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Synthesis and molecular structures of chromium–iron–sulfide $Cp_3Cr_3(\mu_3\text{-}S)_4FeSPh$ and $[Cp_3Cr_3(\mu_3\text{-}S)_4Fe]_2Fe(CO)_3S \cdot C_6H_6$ clusters with tetrahedral metal frameworks

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Abstract

Oxidative decarbonylation of $Fe_2(CO)_6(\mu\text{-}SPh)_2$ under the action of $Cp_2Cr_2(SCMe_3)_2S$ produced the tetrahedral $Cp_3Cr_3(\mu_3\text{-}S)_4Fe(SPh)$ cluster (III) and the unique nonanuclear $[Cp_3Cr_3(\mu_3\text{-}S)_4Fe]_2Fe(CO)_3S \cdot C_6H_6$ cluster (IV), depending on the molecular ratio of the reagents. Both complexes were characterized by X-ray structural analysis. In IV two heterometallotetrahedra are connected via a bridging $Fe(CO)_3S$ group and Fe–Fe bond (3.110 Å).

Cluster III may be considered as a model of ferredoxin while cluster IV could be seen as a model nitrogen fixing system.

Introduction

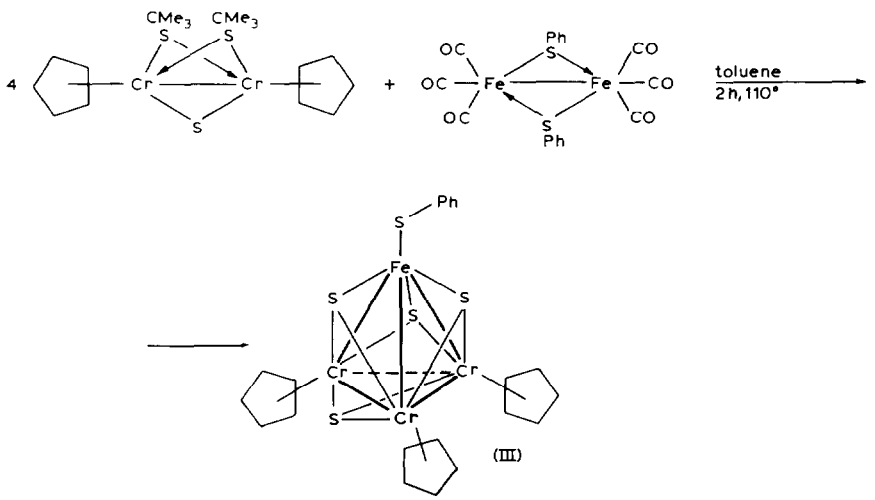
We have recently shown the possibility of enlarging heterometallic cluster frameworks by oxidative decarbonylation of a triangular $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Fe(CO)_3$ cluster under the action of selenium or iodine. Respectively the products are a neutral $[Cp_2Cr_2SCMe_3(\mu_3\text{-}S)_2]_2Fe_2Se_2$ cluster with an unusual framework of "kayak oar" type or a cationic cluster, $[Cp_2Cr_2SCMe_3(\mu_3\text{-}S)_2]_2Fe^+FeI_4^-$, with a heterometallospirane Cr_2FeCr_2 core [1]. In the latter case an intermediate cluster, $[Cp_2Cr_2SCMe_3(\mu_3\text{-}S)_2FeI]_2$, is probably formed, whose oxidation with excess iodine and subsequent disproportionation presumably results in the final product.

Results and discussion

In an attempt to obtain a cluster with the framework of "kayak oar" type $Cr_2Fe\text{–}FeCr_2$ and bridging SPh between the central iron atoms we have studied the

oxidative decarbonylation of the binuclear complex $Fe_2(SPh)_2(CO)_6$ (I) under the action of a binuclear antiferromagnetic complex of Cr^{III}, $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (II) (Cr–Cr 2.689 Å, $-2J = 430\ cm^{-1}$) [2].

It turned out however that interaction of the reagents in molar ratio of 1 : 4 in refluxing toluene for 2 h results in formation of a large brown single crystals of a tetrahedral complex $Cp_3Cr_3(\mu_3\text{-}S)_4FeSPh$ (III)



According to X-ray structural analysis (Fig. 1, Table 1–3) the framework of III contains a tetrahedron Cr_3Fe (Cr–Cr 2.869(5), 2.838(5), 2.841(5) Å; Fe–Cr 2.721(4), 2.768(5) Å), with each face coordinated by bridging μ_3-S sulfur atoms (Fe–S 2.215(6), $2 \times 2.222(6)$ Å, $Cr\text{–}S_{mean}$ 2.252 Å). Each Cr^{III} atom is bonded to a

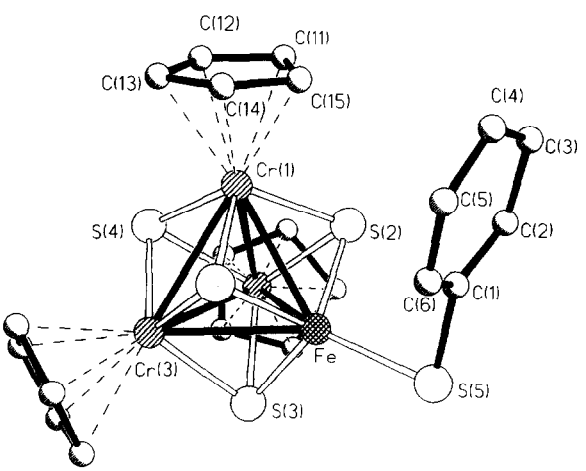


Fig. 1. The molecular structure of $Cp_3Cr_3(\mu_3\text{-}S)_4FeSPh$ (III).

