The effects of steric factors and of the nature of the $M(CO)_n$ fragments on the chemical transformations of $(C_5H_5CrSCMe_3)_2S \cdot M(CO)_n$ are discussed.

* For Part III see ref. 2.

Introduction

In the preceding communication [2], we described the use of the binuclear complex $(CpCrSCMe_3)_2S$ (I) where Cp is π-C_5H_5 (containing a Cr—Cr bond 2.869 Å long [1]) as an unusual antiferromagnetic ligand (L) in the complexes of the type $M(CO)_5L$ (II) where M is Cr, Mo or W. The structure of I was shown to remain almost unaffected in the formation of those adducts where the ligand is attached to M via the bridging sulphur atom only. The absence of additional coordinative bonding at the thiolate sulphur atom was explained by remoteness of the M atoms (the M—S bond length 2.58 Å) caused by the large Mo and W covalent radii (1.58 Å) [3], and by hindrance to approach of the $SCMe_3$ group to the electronically saturated octahedral M atom of the $M(CO)_5L$ group. We deemed it interesting to study the reaction of I with $Fe(CO)_5$ which would make it possible not only to attach one more heteroatom to the dichromium system but also to determine the effect of a decrease of the covalent radius of M (*r* Fe 1.34 Å [3]) and of its coordination number (to 5) on the structure and properties of the expected adduct $Fe(CO)_4L$.

Results

a) Synthesis

The results obtained in this work show that the photochemical reaction between complex I and $Fe(CO)_5$ in THF at 5°C results in the elimination of two CO and one tert.-butyl groups with the formation of complex III:

$$\underset{(I)}{(CpCrSCMe_3)_2S} + Fe(CO)_5 \xrightarrow[\text{THF, 5°C}]{h\nu} \underset{(III)}{(CpCr)_2(SCMe_3)(S)_2 \cdot Fe(CO)_3}$$

Complex III was isolated by chromatography on Al_2O_3 as black prisms, stable in air, which decompose at 160°C without melting. The IR spectrum of III contains three CO stretches at 2030, 1964 and 1944 cm^{-1}, as well as the bands of C_5H_5 (810, 1012, 1440 cm^{-1}) and of the CMe_3 group (1160 and 2900—3000 cm^{-1}).

b) Structure

A complete X-ray structure analysis was performed to determine the structure of complex III unambiguously (Fig. 1). The unit cell parameters were found to be: a = 11.688(4), b = 18.802(5), c = 9.955(3) Å, β = 108.77(3)°, V = 2071 Å^3, $D_{exptl.}$ = 1.70, $D_{calcd.}$ = 1.69 g/cm^3, Z = 4, space group $P2_1/n$.

The structure was solved by the direct method. The final atomic coordinates are given in Table 1, the anisotropic temperature factors in Table 2, the bond lengths in Table 3, and the valence angles in Table 4.

Two C_5H_5Cr fragments are linked by a direct Cr—Cr bond 2.707 Å long and by the tert.-butylthiolate and two sulphide bridges (average Cr—S(sulphide) and Cr—S(thiolate) bond lengths are 2.30 and 2.35 Å, respectively). Both sulphide sulphur atoms are also linked with the $Fe(CO)_3$ fragment (average Fe—S bond length 2.30 Å). The Fe atom is positioned asymmetrically with

