Formation of antiferromagnetic heteronuclear thiolate and sulfide bridged complexes

II. Synthesis, magnetic properties, and molecular structures of the clusters $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_4\text{-}S)W_2(\mu\text{-}I)_2(CO)_4(NO)_2$ and $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2W(SCMe_3)(NO)$

Igor L. Eremenko, Heinz Berke and Adolphus A.H. van der Zeijden

Institute of Inorganic Chemistry, Zurich University, Winterthurerstr. 190, CH-8057 Zurich (Switzerland)

Boris I. Kolobkov and Vladimir M. Novotortsev

Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Leninsky prosp. 31, 117907 Moscow (Russian Federation)

(Received September 8, 1993)

Abstract

The reaction between the antiferromagnetic complex $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (**1**) and $WI(CO)_4(NO)$ (**2**) was studied. At 40–50°C the predominant product was the antiferromagnetic adduct $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_4\text{-}S)W_2(\mu\text{-}I)_2(CO)_4(NO)_2$ (**3**) (Cr–Cr 2.764(4) Å, W ··· W 3.559(1) Å, $-2J = 338\ cm^{-1}$), in which a sulfur atom bridges all four metal atoms. Further heating of **3** in the presence of an excess of **1** afforded the trinuclear antiferromagnetic cluster $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2W(SCMe_3)(NO)$ (**7**) (W–Cr 3.090(1) Å, Cr–Cr 3.027(1) Å, $-2J = 246\ cm^{-1}$) which can also be prepared by direct reaction between **1** and **2** (ratio 3:2) at 80°C in toluene. It is suggested that this process *via* the formation of an unstable intermediate $CpCr(\mu\text{-}SCMe_3)_2(\mu\text{-}S)W(CO)_2(NO)$. In an attempt to use the trinuclear cluster $Fe_3S_2(CO)_9$ as a metal containing ligand for **2**, the known iron clusters $Fe_2S_2(CO)_6$ and $(ON)_4Fe_4S_4$ were isolated. All products, including the two iron clusters, were characterized by X-ray diffraction studies at −60°C.

Key words: Chromium; Tungsten; Bridging ligand; Thiolate; Nitrosyl; Cluster

1. Introduction

Recently we have shown, that the binuclear antiferromagnetic complex $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (**1**) can act as an unusual metal-containing ligand towards a variety of unsaturated metal fragments ML_n following cluster "block building" [1,2] sequences. For instance, **1** and $[ReCl_2(CO)_2(NO)]$ as ML_n, generated from its dimer, can be used for the preparation of thiolate- and sulfide-bridged Cr,Re clusters, bearing a Re(NO)(CO) unit [2]. For this process to take place an initial remetallation process must occur. The tetranuclear paramagnetic unit $[CpCr(\mu\text{-}SCMe_3)_2(\mu_3\text{-}S)Re(CO)(NO)]_2$ is presumably formed via the unstable precursor $CpCr(\mu\text{-}SCMe_3)_2(\mu\text{-}S)Re(CO)_2(NO)$. In this paper we report on the syntheses of new Cr,W clusters prepared by reaction of **1** with $WI(CO)_4(NO)$ (**2**). By loss of CO **2** can serve as a source of unsaturated ML_n units, but, in contrast to $[ReCl_2(CO)_2(NO)]$, it contains only a single halogen atom as a potentially connecting ligand, initiating cluster formation with various topological patterns.

Correspondence to: Professor I.L. Eremenko or Professor H. Berke.

2. Results and discussion

Upon gentle heating and in the presence of PR_3 ligands the mononuclear complex $WI(CO)_4(NO)$ (**2**) [3] very easily loses two CO groups and gives complexes of the type $WI(CO)_2(PR_3)_2(NO)$ [4], which are isoelec-