Table 1

Atomic coordinates ($\times 10^3$) (for Cr, Fe and S $\times 10^4$) for the cluster $Cp_3Cr_3(\mu_3\text{-}S)_4FeSPh$ (III)

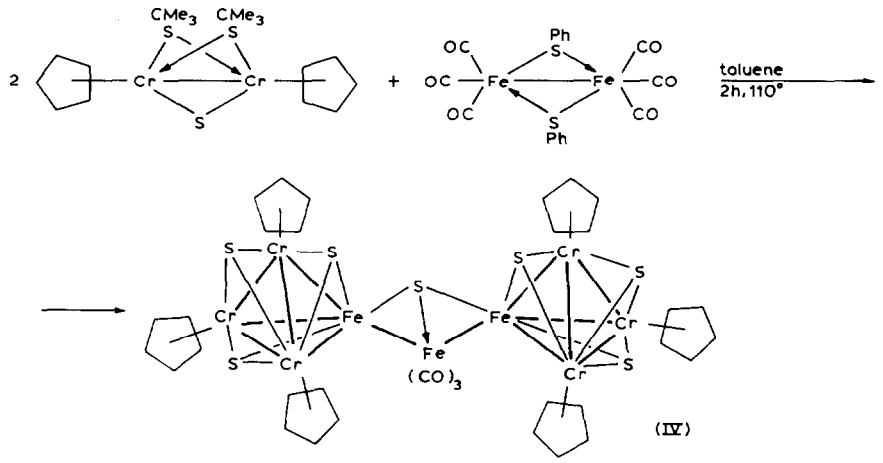
Atom	x	y	z
Fe	−2242(4)	7415(2)	8284(2)
Cr(1)	594(4)	7473(2)	9405(2)
Cr(2)	−1791(4)	6432(2)	9584(2)
Cr(3)	241(4)	6494(2)	8021(2)
S(1)	362(7)	7582(3)	7852(4)
S(2)	−2105(6)	7518(3)	9813(4)
S(3)	−2592(7)	6350(3)	8056(4)
S(4)	1033(7)	6386(3)	9528(4)
S(5)	−4124(9)	8123(3)	7651(5)
C(11)	121(3)	804(1)	1069(2)
C(12)	252(3)	760(1)	1057(2)
C(13)	331(3)	776(1)	968(2)
C(14)	240(3)	830(1)	933(2)
C(15)	112(3)	848(1)	987(2)
C(21)	−248(3)	623(1)	1105(2)
C(22)	−395(3)	626(1)	1050(2)
C(23)	−395(3)	578(1)	986(2)
C(24)	−250(3)	541(1)	995(2)
C(25)	−155(3)	571(1)	107(2)
C(31)	14(3)	600(1)	661(2)
C(32)	266(3)	623(1)	741(2)
C(33)	155(3)	645(1)	667(2)
C(34)	201(3)	565(1)	780(2)
C(35)	47(3)	551(1)	733(2)
C(1)	−300(3)	883(1)	800(2)
C(2)	−331(3)	910(1)	892(2)
C(3)	−232(4)	968(1)	923(2)
C(4)	−110(4)	994(1)	863(2)
C(5)	−99(4)	966(1)	779(2)
C(6)	−192(3)	914(1)	746(2)

Cp-ligand and each Fe^{III} ion to a SPh group (Fe–S 2.247(7) Å, S–C 1.80(2) Å, Fe–S–C angle is 93.9(8)°.

It is noteworthy that this cluster has practically the same structure as the tetrahedral $Cp_3Cr_3(\mu_3\text{-}S)_4\text{-}Fe(OOCCMe_3)$ cluster which we obtained by the action of pivalic acid on the triangular $Cp_2Cr_2SCMe_3(\mu_3\text{-}S)_2Fe(CO)_3$ cluster [3]. Furthermore, III is interesting as an intermediate in the series from electronsaturated $Cp_4Cr_4S_4$ [4] to highly electron-deficient $(RS)_4Fe_4S_4^{n-}$ [5], which models 4Fe4S ferredoxin.