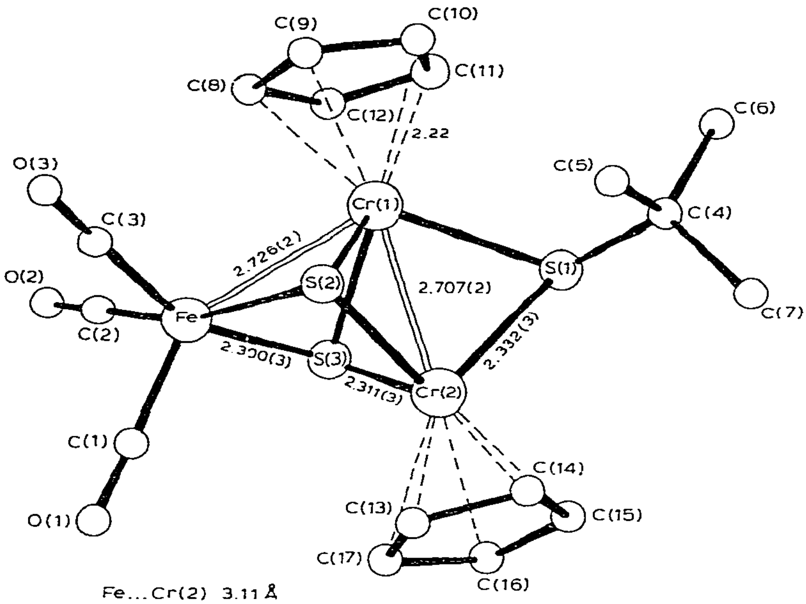
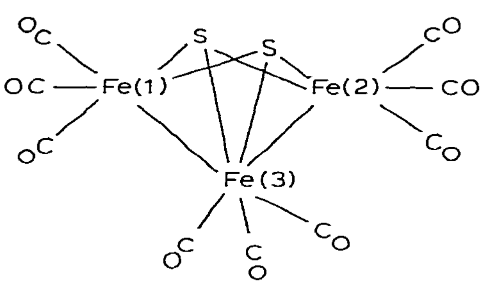


Fig. 1. The structure of $(C_5H_5Cr)_2(SCMe_3)(S)_2 \cdot Fe(CO)_3$.

respect to the chromium atoms: at a bonded distance of 2.726 Å from Cr(1) and non-bonded distance of 3.110 Å from Cr(2). The Cr—S—Cr angles of 70.46° and 72.37° and Cr(1)—S—Fe angles of 72.90° and 72.73° reflect the presence of the Cr—Cr and Cr(1)—Fe bonds, whereas the Fe—S—Cr(2) angles in the absence of a Fe—Cr(2) bond are 87.71° and 87.50°.

The previously studied trinuclear complex $Fe_3S_2(CO)_9$ [4] shows similar features. The Fe—S—Fe angles involving bonded Fe atoms in this compound



Fe(1)–Fe(3)	2.582(9) Å
Fe(2)–Fe(3)	2.609(10) Å
Fe(1)...Fe(2)	3.371 (10) Å
Fe(1)SFe(3)	70.7°
Fe(2)SFe(3)	71.6°
Fe(1)SFe(2)	98.4°

are similar to Cr—S—Cr and Cr(1)—S—Fe angles in III, whereas the Fe(1)—S—Fe(2) angle, involving non-bonded Fe atoms, is much larger.

c) Magnetic properties

Complex III is antiferromagnetic, the χ_M and $\mu_{eff.}$ values are listed in Table 5.

The magnetic properties of III were interpreted by fitting the theoretical magnetic susceptibility values calculated using the spin-Hamiltonian

$$\hat{H} = -2J_{12}S_1S_2 - 2J_{23}S_2S_3 - 2J_{13}S_1S_3 + \beta H[g_1S_1 + g_2S_2 + g_3S_3]$$

TABLE 1

ATOMIC COORDINATES (X 10^4)

Atom	X	Y	Z
Fe	2212(1)	1381(1)	8760(1)
Cr(1)	2316(1)	495(1)	6634(1)
Cr(2)	2245(1)	−314(1)	8855(1)
S(1)	2016(2)	−748(1)	6589(2)
S(2)	3667(2)	536(1)	8879(2)
S(3)	824(2)	520(1)	7675(2)
O(1)	4152(7)	2397(4)	9029(9)
O(2)	2203(8)	1478(4)	11703(8)
O(3)	232(7)	2380(4)	7502(10)
C(1)	3386(2)	2013(5)	8929(10)
C(2)	2204(8)	1418(5)	10560(10)
C(3)	1023(9)	2008(5)	8014(11)
C(4)	3272(8)	−1330(5)	6407(10)
C(5)	3036(10)	1415(6)	4841(11)
C(6)	3147(10)	−2037(6)	7066(13)
C(7)	4502(9)	−1014(6)	7118(11)
C(8)	3349(10)	1206(7)	5631(11)
C(9)	3111(12)	572(7)	4888(12)
C(10)	1887(13)	516(8)	4312(10)
C(11)	1351(10)	1093(8)	4686(13)
C(12)	2284(13)	1537(6)	5511(12)
C(13)	1161(8)	−913(6)	9984(11)
C(14)	1993(10)	−1380(5)	9763(10)
C(15)	3140(9)	−1149(6)	10463(11)
C(16)	3031(9)	−521(7)	11191(10)
C(17)	1809(11)	−369(5)	10873(11)
H(501)	3239	−1885	4515
H(502)	3519	−1050	4489
H(503)	2158	−1325	4314
H(601)	3743	−2399	6947
H(602)	3793	−1905	8173
H(603)	2317	−2221	6822
H(701)	4750	−750	8250
H(702)	5324	−1483	7497
H(703)	4520	−635	6407
H(8)	4539	1414	6218
H(9)	3773	215	4837
H(10)	1430	108	3674
H(11)	442	1209	4355
H(12)	2184	2002	5960
H(13)	270	−997	9582
H(14)	1824	−1845	9114
H(15)	3958	−1402	10528
H(16)	3750	−247	11846
H(17)	1437	57	11221