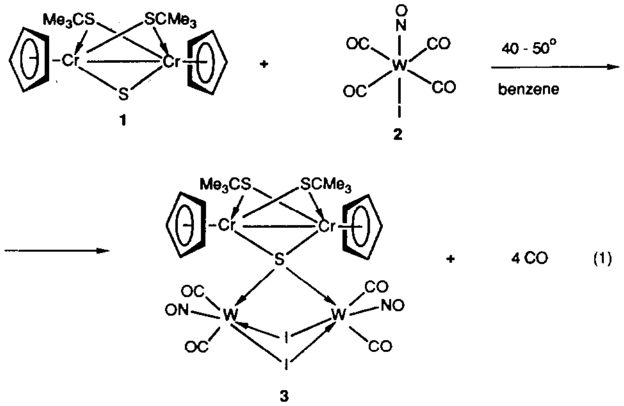
0022-328X/94/$7.00
SSDI 0022-328X(93)24236-X

tron with the Re containing complexes $ReCl_2(PR_3)_2(CO)(NO)$ [5]. We therefore expected that $WI(CO)_4(NO)$ would be a valuable starting material for the construction of new chromium and tungsten containing antiferromagnetic complexes. The first syntheses of $WX(CO)_4(NO)$ (X = Cl, Br, I) were reported in 1973 [3a], but the 80% yield reported for $WBr(CO)_4(NO)$ could not be reproduced by us or others [3b]. Other attempts to synthesize $WX(CO)_4(NO)$ resulted in low yields ($\leq 25\%$) and contamination with $W(CO)_6$ [3]. There was thus an obvious need for a high yield synthesis of this interesting class of compound. The main problem appeared to be the reaction of the starting compound $[R_4N][WX(CO)_5]$ [6] with nitrosylating reagents, giving varying yields of $W(CO)_6$ as a major by-product. We found that dry $NOBF_4$ or $NOPF_6$ in CH_2Cl_2 are the best reagents, but the yield of $WX(CO)_4(NO)$ is strongly dependent on X and falls on going from I to Cl from *ca.* 80 to 20%. The method thus seems to be limited to the synthesis of $WI(CO)_4(NO)$ (**2**). The contamination by *ca.* 20% of $W(CO)_6$ may not present a big problem, since the replacement of CO groups in **2** proceeds at much lower temperatures (≤ 40°C) than in the case of $W(CO)_6$, which requires more violent conditions (boiling THF and UV-irradiation) to give $Cp_2Cr_2(SCMe_3)_2(\mu_3\text{-}S)W(CO)_5$ [7].

2.1. Formation of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_4\text{-}S)W_2(\mu\text{-}I)_2(CO)_4(NO)_2$ (3)

Complex **1** reacts with **2** in benzene at 40–50°C (ratio 1:2) with visible elimination of CO and formation of a single product, the tetranuclear species $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_4\text{-}S)W_2(\mu\text{-}I)_2(CO)_4(NO)_2$ (**3**) (eqn. (1)).

The IR spectrum of **3** exhibits characteristic ν(CO) (2000 and 1909 cm^{-1}) and ν(NO) (1638 cm^{-1}) bands.



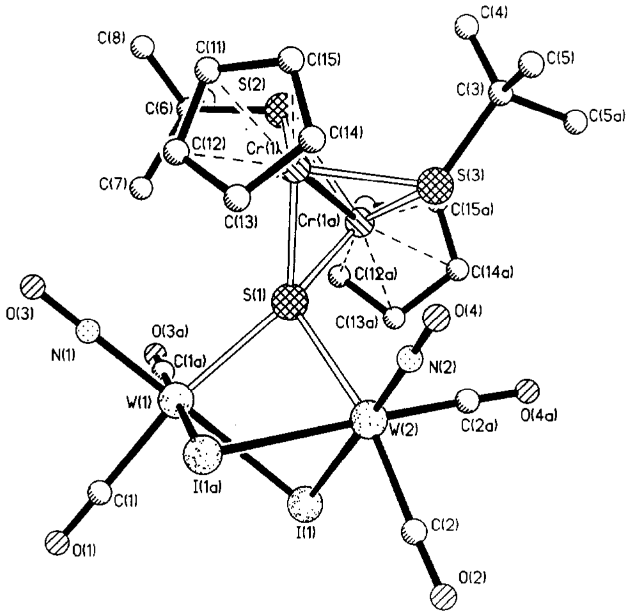


Fig. 1. Molecular structure of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_4\text{-}S)W_2(\mu\text{-}I)_2(CO)_4(NO)_2$ (**3**).