Changing the ratio of the reagents to 1 : 2 (reducing the excess of chromium atoms) under the same conditions of refluxing for 2 h in toluene results in formation of large black single crystals of the unique nonanuclear cluster $[Cp_3Cr_3(\mu_3\text{-}S)_4Fe]_2(\mu\text{-}(CO)_3FeS)$ (IV):

X-ray studies (Fig. 2, Table 4–6) of IV reveal two tetrahedra $Cp_3Cr_3(\mu_3\text{-}S)_4Fe$ (Cr–Cr 2.807(4), 2.774(5), 2.808(4) Å; Fe–Cr 2.779(4), 2.757(4), 2.805(3) Å, $Cr\text{–}S_{mean}$



2.235 Å, Fe–S 2.335, 2 × 2.224(6) Å), which are connected with each other via iron and sulfur atoms of an unusual bridging group [S → $Fe(CO)_3$] (Fe–Fe_{tetr} 2.679(3), 2.649(3) Å; Fe–S 2.159(6) Å; Fe_{tetr}–S 2.235(5), 2.247(6) Å). A degree of shortening, by 0.1 Å, of the Fe–S bond of the bridging fragment [S → $Fe(CO)_3$] is observed. Coordination of [$SFe(CO)_3$] may presumably be described as a π-interaction of the

Table 2

Bond lengths (Å) for the cluster $Cp_3Cr_3(\mu_3\text{-}S)_4FeSPh$ (III)

Fe–Cr(1)	2.721(4)	Fe–Cr(2)	2.768(5)
Fe–Cr(3)	2.768(5)	Fe–S(1)	2.215(6)
Fe–S(2)	2.223(6)	Fe–S(3)	2.221(7)
Fe–S(5)	2.247(7)	Cr(1)–Cr(2)	2.869(5)
Cr(1)–Cr(3)	2.838(5)	Cr(1)–S(1)	2.259(7)
Cr(1)–S(2)	2.252(6)	Cr(1)–S(4)	2.256(7)
Cr(2)–Cr(3)	2.841(5)	Cr(2)–S(2)	2.261(7)
Cr(2)–S(3)	2.282(7)	Cr(2)–S(4)	2.251(4)
Cr(3)–S(1)	2.242(7)	Cr(3)–S(3)	2.273(7)
Cr(3)–S(4)	2.254(7)	S(5)–C(1)	1.80(2)
C(11)–C(12)	1.39(3)	C(11)–C(15)	1.50(3)
C(12)–C(13)	1.49(3)	C(13)–C(14)	1.40(3)
C(14)–C(15)	1.36(3)	C(21)–C(22)	1.38(4)
C(21)–C(25)	1.41(4)	C(22)–C(23)	1.35(4)
C(23)–C(24)	1.38(4)	C(25)–C(25)	1.44(4)
C(31)–C(33)	1.44(3)	C(31)–C(35)	1.47(3)
C(32)–C(33)	1.43(3)	C(33)–C(34)	1.43(3)
C(34)–C(35)	1.40(3)	C(1)–C(2)	1.36(3)
C(1)–C(6)	1.41(3)	C(2)–C(3)	1.49(4)
C(3)–C(4)	1.42(4)	C(4)–C(5)	1.35(4)
C(5)–C(6)	1.38(4)		

Table 3

Bond angles (°) for the cluster $Cp_3Cr_3(\mu_3\text{-}S)_4FeSPh$ (III)