to the experimental values with the help of the programme described in ref. 5. In the Hamiltonian index, I refers to the Fe^{I} centre having spin of 1/2, and indices 2 and 3 to the Cr^{III} centre with spins $S_2 = S_3 = 3/2$. Accordingly, the parameters $-2J_{12}$ and $-2J_{13}$ describe interactions between the Cr^{III} and Fe^{I} centres, and the parameter $-2J_{23}$ between the two Cr^{III} centres. The g-factors of the Fe^{I} and two Cr^{III} centres are denoted g_1, g_2 and g_3, respectively.

The best fit between the experimental and theoretical temperature depen-

TABLE 2

ANISOTROPIC TEMPERATURE FACTORS (X 10^2) IN THE FORM $T = \exp[-1/4(B_{11}h^2a^{*2} + ... + 2B_{23}klb^*c^*)]$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	302(5)	260(6)	310(6)	—5(5)	116(5)	—9(5)
Cr(1)	276(5)	316(6)	210(5)	—37(5)	100(4)	23(5)
Cr(2)	267(6)	277(6)	250(6)	—24(5)	123(5)	10(5)
S(1)	306(10)	306(10)	314(11)	—66(8)	121(8)	—75(8)
S(2)	222(8)	265(9)	264(9)	—16(8)	75(6)	—2(8)
S(3)	228(8)	310(9)	325(10)	—8(8)	104(7)	5(9)
O(1)	578(39)	465(40)	1027(58)	—215(34)	415(40)	—120(39)
O(2)	944(5)	717(49)	455(40)	—81(42)	359(39)	—76(37)
O(3)	553(38)	522(40)	1017(61)	—200(34)	59(40)	—31(40)
C(1)	479(50)	292(44)	490(53)	—17(40)	231(43)	—21(38)
C(2)	407(47)	392(47)	377(47)	377(47)	—5(39)	81(42)
C(3)	460(51)	414(51)	472(54)	—24(42)	99(43)	—57(42)
C(4)	407(43)	351(44)	389(47)	16(36)	207(38)	—132(38)
C(5)	679(65)	658(65)	418(52)	91(52)	245(48)	—154(48)
C(6)	640(63)	394(54)	830(76)	95(46)	316(58)	—58(51)
C(7)	381(46)	587(59)	519(57)	86(43)	124(41)	—124(48)
C(8)	478(53)	698(72)	352(51)	—220(52)	79(43)	211(48)
C(9)	793(73)	583(64)	470(58)	—23(62)	425(56)	96(55)
C(10)	855(80)	795(79)	222(44)	—393(73)	133(48)	—30(53)
C(11)	391(53)	1015(94)	408(59)	94(60)	125(46)	437(61)
C(12)	829(79)	443(57)	440(55)	118(57)	323(55)	209(47)
C(13)	322(44)	623(62)	519(58)	—46(44)	179(41)	314(50)
C(14)	612(62)	322(46)	454(52)	—59(44)	181(47)	133(41)
C(15)	432(51)	435(53)	487(56)	111(43)	201(44)	181(44)
C(16)	431(48)	664(62)	272(41)	—166(50)	30(35)	226(48)
C(17)	806(56)	421(56)	374(49)	140(49)	413(50)	93(41)