The structure of the molecule was established by an X-ray diffraction study (Fig. 1, Table 1). The two $W(CO)_2(NO)$ fragments in **3** are joined together by two bridging iodine atoms (W–I 2.889(2) and 2.886(2) Å, W–I–W 76.1(1)°) and one bridging sulfur atom (W–S 2.551(5) Å, W–S–W 88.1(2)°). The latter atom also

TABLE 1. Selected bond lengths (Å) and angles (°) in 3

W(1)–I(1)	2.889(2)	W(1)–S(1)	2.551(5)
W(1)–N(1)	1.905(12)	W(1)–C(1)	2.027(23)
W(2)–I(1)	2.886(2)	W(2)–S(1)	2.566(5)
W(2)–N(2)	1.870(13)	W(2)–C(2)	2.001(20)
Cr(1)–S(1)	2.357(5)	Cr(1)–S(2)	2.351(5)
Cr(1)–S(3)	2.362(5)	Cr(1)–Cr(1A)	2.764(4)
O(1)–C(1)	1.115(30)	O(2)–C(2)	1.144(26)
O(3)–N(1)	1.169(17)	O(4)–N(2)	1.195(17)
W(1)···W(2)	3.559(1)	W(1)···Cr(1)	4.490(2)
W(2)···Cr(1)	4.225(2)		
I(1)–W(1)–S(1)	82.4(1)	I(1)–W(1)–N(1)	178.0(4)
S(1)–W(1)–N(1)	97.8(4)	I(1)–W(1)–C(1)	89.6(5)
S(1)–W(1)–C(1)	169.1(7)	N(1)–W(1)–C(1)	89.9(6)
I(1)–W(1)–I(1A)	84.5(1)	I(1)–W(2)–S(1)	82.2(1)
I(1)–W(2)–N(2)	177.2(4)	S(1)–W(2)–N(2)	97.3(4)
I(1)–W(2)–C(2)	89.7(4)	S(1)–W(2)–C(2)	169.0(6)
N(2)–W(2)–C(2)	90.5(6)	W(1)–I(1)–W(2)	76.1(1)
S(1)–Cr(1)–S(2)	95.3(2)	S(1)–Cr(1)–S(3)	81.8(2)
S(2)–Cr(1)–S(3)	89.3(2)	W(1)–S(1)–W(2)	88.1(2)
W(1)–S(1)–Cr(1)	132.3(1)	W(2)–S(1)–Cr(1)	118.2(2)
Cr(1)–S(1)–Cr(1A)	71.8(2)	Cr(1)–S(2)–Cr(1A)	72.0(2)
Cr(1)–S(3)–Cr(1A)	71.6(2)	W(1)–N(1)–O(3)	178.6(9)
W(2)–N(2)–O(4)	178.2(12)	W(1)–C(1)–O(1)	179.2(14)
W(2)–C(2)–O(2)	177.9(18)		

connects the two Cr centers (Cr–S 2.357(5) Å, Cr–S–Cr 71.8(2)°). As a consequence of π electron donation from the S atom to the W centers bearing the acceptor NO ligands, there is a weakening of the Cr–Cr bond (Cr–Cr 2.764(4) Å, Cp(centroid)CrCr 179.3(1)°). This Cr–Cr distance is longer than that in **1** (Cr–Cr 2.689(8) Å, Cp(centroid)CrCr 177.5(9)°) [8] or in the $Cp_2Cr_2(\mu$-$SCMe_3)_2(\mu_3$-$S)W(CO)_5$ adduct (**4**) containing CO ligands only (Cr–Cr 2.73(1) Å, Cp(centroid)CrCr 178.6(11)°) [7]. A similar effect is found in the two isomers of $Cp_2Cr_2(\mu$-$SCMe_3)_2(\mu_3$-$S)ReCl_2(CO)_2(NO)$ (**5**) in which the Cr–Cr separations (**5a** (isomer with a *cis* SRe(NO) unit), Cr–Cr 2.777(6) Å, Cp(centroid)CrCr 177.0(4)°; **5b** (isomer with a trans SRe(NO) unit), Cr–Cr 2.788(3) Å, Cp(centroid)CrCr 179.7(1)°) [2] are significantly longer than those in **1** or in $Cp_2Cr_2(\mu$-$SCMe_3)_2(\mu_3$-$S)Re_2(CO)_9$ (**6**) (Cr–Cr 2.732(2) Å, Cp(centroid)CrCr 176.7(1)°) [9]. However, the relatively small geometrical changes within the dichromium unit of **1** in **3**, **5a** and **5b** have a strong effect on the