Cr(1)FeCr(2)	63.0(1)	Cr(1)FeCr(3)	62.3(1)
Cr(1)FeS(1)	53.3(2)	Cr(1)FeS(2)	53.0(2)
Cr(1)FeS(3)	103.0(2)	Cr(1)FeS(5)	137.2(2)
Cr(2)FeCr(3)	61.7(1)	Cr(2)FeS(1)	102.1(2)
Cr(2)FeS(2)	52.5(2)	Cr(2)FeS(3)	53.1(2)
Cr(2)FeS(5)	144.0(2)	Cr(3)FeS(1)	52.0(2)
Cr(3)FeS(2)	101.4(2)	Cr(3)FeS(3)	52.8(2)
Cr(3)FeS(5)	148.1(2)	S(1)FeS(2)	105.2(2)
S(1)FeS(3)	102.8(2)	S(1)FeS(5)	113.5(3)
S(2)FeS(3)	103.9(2)	S(2)FeS(5)	110.3(3)
S(3)FeS(5)	119.7(3)	FeCr(1)Cr(2)	59.3(1)
FeCr(1)Cr(3)	59.7(1)	FeCr(1)S(1)	51.8(2)
FeCr(1)S(2)	52.1(2)	Cr(2)Cr(1)Cr(3)	59.7(1)
Cr(2)Cr(1)S(1)	98.0(2)	Cr(2)Cr(1)S(2)	50.7(2)
Cr(2)Cr(1)S(4)	50.4(2)	Cr(3)Cr(1)S(1)	50.6(2)
Cr(3)Cr(1)S(2)	98.6(2)	Cr(3)Cr(1)S(4)	51.0(2)
S(1)Cr(1)S(2)	102.8(2)	S(1)Cr(1)S(4)	100.4(2)
S(2)Cr(1)S(4)	99.5(2)	FeCr(2)Cr(1)	57.7(1)
FeCr(2)Cr(3)	59.1(1)	FeCr(2)S(2)	51.3(2)
FeCr(2)S(3)	51.1(2)	FeCr(2)S(4)	96.0(2)
Cr(1)Cr(2)Cr(3)	59.6(1)	Cr(1)Cr(2)S(2)	50.4(2)
Cr(1)Cr(2)S(3)	97.1(2)	Cr(1)Cr(2)S(4)	50.5(2)
Cr(3)Cr(2)S(2)	98.3(2)	Cr(3)Cr(2)S(3)	51.3(2)
Cr(3)Cr(2)S(4)	51.0(2)	S(2)Cr(2)S(3)	100.8(2)
S(2)Cr(2)S(4)	99.4(2)	S(3)Cr(2)S(4)	101.4(2)
FeCr(3)Cr(1)	58.1(1)	FeCr(3)Cr(1)	59.1(1)
FeCr(3)S(1)	51.2(2)	FeCr(3)S(3)	51.1(2)
FeCr(3)S(4)	95.9(2)	Cr(1)Cr(3)Cr(2)	60.7(1)
Cr(1)Cr(3)S(1)	51.2(2)	Cr(1)Cr(3)S(3)	98.2(2)
Cr(1)Cr(3)S(4)	51.0(2)	Cr(2)Cr(3)S(1)	99.2(2)
Cr(2)Cr(3)S(3)	51.6(2)	Cr(2)Cr(3)S(4)	50.9(2)
S(1)Cr(3)S(3)	100.3(2)	S(1)Cr(3)S(4)	101.0(2)
S(3)Cr(3)S(4)	101.5(2)	FeS(1)Cr(1)	74.9(2)
FeS(1)Cr(3)	76.8(2)	Cr(1)S(1)Cr(3)	78.2(2)
FeS(2)Cr(1)	74.9(2)	FeS(2)Cr(2)	76.2(2)
Cr(1)S(2)Cr(2)	79.0(2)	FeS(3)Cr(2)	75.9(2)
FeS(3)Cr(3)	76.0(2)	Cr(2)S(3)Cr(3)	77.2(2)
Cr(1)S(4)Cr(2)	79.1(2)	Cr(1)S(4)Cr(3)	78.0(2)
Cr(2)S(4)Cr(3)	78.2(2)	FeS(5)C(1)	93.9(8)
S(5)C(1)C(2)	122(2)	S(5)C(1)C(6)	116(2)

partially triple Fe≡S bond with two iron atoms located in the vertices of the tetrahedra.

The structure of cluster IV resembles the nonanuclear cluster $[Mo_2Fe_7S_8(CO)_{22}]$ [6] with the framework:

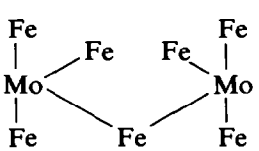


Table 4

Atomic coordinates ($\times 10^4$) for the cluster $[Cp_3Cr_3(\mu_3\text{-}S)_4\text{-}Fe]_2Fe(CO)_3S\cdot C_6H_6$ (IV)

Atom	x	y	z
Fe(1)	8068(2)	1664(1)	5903(1)
Fe(2)	5994(2)	2301(1)	5414(1)
Fe(3)	6524(2)	1141(2)	4766(2)
Cr(1)	9277(2)	503(2)	6582(2)
Cr(2)	10043(2)	1870(2)	6345(2)
Cr(3)	9201(2)	1746(2)	7487(2)
Cr(4)	5665(2)	3561(2)	6179(2)
Cr(5)	4113(2)	2821(2)	5085(2)
Cr(6)	5092(2)	2146(2)	6521(2)
S(1)	10488(3)	1145(3)	7405(3)
S(2)	8014(3)	944(3)	6877(3)
S(3)	8939(3)	2618(2)	6557(3)
S(4)	9107(3)	1087(3)	5459(3)
S(5)	7114(3)	2244(3)	4836(3)
S(6)	4262(3)	3209(3)	6284(3)
S(7)	5368(3)	3392(3)	4892(3)
S(8)	4690(3)	1658(3)	5320(3)
S(9)	6580(3)	2564(3)	6683(3)
O(1)	4748(11)	1186(9)	3423(9)
O(2)	7498(11)	104(9)	4055(9)
O(3)	6058(11)	20(9)	5749(9)
C(1)	5456(14)	1158(11)	3972(11)
C(2)	7094(14)	538(11)	4339(11)
C(3)	6254(15)	444(12)	5364(12)
C(11)	8572(20)	−612(15)	6437(16)
C(12)	9041(18)	−552(13)	5919(14)
C(13)	10038(19)	−474(14)	6314(15)
C(14)	10100(21)	−494(15)	7116(16)
C(15)	9207(21)	−588(15)	7154(16)
C(21)	10449(16)	2743(13)	5664(12)
C(22)	10731(16)	2094(13)	5454(13)
C(23)	11387(16)	1733(12)	6056(13)
C(24)	11586(16)	2176(12)	6728(12)
C(25)	11027(16)	2830(12)	6507(12)
C(31)	8900(15)	2629(12)	8243(11)
C(32)	9912(14)	2512(11)	8476(11)
C(33)	10099(13)	1763(10)	8760(10)
C(34)	9189(13)	1443(10)	8691(10)
C(35)	8468(13)	1983(10)	8366(10)
C(41)	5473(14)	4794(11)	6229(11)
C(42)	5636(16)	4495(12)	6998(13)
C(43)	6570(16)	4190(12)	7240(12)
C(44)	6960(16)	4287(12)	6620(13)
C(45)	6270(17)	4661(12)	6009(13)
C(51)	3226(14)	3284(11)	3894(11)
C(52)	3129(16)	2482(12)	3914(13)
C(53)	2660(14)	2305(11)	4464(11)
C(54)	2520(14)	2965(11)	4821(11)
C(55)	2881(14)	3582(10)	4478(11)
C(61)	4152(16)	1452(12)	6945(12)
C(62)	4504(15)	2006(12)	7479(12)
C(63)	5504(16)	1916(12)	7792(12)
C(64)	5742(16)	1277(12)	7405(12)