TABLE 3

BOND LENGTHS

Bond	d(Å)	Bond	d(Å)
Fe—Cr(1)	2.726(2)	Cr(2)—C(13)	2.25(1)
Cr(1)—Cr(2)	2.707(2)	Cr(2)—C(14)	2.26(1)
Fe—S(2)	2.303(2)	Cr(2)—C(15)	2.24(1)
Fe—S(3)	2.300(3)	Cr(2)—C(16)	2.24(1)
Cr(1)—S(1)	2.361(3)	Cr(2)—C(17)	2.23(1)
Cr(1)—S(2)	2.286(2)	C(1)—O(1)	1.13(1)
Cr(1)—S(3)	2.297(2)	C(2)—O(2)	1.14(1)
Cr(2)—S(1)	2.332(3)	C(3)—O(3)	1.14(1)
Cr(2)—S(2)	2.300(3)	S(1)—C(4)	1.89(1)
Cr(2)—S(3)	2.311(3)	C(4)—C(5)	1.50(1)
Fe—C(1)	1.78(1)	C(4)—C(6)	1.51(1)
Fe—C(2)	1.80(1)	C(4)—C(7)	1.51(1)
Fe—C(3)	1.79(1)	C(8)—C(9)	1.38(2)
Cr(1)—C(8)	2.24(1)	C(9)—C(10)	1.36(2)
Cr(1)—C(9)	2.22(1)	C(10)—C(11)	1.36(2)
Cr(1)—C(10)	2.20(1)	C(11)—C(12)	1.41(2)
Cr(1)—C(11)	2.21(1)	C(12)—C(8)	1.36(2)
Cr(1)—C(12)	2.25(1)	C(13)—C(14)	1.38(2)
		C(14)—C(15)	1.37(2)
		C(15)—C(16)	1.40(2)
		C(16)—C(17)	1.39(2)
		C(17)—C(13)	1.40(2)

TABLE 4

BOND ANGLES

Angle	ω (°)	Angle	ω (°)	Angle	ω (°)
FeCr(1)Cr(2)	71.88(5)	Cr(1)S(1)C(4)	117.5(3)	C(14)C(13)C(17)	107.4(10)
Cr(1)FeS(2)	53.26(6)	Cr(1)S(1)Cr(2)	70.46(8)	C(13)C(14)C(15)	109.5(10)
Cr(1)FeS(3)	53.58(7)	Cr(2)S(1)C(4)	116.4(3)	C(14)C(15)C(16)	107.4(9)
S(2)FeS(3)	86.31(9)	FeS(2)Cr(1)	72.90(8)	C(15)C(16)C(17)	108.1(10)
C(1)FeC(2)	97.5(5)	FeS(2)Cr(2)	87.71(8)	C(16)C(17)C(13)	107.5(10)
C(2)FeC(3)	97.8(5)	Cr(1)S(2)Cr(2)	72.37(8)		
C(3)FeC(1)	94.1(5)	FeS(3)Cr(1)	72.73(8)		
Cr(2)Cr(1)S(1)	54.26(7)	FeS(3)Cr(2)	87.50(9)		
FeCr(1)S(1)	125.18(8)	Cr(1)S(3)Cr(2)	71.95(8)		
S(2)Cr(1)S(1)	95.92(9)	FeC(1)O(1)	177.9(9)		
Cr(2)Cr(1)S(2)	54.06(7)	FeC(2)O(2)	176.5(9)		
Cr(2)Cr(1)S(3)	54.26(7)	FeC(3)O(3)	176.7(10)		
FeCr(1)S(2)	53.84(6)	C(5)C(4)S(1)	105.8(7)		
FeCr(1)S(3)	53.69(7)	C(6)C(4)S(1)	106.4(7)		
S(3)Cr(1)S(1)	84.21(9)	C(7)C(4)S(1)	112.4(7)		
S(3)Cr(1)S(2)	86.79(9)	C(5)C(4)C(6)	110.3(9)		
Cr(2)Cr(1)Cp*(1)	174.8(5)	C(6)C(4)C(7)	110.8(8)		
Cr(1)Cr(2)Cp(2)	178.0(5)	C(5)C(4)C(7)	111.0(8)		
		C(9)C(8)C(12)	109.1(11)		
		C(8)C(9)C(10)	107.1(11)		
		C(9)C(10)C(11)	109.6(12)		
		C(10)C(11)C(12)	107.1(12)		
		C(11)C(12)C(8)	107.1(11)		