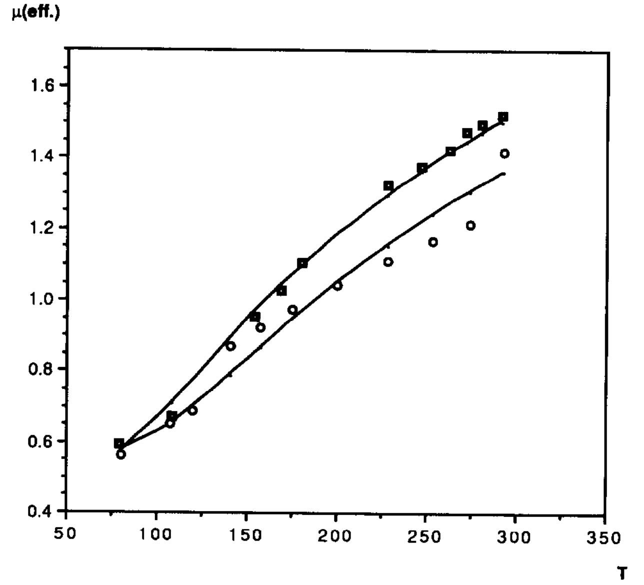
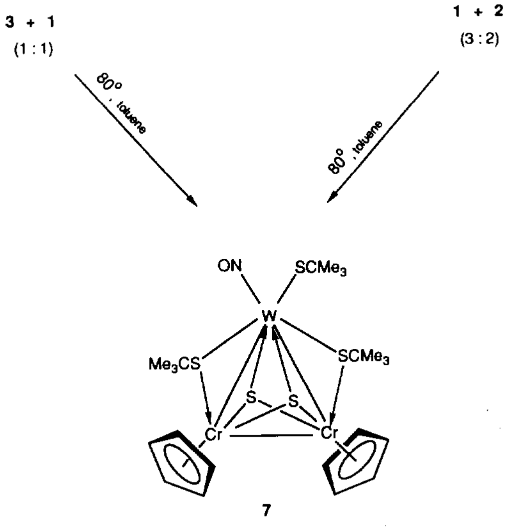


Fig. 2. Plot of the theoretical (line) and experimental dependence of the magnetic moment μ_{eff} for **3** (○) and **7** (□).

TABLE 2. Geometric parameters and magnetic properties of the Cp_2Cr_2 moiety in the adducts $Cp_2Cr_2(\mu$-$SCMe_3)_2(\mu_m$-$S)ML_n$ and clusters $Cp_2Cr_2(\mu_3$-$S)_2(\mu$-$SCMe_3)_2ML_n$ (M = Re, W)

N	ML_n	Cr–Cr dist. (Å)	Cp(cen)CrCr (°), av.	μ_{eff}/Cr at. μ_B, (temp. range, K)	Exchange parametr −2J (cm^{-1})	Least sq. err. (%)	Ref
1	–	2.689(8)	177.5(9)	0.98–0.02 (297–79)	430	3.2	6
$Cp_2Cr_2(\mu$-$SCMe_3)_2(\mu_m$-$S)ML_n$ adducts							
4	$W(CO)_5$ ($m = 3$)	2.73(1)	178.2(9)	1.09–0.04 (295–77)	440	3.8	7
6	$Re_2(CO)_9$ ($m = 3$)	2.732(2)	176.7(1)	1.29–0.32 (296–77)	424	3.8	8
3	$W_2J_2(CO)_4$-$(NO)_2$ ($m = 4$)	2.764(4)	179.3(4)	1.42–0.56 (291–79)	338	4.9	This work
5a	$ReCl_2(CO)_2$-(NO)(*cis*-SRe(NO)) ($m = 3$)	2.777(6)	177.0(5)	1.36–0.60 (291–79)	328	4.7	2
5b	$ReCl_2(CO)_2$-(NO)(*trans*-SRe(NO)) ($m = 3$)	2.788(3)	179.3(1)	1.39–0.62 (291–79)	328	2.2	2
$Cp_2Cr_2(\mu_3$-$S)_2(\mu$-$SCMe_3)_2ML_n$ clusters							
9	$Re_2(CO)_6$	2.96(1)	137.5(9)	1.50–0.72 (292–79)	302	3.0	8
8	Re(CO)(NO)	3.010(6)	126.5(6)	1.67–0.55 (288–79)	231	2.4	2
7	$W(SCMe_3)(NO)$	3.027(1)	126.9(1)	1.52–0.59 (291–79)	246	2.4	This work