Table 4 (continued)

Atom	x	y	z
C(65)	4887(17)	975(13)	6899(13)
C(1B)	8769(14)	4759(11)	5241(11)
C(2B)	8035(15)	4239(12)	5032(12)
C(3B)	7271(14)	4359(11)	4331(11)
C(4B)	7214(15)	4925(12)	3855(12)
C(5B)	7976(14)	5445(11)	4052(11)
C(6B)	8748(14)	5366(11)	4734(12)

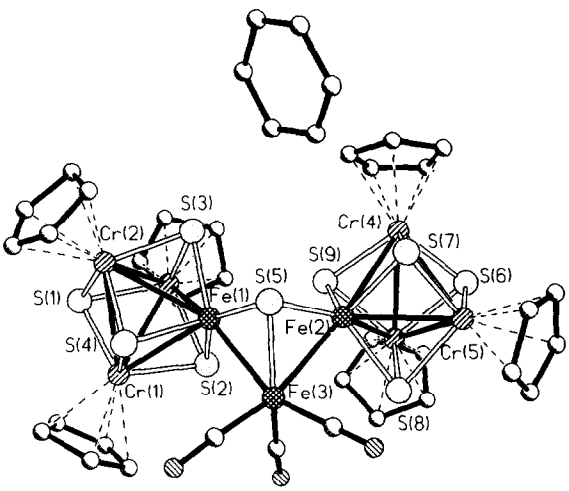


Fig. 2. The molecular structure of $[Cp_3Cr_3(\mu_3\text{-}S)_4Fe]_2Fe(CO)_3S\cdot C_6H_6$ (IV).

Table 5

Bond lengths (Å) for the cluster $[Cp_3Cr_3(\mu_3\text{-}S)_4Fe]_2Fe(CO)_3S\cdot C_6H_6$ (IV)

Fe(1)–Fe(3)	2.679(3)	Fe(1)–Cr(2)	2.779(4)
Fe(1)–S(2)	2.224(6)	Fe(1)–S(4)	2.224(6)
Fe(2)–Fe(3)	2.649(4)	Fe(2)–Cr(5)	2.802(4)
Fe(2)–S(5)	2.247(6)	Fe(2)–S(8)	2.209(6)
Fe(3)–S(5)	2.159(6)	Fe(3)–C(2)	1.716(23)
Cr(1)–Cr(2)	2.807(4)	Cr(1)–S(1)	2.229(5)
Cr(1)–S(4)	2.238(6)	Cr(2)–Cr(3)	2.774(5)
Cr(2)–S(3)	2.251(6)	Cr(3)–S(2)	2.255(5)
Cr(4)–Cr(6)	2.824(4)	Cr(4)–S(7)	2.255(6)
Cr(5)–S(6)	2.232(6)	Cr(5)–S(8)	2.249(5)
Cr(6)–S(6)	2.237(6)	Cr(6)–S(9)	2.250(6)
Fe(1)–Cr(1)	2.757(4)	Fe(1)–Cr(3)	2.805(3)
Fe(1)–S(3)	2.235(5)	Fe(1)–S(5)	2.235(5)
Fe(2)–Cr(4)	2.795(4)	Fe(2)–Cr(6)	2.787(5)
Fe(2)–S(7)	2.242(5)	Fe(2)–S(9)	2.228(5)
Fe(3)–C(1)	1.743(17)	Fe(3)–C(3)	1.794(23)
Cr(1)–Cr(3)	2.808(4)	Cr(1)–S(2)	2.258(6)
Cr(2)–S(1)	2.238(6)	Cr(2)–S(4)	2.236(5)
Cr(3)–S(1)	2.241(6)	Cr(3)–S(3)	2.246(5)
Cr(4)–Cr(5)	2.813(4)	Cr(4)–S(6)	2.240(6)
Cr(4)–S(9)	2.251(5)	Cr(5)–Cr(6)	2.799(4)
Cr(5)–S(7)	2.254(6)	Cr(6)–S(8)	2.242(6)
		Fe(1)–Fe(2)	3.110(4)