TABLE 5

THE MAGNETIC PROPERTIES OF $(C_5H_5Cr)_2(\mu^2\text{-}SCMe_3)(\mu^3\text{-}S)_2Fe(CO)_3$

No	T (K)	$\chi_M \times 10^6$ (cm^3/mol)	$\mu_{eff.}$ (B.M.)	Monomer admixture (%)	$-2J$(Cr—Cr) (cm^{-1})	$-2J$(Cr(1)—Fe) (cm^{-1})	$-2J$(Cr(2)—Fe) (cm^{-1})
	298	633	1.22				
III	227	714	1.14	1.8	380	2600	170
	80	1822	1.08				

dences of magnetic susceptibility was obtained with the following parameter values: $-2J_{12} = 2600$ cm^{-1}, $-2J_{23} = 380$ cm^{-1}, $-2J_{13} = 170$ cm^{-1}; $g_1 = 2.18$, $g_2 = g_3 = 1.98$; monomer admixture 1.8%. The mean square deviation was 1.7%.

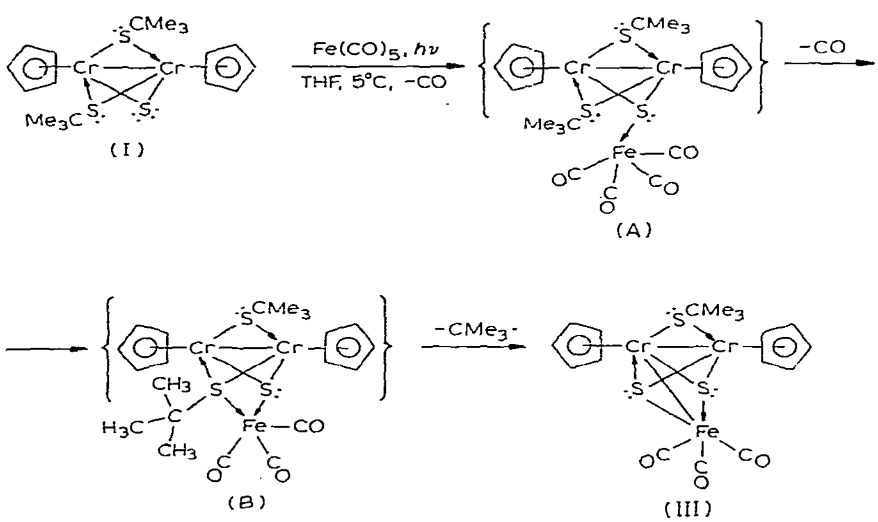
Discussion

The structural transformation of the initial binuclear complex $(CpCrSCMe_3)_2S$ (I), which loses one tert.-butyl group, is a particularly interesting feature of the reaction leading to $(CpCr)_2(SCMe_3)(S)_2 \cdot Fe(CO)_3$ (III). As mentioned in the Introduction, this reaction differs from those leading to the adducts $(CpCrSCMe_3)_2S \cdot M(CO)_5$ (II), where M is Cr, Mo and W [2], in that the Fe covalent radius (1.34 Å [3]) is smaller than the radii of Cr (1.46 Å), Mo or W