7

(2)

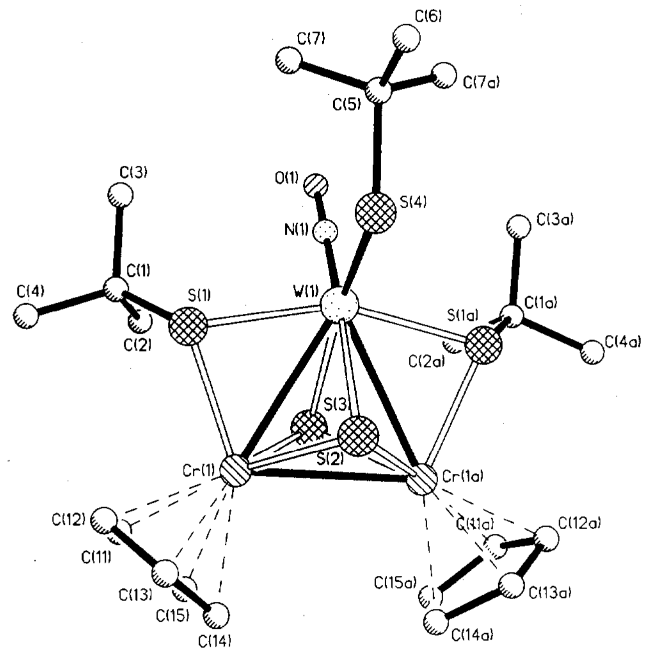


Fig. 3. Molecular structure of $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2\text{-}W(SCMe_3)(NO)$ (7).

magnetic properties (Fig. 2, Table 2). The energy of the spin-spin exchange interaction between the two Cr^{III} atoms in 3 ($-2J = 338$ cm^{-1}) is essentially lower than that in the inital 1 ($-2J = 430$ cm^{-1}) [8], 4 ($-2J = 440$ cm^{-1}) [7] or 6 ($-2J = 424$ cm^{-1}) [9] but is close to the value for **5a** and **5b** ($-2J = 328$ cm^{-1} for both isomers) [2].

The formation of **3** containing a dimeric W_2I_2 unit is presumably the essential step in the process of Cr,W cluster formation. Use of an stoichiometric excess of **1** or **2** does not change the type of products in the reaction of **1** with **2**. An increase of the reaction temperature from 40–50°C (benzene) to 80°C (toluene), however, has a strong influence on the product selectivity.

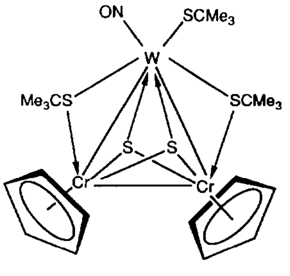
2.2. *Formation of* $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2\text{-}W(SCMe_3)(NO)$ *(7)*

If **3** is treated with an equimolar amount of **1** or if **1** and **2** are mixed in the molar ratio 3:2 at 80°C in toluene, a new cluster $Cp_2Cr_2(\mu_3\text{-}S)(\mu\text{-}SCMe_3)_2\text{-}W(SCMe_3)(NO)$ (**7**) is formed as the major product (eqn. (2)).

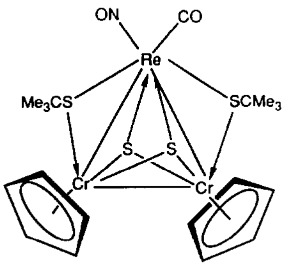
The IR spectrum of **7** shows a characteristic ν(NO) band (1588 cm^{-1}), but no ν(CO) absorption. The X-ray diffraction study reveals (Fig. 3, Table 3) that two sulfur atoms bridge a Cr_2W triangle (Cr–S 2.338(2) and 2.307(2) Å, W–S 2.582(2) and 2.590(2) Å). A crystallographic mirror plane contains the two sulfur atoms, the tungsten atom, the terminal $SCMe_3$ group (W–S 2.323(2) Å), and the NO ligand (W–N 1.776(7) Å, N–O 1.213(10) Å). The tungsten(II) atom in **7** possesses a 16 valence electron configuration (3 electrons from NO, 3e from 3SR groups, 4e from 2S and 6 own electrons) in contrast to the rhenium(I) atom in the comparable cluster $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2Re(CO)(NO)$ (**8**) [2] (Chart 1), in which the Re center is assigned an 18 electron environment (3 electrons from NO, 2e from CO, 2e from 2SR groups, 4e from 2S and 7 own