Table 6

Bond angles (°) for the cluster $[Cp_3Cr_3(\mu_3\text{-}S)_4Fe]_2Fe(CO)_3S\cdot C_6H_6$ (IV)

Fe(3)Fe(1)Cr(1)	109.4(1)	Fe(3)Fe(1)Cr(2)	143.8(2)
Cr(1)Fe(1)Cr(2)	60.9(1)	Fe(3)Fe(1)Cr(3)	150.2(1)
Cr(1)Fe(1)Cr(3)	60.6(1)	Cr(2)Fe(1)Cr(3)	59.6(1)
Fe(3)Fe(1)S(2)	99.1(2)	Cr(1)Fe(1)S(2)	52.6(2)
Cr(2)Fe(1)S(2)	99.6(2)	Cr(3)Fe(1)S(2)	51.7(1)
Fe(3)Fe(1)S(3)	150.3(2)	Cr(1)Fe(1)S(3)	100.2(1)
Cr(2)Fe(1)S(3)	52.0(2)	Cr(3)Fe(1)S(3)	51.4(1)
S(2)Fe(1)S(3)	101.2(2)	Fe(3)Fe(1)S(4)	93.9(2)
Cr(1)Fe(1)S(4)	52.0(2)	Cr(2)Fe(1)S(4)	51.7(1)
Cr(3)Fe(1)S(4)	98.9(1)	S(2)Fe(1)S(4)	103.6(2)
S(3)Fe(1)S(4)	102.1(2)	Fe(3)Fe(1)S(5)	51.1(1)
Cr(1)Fe(1)S(5)	150.1(2)	Cr(2)Fe(1)S(5)	118.7(2)
Cr(3)Fe(1)S(5)	148.1(2)	S(2)Fe(1)S(5)	141.6(2)
S(3)Fe(1)S(5)	100.5(2)	S(4)Fe(1)S(5)	102.3(2)
Fe(3)Fe(2)Cr(4)	173.3(1)	Fe(3)Fe(2)Cr(5)	126.3(1)
Cr(4)Fe(2)Cr(5)	60.3(1)	Fe(3)Fe(2)Cr(6)	122.1(1)
Cr(4)Fe(2)Cr(6)	60.8(1)	Cr(5)Fe(2)Cr(6)	60.1(1)
Fe(3)Fe(2)S(5)	51.5(2)	Cr(4)Fe(2)S(5)	123.6(2)
Cr(5)Fe(2)S(5)	138.8(2)	Cr(6)Fe(2)S(5)	161.0(2)
Fe(3)Fe(2)S(7)	130.3(2)	Cr(4)Fe(2)S(7)	51.8(1)
Cr(5)Fe(2)S(7)	51.6(2)	Cr(6)Fe(2)S(7)	99.4(2)
S(5)Fe(2)S(7)	96.1(2)	Fe(3)Fe(2)S(8)	86.3(2)
Cr(4)Fe(2)S(8)	99.7(2)	Cr(6)Fe(2)S(8)	51.7(1)
Cr(6)Fe(2)S(8)	51.8(2)	S(5)Fe(2)S(8)	134.8(2)
S(7)Fe(2)S(8)	101.7(2)	Fe(3)Fe(2)S(9)	124.1(2)
Cr(4)Fe(2)S(9)	51.8(1)	Cr(5)Fe(2)S(9)	99.0(2)
Cr(6)Fe(2)S(9)	51.9(2)	S(5)Fe(2)S(9)	114.1(2)
S(7)Fe(2)S(9)	102.2(2)	S(8)Fe(2)S(9)	102.3(2)
Fe(1)Fe(3)Fe(2)	71.4(1)	Fe(1)Fe(3)S(5)	53.7(1)
Fe(2)Fe(3)S(5)	54.6(2)	Fe(1)Cr(1)Cr(2)	59.9(1)
Fe(1)Cr(1)Cr(3)	60.5(1)	Cr(2)Cr(1)Cr(3)	59.2(1)
Fe(1)Cr(1)S(1)	99.1(2)	Cr(2)Cr(1)S(1)	51.2(2)
Cr(3)Cr(1)S(1)	51.3(2)	Fe(1)Cr(1)S(2)	51.5(1)
Cr(2)Cr(1)S(2)	98.0(2)	Cr(3)Cr(1)S(2)	51.5(1)
S(1)Cr(1)S(2)	101.4(2)	Fe(1)Cr(1)S(4)	51.6(2)
Cr(2)Cr(1)S(4)	51.1(1)	Cr(3)Cr(1)S(4)	98.5(2)
S(1)Cr(1)S(4)	100.7(2)	S(2)Cr(1)S(4)	102.0(2)
Fe(1)Cr(2)Cr(1)	59.2(1)	Fe(1)Cr(2)Cr(3)	60.7(1)
Cr(1)Cr(2)Cr(3)	60.4(1)	Fe(1)Cr(2)S(1)	98.3(2)
Cr(1)Cr(2)S(1)	50.9(1)	Cr(3)Cr(2)S(1)	51.8(2)
Fe(1)Cr(2)S(3)	51.5(1)	Cr(1)Cr(2)S(3)	98.3(2)
Cr(3)Cr(2)S(3)	51.8(2)	S(1)Cr(2)S(3)	102.7(2)
Fe(1)Cr(2)S(4)	51.3(2)	Cr(1)Cr(2)S(4)	51.2(2)
Cr(3)Cr(2)S(4)	99.5(2)	S(1)Cr(2)S(4)	100.5(2)
S(3)Cr(2)S(4)	101.2(2)	Fe(1)Cr(3)Cr(1)	58.8(1)
Fe(1)Cr(3)Cr(2)	59.8(1)	Cr(1)Cr(3)Cr(2)	60.4(1)
Fe(1)Cr(3)S(1)	97.4(2)	Cr(1)Cr(3)S(1)	50.9(1)
Cr(2)Cr(3)S(1)	51.7(2)	Fe(1)Cr(3)S(2)	50.7(1)
Cr(1)Cr(3)S(2)	51.6(2)	Cr(2)Cr(3)S(2)	99.0(2)
S(1)Cr(3)S(2)	101.2(2)	Fe(1)Cr(3)S(3)	51.1(1)
Cr(1)Cr(3)S(3)	98.4(2)	Cr(2)Cr(3)S(3)	52.0(2)
S(1)Cr(3)S(3)	102.8(2)	S(2)Cr(3)S(3)	99.9(2)
Fe(2)Cr(4)Cr(5)	60.0(1)	Fe(2)Cr(4)Cr(6)	59.5(1)
Cr(5)Cr(4)Cr(6)	59.6(1)	Fe(2)Cr(4)S(6)	97.8(2)
Cr(5)Cr(4)S(6)	50.9(1)	Cr(6)Cr(4)S(6)	50.9(2)