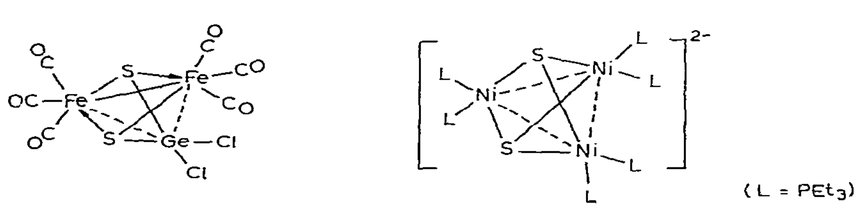
(1.58 Å [3]) and the Fe coordination number is decreased to 5 from 6 for Cr, Mo and W. These two differences may play a decisive role, providing a possibility for the formation of the chelate system Cr_2S_2Fe. In fact, it appears that the formation of III (Scheme 1) involves first coordination of the $Fe(CO)_4$ fragment generated photochemically at the bridging sulphide sulphur atom (A), like that observed for $M(CO)_5$ in complexes II. With the smaller Fe atom, however, the Fe—S distance should be shorter by some 0.2 Å than the M—S distances in II, which facilitates approach of the Fe atom to the thiolate bridge leading to the formation of complex B. One more point favouring this process is the presence of a coordination vacancy in the trigonal-bipyramidal Fe environment in intermediate A. The formation of chelate B with the elimination of one more carbonyl group from $Fe(CO)_4$ should, however, result in a drastic increase of steric strain, due to the proximity of the $Fe(CO)_3$ and CMe_3 groups. The removal of the strain by the elimination of the t-butyl group eventually gives III.

SCHEME 1

POSSIBLE PATHWAY TO III



The basic feature of the structure of III is the asymmetrical trimetallic triangle Cr_2Fe with the μ^3-sulphide bridges on the opposite sides of it. Such structures are known for sulphur-containing clusters [6], in particular, the complexes $Fe_2(CO)_6S_2 \cdot GeCl_2$ (IV) [7] and $[(PEt_3)_6Ni_3S_2]^{2-}$ (V) [8] have been described recently:



The distances between the M atoms in the trigonal bipyramidal skeleton may, depending on the nature of M and other ligands, vary from purely non-bonded (average Ni—Ni distance in V is 2.91 Å) to short M—M bonds (two Fe—Fe bonds of 2.59 Å (average) in $Fe_3(CO)_9S_2$, mentioned above, and the Fe—Fe bond of 2.480 Å in IV).

The molecule III contain two short non-equivalent M—M bonds (Cr—Cr 2.707 Å and Cr(I)—Fe 2.726 Å) whereas the Cr(2) and Fe atoms are only linked through the sulphide bridges (Cr(2)...Fe 3.110 Å).

The magnetochemical data on III agree well with the results of the structure determination. In fact, the $-2J_{23}$ exchange parameter for the Cr(2)...Fe pair involving no direct M—M bond is equal to 170 cm^{-1}, a value typical for indirect exchange through monoatomic bridges only. Thus, the $-2J$ value in the binuclear Fe^{III} complex (complex VI), involving thiolate-bridges (Fe—S 2.303 and 2.265 Å) and non-bonded Fe...Fe distances (3.410 Å) is equal to 108 cm^{-1} [9].

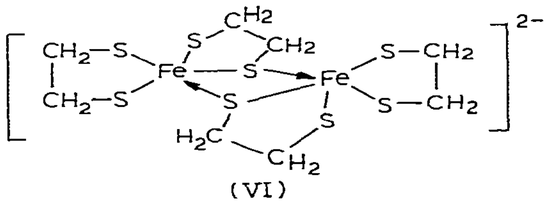
Comparison of exchange interactions summed over all exchange channels, $-2J_\Sigma$, is a more correct approach than comparison of the $-2J$ values, as it takes into account spins of the interacting paramagnetic ions a and b (see refs. 10—13):

$$-2J_\Sigma = -2J \times 4S_aS_b$$

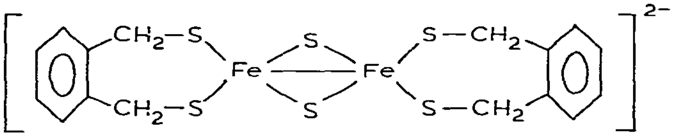
This gives for VI, containing Fe^{III} ions with spins of 3/2, the $-2J_\Sigma$ value of $108 \times 4 \times 3/2 \times 3/2 = 972$ cm^{-1} and for Cr(2)...Fe interactions in III (spins S(Cr) = 3/2 and S(Fe) = 1/2) the value of $170 \times 4 \times 3/2 \times 1/2 = 510$ cm^{-1}. Indirect exchange through bridge sulphur atoms in III and VI is thus of the same order of magnitude despite the differences in the nature of the metal atoms and bridge ligands.