TABLE 3. Selected bond lengths (Å) and angles (°) in 7

W(1)–Cr(1)	3.090(1)	W(1)–S(1)	2.461(1)
W(1)–S(2)	2.582(2)	W(1)–S(4)	2.323(2)
W(1)–S(3)	2.590(2)	W(1)–N(1)	1.776(7)
Cr(1)–Cr(1A)	3.027(1)	Cr(1)–S(1)	2.380(2)
Cr(1)–S(2)	2.338(2)	Cr(1)–S(3)	2.307(2)
O(1)–N(1)	1.213(10)		
Cr(1)–W(1)–S(1)	49.2(1)	Cr(1)–W(1)–S(2)	47.7(1)
S(1)–W(1)–S(2)	80.4(1)	Cr(1)–W(1)–S(4)	120.2(1)
S(1)–W(1)–S(4)	95.6(1)	S(2)–W(1)–S(4)	85.8(1)
Cr(1)–W(1)–S(3)	46.9(1)	S(1)–W(1)–S(3)	81.8(1)
S(2)–W(1)–S(3)	77.8(1)	S(4)–W(1)–S(3)	163.6(1)
Cr(1)–W(1)–N(1)	127.3(2)	S(1)–W(1)–N(1)	98.8(1)
S(2)–W(1)–N(1)	173.4(2)	S(4)–W(1)–N(1)	100.8(2)
S(3)–W(1)–N(1)	95.6(2)	Cr(1)–W(1)–Cr(1A)	58.7(1)
S(1)–W(1)–Cr(1A)	107.8(1)	S(2)–W(1)–Cr(1A)	47.7(1)
S(4)–W(1)–Cr(1A)	120.2(1)	S(3)–W(1)–Cr(1A)	46.9(1)
N(1)–W(1)–Cr(1A)	127.3(2)	W(1)–Cr(1)–S(1)	51.5(1)
W(1)–Cr(1)–S(2)	54.7(1)	S(1)–Cr(1)–S(2)	87.2(1)
W(1)–Cr(1)–S(3)	55.1(1)	S(1)–Cr(1)–S(3)	89.8(1)
S(2)–Cr(1)–S(3)	88.8(1)	W(1)–S(1)–Cr(1)	79.3(1)
W(1)–S(2)–Cr(1)	77.6(1)	Cr(1)–S(2)–Cr(1A)	80.7(1)
W(1)–S(3)–Cr(1)	78.0(1)	Cr(1)–S(3)–Cr(1A)	82.0(1)
W(1)–N(1)–O(1)	178.6(6)		



7



8

Chart 1.

electrons). The electron deficiency of the W^{II} center apparently leads to a significant weakening of the $Cr \leftarrow W$ donor bonding in **7** (3.090(1) Å) compared with that of the $Cr \leftarrow Re$ bond (2.900(5) Å) (tungsten and rhenium atoms have similar covalent radii [10], 1.58 and 1.59 Å. In **8** the $Cr \leftarrow SCMe_3$ bond is elongated (2.759 Å), presumably because the bonding of the SR groups is in strong competition with the binding of the electron donating Re moiety [2]. Correspondingly, the weakening of the $Cr \leftarrow W$ bond in **7** strengthens the $Cr \leftarrow SCMe_3$ interactions (Cr–S 2.380(2) Å). The Cp_2Cr_2 fragment in **7** as in **8**, adopts a bent geometry (Cp(centroid)CrCr 126.9(1)°) that does not allow effective overlap of the σ type orbitals of the chromium atoms [11]. For this reason the Cr–Cr distance (3.027(1) Å) is very long. The magnetic properties of **7** (Fig. 2, Table 2) and **8** are similar, as demonstrated by their exchange parameters (**7**, $-2J = 338$ cm^{-1}; **8**, $-2J = 328$ cm^{-1}). These values are lower than those for $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu_3\text{-}SCMe_3)_2Re_2(CO)_6$ (**9**) ($-2J = 302$ cm^{-1}) which contains no nitrosyl ligands. Its Cp_2Cr_2 fragment lies closer to a linearly arranged unit (Cp(centroid)CrCr 137.5(9)°) giving rise to a shorter Cr–Cr distance (2.96(1) Å) [9]. Thus in clusters **7**, **8**, and **9**, containing the same magnetic core, $Cp_2Cr_2S_2$, but having different $(Me_3CS)_2ML_n$ moieties (**7**, ML = W(SCMe$_3$)(NO); **8**, ML_n = Re(CO)(NO) [2]; **9**, $ML_n = Re_2(CO)_6$ [9]), there is a clear correlation between magnetic properties and the Cr–Cr distances in the paramagnetic units (Table 2).