Table 6 (continued)

Fe(2)Cr(4)S(7)	51.4(1)	Cr(5)Cr(4)S(7)	51.4(2)
Cr(6)Cr(4)S(7)	98.0(2)	S(6)Cr(4)S(7)	101.1(2)
Fe(2)Cr(4)S(9)	51.0(1)	Cr(5)Cr(4)S(9)	98.2(2)
Cr(6)Cr(4)S(9)	51.1(0)	S(6)Cr(4)S(9)	100.7(2)
S(7)Cr(4)S(9)	101.1(2)	Fe(2)Cr(5)Cr(4)	59.7(1)
Fe(2)Cr(5)Cr(6)	59.7(1)	Cr(4)Cr(5)Cr(6)	60.4(1)
Fe(2)Cr(5)S(6)	97.8(2)	Cr(4)Cr(5)S(6)	51.2(2)
Cr(6)Cr(5)S(6)	51.3(1)	Fe(2)Cr(5)S(7)	51.3(1)
Cr(4)Cr(5)S(7)	51.4(1)	Cr(6)Cr(5)S(7)	98.9(1)
S(6)Cr(5)S(7)	101.4(2)	Fe(2)Cr(5)S(8)	50.4(2)
Cr(4)Cr(5)S(8)	98.2(1)	Cr(6)Cr(5)S(8)	51.3(1)
S(6)Cr(5)S(8)	101.6(2)	S(7)Cr(5)S(8)	100.1(2)
Fe(2)Cr(6)Cr(4)	59.8(1)	Fe(2)Cr(6)Cr(5)	60.2(1)
Cr(4)Cr(6)Cr(4)	60.0(1)	Fe(2)Cr(6)S(6)	98.1(2)
Cr(4)Cr(6)Cr(5)	50.9(2)	Cr(5)Cr(6)S(6)	51.1(1)
Fe(2)Cr(6)S(8)	50.7(2)	Cr(4)Cr(6)S(8)	98.0(2)
Cr(5)Cr(6)S(8)	51.6(1)	S(6)Cr(6)S(8)	101.7(2)
Fe(2)Cr(6)S(9)	51.2(1)	Cr(4)Cr(6)S(9)	51.2(1)
Cr(5)Cr(6)S(9)	98.6(2)	S(6)Cr(6)S(9)	100.8(2)
S(8)Cr(6)S(9)	100.5(2)	Cr(1)S(1)Cr(2)	77.9(2)
Cr(1)S(1)Cr(3)	77.8(2)	Cr(2)S(1)Cr(3)	76.5(2)
Fe(1)S(2)Cr(1)	75.9(2)	Fe(1)S(2)Cr(3)	77.6(2)
Cr(1)S(2)Cr(3)	76.9(2)	Fe(1)S(3)Cr(2)	76.6(2)
Fe(1)S(3)Cr(3)	77.5(2)	Cr(2)S(3)Cr(3)	76.2(2)
Fe(1)S(4)Cr(1)	76.3(2)	Fe(1)S(4)Cr(2)	77.1(2)
Cr(1)S(4)Cr(2)	77.7(2)	Fe(1)S(5)Fe(2)	87.9(2)
Fe(1)S(5)Fe(3)	75.1(2)	Fe(2)S(5)Fe(3)	73.9(2)
Cr(4)S(6)Cr(5)	78.0(2)	Cr(4)S(6)Cr(6)	78.2(2)
Cr(5)S(6)Cr(6)	77.6(2)	Fe(2)S(7)Cr(4)	76.9(2)
Fe(2)S(7)Cr(5)	77.1(2)	Cr(4)S(7)Cr(5)	77.2(2)
Fe(2)S(8)Cr(5)	77.9(2)	Fe(2)S(8)Cr(6)	77.5(2)
Cr(5)S(8)Cr(6)	77.1(2)	Fe(2)S(9)Cr(4)	77.2(2)
Fe(2)S(9)Cr(6)	77.0(2)	Cr(4)S(9)Cr(6)	77.7(2)
Fe(3)C(1)O(1)	177.7(20)	Fe(3)C(2)O(2)	178.5(17)
Fe(3)C(3)O(3)	177.4(20)		