Exchange coupling across the direct Cr—Cr bond in III ($-2J_{23} = 380$ cm^{-1}) differs only slightly from exchange coupling in I ($-2J$(Cr—Cr) = 430 cm^{-1} [I]) involving the Cr—Cr bond which is almost as short (2.689 Å) as it is in III. Since interactions between paramagnetic ions in complexes involving metal—metal bonds are predominantly due to direct exchange [2], the proximity of the two values seems quite natural. The summed contribution from exchange interactions over all the channels in III (S(Cr) = 3/2) is equal to $380 \times 4 \times 3/2 \times 3/2 = 3420$ cm^{-1}. This value far exceeds the contribution from purely indirect exchange via bridging sulphur atoms.

Lastly, the exchange parameter $-2J_{12}$ for the Fe^I—Cr^{III} pair, linked by the Fe—Cr bond 2.726 Å long, is equal to 2600 cm^{-1} which corresponds to the summed exchange of $-2J_\Sigma = 2600 \times 4 \times 3/2 \times 1/2 = 7800$ cm^{-1}. It is worthwhile mentioning that the Fe^{III} complex (complex VII) [14], having a similar geometry of the exchange skeleton and containing M—M bonds of approximately



(VI)



(VII)

the same length (Fe—Fe 2.69 Å) is characterized by a $-2J$ value of 300 cm^{-1}, which corresponds to the summed exchange of $-2J_{\Sigma} = 300 \times 4 \times 5/2 \times 5/2 =$ 7500 cm^{-1} (the spins of the Fe^{III} ions being equal to 5/2).

Comparison of the $-2J_{\Sigma}$ values characterizing exchange interactions across the direct Cr—Cr, Fe—Cr and Fe—Fe bonds shows that the direct exchange is far stronger than indirect exchange involving bridging ligands. Its magnitude, however, depends strongly on the nature of the interacting ions.

It should be emphasized that complex III is a rather rare example of an asymmetrical triangular exchange cluster and is unique in that it provides a possibility of obtaining a reliable estimate of the relative contributions to exchange from direct and indirect interactions, in particular, those between Cr^{III} and Fe^{I} ions.

Experimental

The initial complex $(CpCrSCMe_3)_2S$ was obtained as described previously [1]. Commercial iron pentacarbonyl was purified by distillation under vacuum. Absolute tetrahydrofuran was obtained by distillation over benzophenoneketyl-sodium under pure argon. UV irradiation was from a high pressure mercury lamp PRK-4. The reaction was carried out in a quartz Schlenk vessel. The IR spectra were measured in KBr pellets on an UR-20 instrument. The magnetic properties were measured by the Faraday technique on an apparatus constructed in this Institute [15]. X-ray diffraction was studied with a Syntex $P2_1$ autodiffractometer (λ Mo-K_{α}, $\theta/2\theta$ scan). 4093 independent reflections were collected; of these 2270 were treated by the full-matrix anisotropic procedure. The hydrogen atoms were located from the differential Fourier series (their coordinates and temperature factors were not refined): $R_1 = 0.059$, $R_W = 0.057$.

Preparation of $(C_5H_5Cr)_2(SCMe_3)(S)_2 \cdot Fe(CO)_3$ (III)

A violet solution of $(CpCrSCMe_3)_2S$ (0.40 g, 0.9 mmol) and $Fe(CO)_5$ (0.22 g, 1.1 mmol) in 25 ml THF was irradiated in a quartz Schlenk vessel jacket cooled by running water and equipped with a magnetic stirrer. During irradiation, the solution gradually turned brownish red. The mixture was chromatographed under argon on a short column (5 × 2 cm) packed with neutral Al_2O_3 and eluted with a benzene/heptane mixture, 1/1. Concentration of the eluate under vacuum led to precipitation of black prisms. These were separated by filtration, washed with pentane and dried under vacuum. The yield was 0.42 g (72%). The product decomposes at 160°C without melting. Found: C, 38.60; H, 3.75. $C_{21}H_{19}Cr_2FeO_3S_3$ calcd.: C, 38.75; H, 3.60%. IR spectrum (ν, cm^{-1}): 470w, 490w, 545m, 575m, 606s, 680w, 810s, 1012m, 1022m, 1070m, 1160m, 1370m, 1440m, 1460m, 1944s, 1965s, 2030s, 2930m, 2970w, 3120w.

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