It is likely that the process of cluster assembly of **7** resembles that of **8** [2]. It presumably proceeds *via* the unstable remetallation intermediate $CpCr(\mu\text{-}SCMe_3)_2\text{-}(\mu\text{-}S)W(CO)_2(NO)$ (**10**), which contains one electron less than its Cr,Re analogue. In the intermediate **10** the tungsten center has an unusual oxidation state of

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for $Fe_2S_2(CO)_6$ [a]

	x	y	z	U_{eq}
Fe(1)	1386(2)	10086(1)	2197(1)	26(1)
Fe(2)	2915(2)	6854(1)	2628(1)	27(1)
S(1)	2389(4)	8046(3)	825(2)	40(1)
S(2)	4720(3)	8777(2)	1428(2)	34(1)
O(1)	5750(11)	3461(8)	2040(7)	66(3)
O(2)	3801(11)	7190(8)	4972(5)	49(2)
O(3)	−1079(10)	5507(8)	3618(7)	61(3)
O(4)	1826(10)	11558(8)	4351(6)	49(2)
O(5)	907(12)	13453(8)	744(7)	63(3)
O(6)	−3104(9)	9776(8)	3197(6)	49(2)
C(1)	4695(13)	4773(10)	2266(8)	42(3)
C(2)	3461(12)	7055(9)	4062(7)	34(2)
C(3)	491(13)	6028(9)	3239(8)	40(3)
C(4)	1675(12)	10969(9)	3514(6)	32(2)
C(5)	1096(13)	12135(10)	1283(7)	39(3)
C(6)	−1359(12)	9917(9)	2806(7)	35(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for $Fe_4S_4(NO)_4$ [a]

	x	y	z	U_{eq}
Fe(1)	4196(2)	1592(2)	3145(1)	21(1)
Fe(2)	2172(2)	1952(2)	1531(1)	22(1)
Fe(3)	1413(2)	969(2)	3556(2)	24(1)
Fe(4)	2125(2)	3234(2)	3474(1)	22(1)
S(1)	3864(4)	3237(3)	2114(3)	26(1)
S(2)	202(4)	2392(3)	2609(3)	27(1)
S(3)	2925(4)	1909(3)	4777(2)	26(1)
S(4)	2914(4)	203(3)	2209(3)	26(1)
O(1)	7215(12)	976(10)	3282(9)	37(3)
O(2)	1986(15)	2125(12)	−943(8)	48(4)
O(3)	−436(15)	−615(11)	4825(10)	51(4)
O(4)	1280(17)	5481(10)	4354(9)	48(4)
N(1)	5971(13)	1233(9)	3243(9)	25(3)
N(2)	1998(14)	2034(9)	72(8)	26(3)
N(3)	342(13)	−4(10)	4276(10)	30(3)
N(4)	1664(16)	4568(10)	3984(10)	34(4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

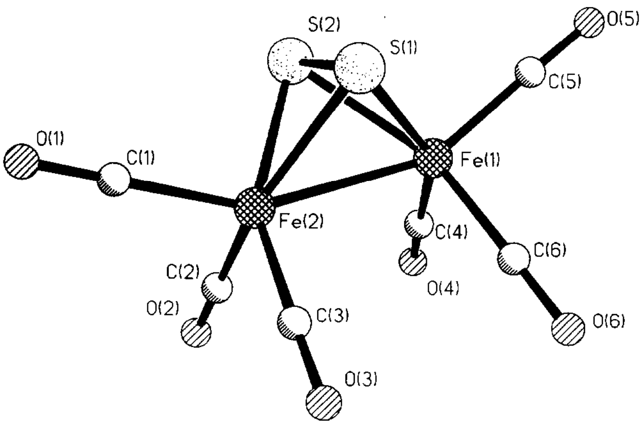


Fig. 4. Molecular structure of $Fe_2S_2(CO)_6$.