whose transformation into a well-known bi-tetrahedral structure $[(SPh)_3Fe_3(\mu_3\text{-}S)_4Mo]_2(\mu\text{-}SPh)_3Fe(\mu\text{-}SPh)_3$ [7] would be quite natural. Taking into account the similarity of $Fe_4(SPh)_4S_4^{n-}$ tetrahedra to $Cp_4Cr_4S_4$, complex IV may be anticipated to model the catalytically active centre of the MoFeS cofactor of nitrogenase, though with different transition elements. From this point of view projection of the benzene solvating molecule in the cavity of the cluster IV seems very interesting. It means that there is in principle a possibility of incorporation of the nitrogen molecule with participation or substitution of the $(CO)_3FeS$ group.

Experimental

All operations connected with synthesis of both initial and final products were performed in a flow of pure dry argon in absolute solvents. $Fe_2(SPh)_2(CO)_6$ was obtained as previously described [8]. IR-spectra of preparations in KBr pellets were measured with a Specord 75 IR instrument.

Table 7

Crystal data for the clusters $Cp_3Cr_3(\mu_3\text{-}S)_4FeSPh$ (III) and $[Cp_3Cr_3(\mu\text{-}S)_4Fe]_2(\mu\text{-}S \equiv Fe(CO)_3)\cdot C_6H_6$ (IV)

	III	IV
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a, Å	7.946(1)	14.800(3)
b, Å	20.549(2)	18.033(4)
c, Å	14.480(1)	18.224(4)
α, °	90	90
β, °	92.5561(8)	109.92(3)
γ, °	90	90
V	2351.6	4573
Z	4	4
$2\theta_{max}$	56	56
Number of reflections measured	2537	4446
Number of independent reflections with $I > 3\sigma(I)$	1162	2450
R_1	0.087	0.056
R_2	0.069	0.065

X-ray structural data were obtained with automatic diffractometers (Hilger & Watts and Siemens) (λ(Mo-K_α), θ-2θ scan, 20 °C). Crystal data are presented in Table 7. The structures were solved by a direct method and refined in full-matrix anisotropic approximation for all non-hydrogen atoms.

$Cp_3Cr_3(\mu_3\text{-}S)_4FeSPh$ (III)

The red-brown solution containing 0.12 g (0.25 mM) of $Fe_2(\mu\text{-}SPh)_2(CO)_6$ in 10 ml of toluene was added to a solution of 0.5 g (1.2 mM) of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2S$ in 10 ml of toluene and refluxed for 2 h. The resulting brown solution was concentrated to 7 ml and left to cool slowly. Large dark-brown crystals were precipitated within a day and were isolated by decantation, washed in cold benzene and dried at room temperature in an argon flow. Yield 0.08 g (51.6% relative $Fe_2(\mu\text{-}SPh)_2(CO)_6$). IR-spectrum ($\nu$, cm^{-1}): 720s, 805s, 1010m, 1440m, 2900–3400w br.

$[Cp_3Cr_3(\mu_3\text{-}S)_4Fe]_2Fe(CO)_3S\cdot C_6H_6$ (IV)

The red-brown solution containing 0.16 g (0.34 mM) of $Fe_2(\mu\text{-}SPh)_2(CO)_6$ in 10 ml of toluene was added to the violet solution of 0.3 g (0.67 mM) of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2S$ in 10 ml of toluene and refluxed for 2 h to give a brown solution. 10 ml of benzene was added to this solution and the mixture was concentrated to 5 ml and left to cool slowly to room temperature. Large black crystals were isolated by decantation, washed in benzene and dried in an argon flow. The yield of the crystals was 0.26 g (65.3%). IR-spectrum (ν, cm^{-1}): 675 m, 810 s, 1000w br, 1095 m br, 1200m br, 1440m br, 1625w br, 1885w br, 1925m, 1990s, 2900–3100w br.

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