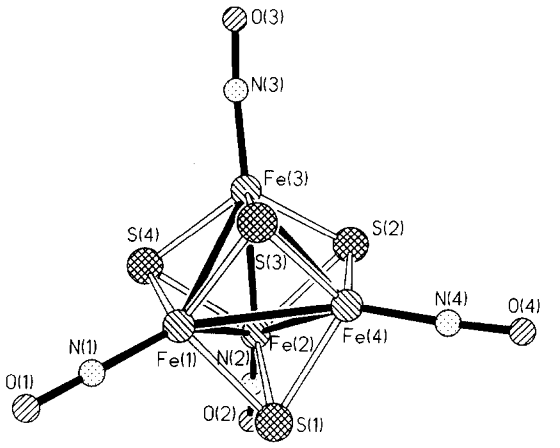


Fig. 5. Molecular structure of $Fe_4S_4(NO)_4$.

+1 and is oxidized in a subsequent reaction step involving **1**.

2.3. *Interaction of $WI(CO)_4(NO)$ with $Fe_3(\mu_3\text{-}S)_2(CO)_9$*

The 50 electron cluster $Fe_3S_2(CO)_9$ (**11**) contains two Fe–Fe bonds (2.582(9) and 2.609(10) Å) [12] and one lone pair on each sulfide bridge that in principle may be used for coordinative interactions with unsaturated metallofragments ML_n. As in the case of $(PPh_3)_2PdCl_2$, a remetallation reaction may take place. The Pd reaction gave a heteronuclear cluster $(PPh_3)_2Pd(\mu_3\text{-}S)_2Fe_2(CO)_6$ [13,14]. In an attempt to prepare analogous Fe,W,S species **2** was treated with **11** but this produced only $Fe_2S_2(CO)_6$ and $Fe_4S_4(NO)_4$ as soluble components and an insoluble brown powder containing no CO and NO groups (IR monitoring) at various temperatures (40–80°C) and in varying reagent ratios (from 2:1 to 1:2). The best result was obtained for a 1:1 reagent ratio with complete conversion of the inital reagents. The known compounds $Fe_2S_2(CO)_6$ [12] and $Fe_4S_4(NO)_4$ [15] were identified by mass and IR spectroscopy and by X-ray diffraction studies at −60°C (Tables 4 and 5, Figs. 4 and 5, [16*]).

Although the formation of an $Fe_4S_4(NO)_4$ compound indicates a ligand exchange process in the reaction of **2** and **11**, there is no noticeable transfer of I atoms. The iodine is a soft-acid ligand and the strong competition between the formation of new M–S and M–I bonds possibly prevents a transfer of I to the iron atom with formation of FeI_2. In this respect the behaviour differs from that of the Pd complex, where a remetallation process yields $FeCl_2$ [13].

* Reference number with asterisk indicates a note in the list of references.

3. Conclusion

The antiferromagnetic clusters $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2M(NO)L$ (**7**, ML = $W(SCMe_3)$; **8**, ML = Re(CO)) can be made starting from **1** and a suitable unsaturated precursor ML_n, which leads to the adducts **3** or **5** bearing two halogen atoms. Subsequent reaction of these adducts in the presence of **1** leads, with remetallation, to $CpCr(\mu\text{-}SCMe_3)_2(\mu\text{-}S)M(CO)_2(NO)$ (M = W, Re). Depending on the electronic nature of M the formal oxidation state may be preserved (M = Re) or increased (M = W). The presence of a NO ligand bonded to M (M = W, Re) has a significant influence on the electron density distribution in the dichromium fragments in the adducts **3** or **5** and clusters **7** and **8**. This can be seen from changes of the Cr–Cr distances and from differences in the bending of the Cp_2Cr_2 moieties. As a consequence these structural changes affect the magnetic properties of these compounds.

4. Experimental details

4.1. *General comments*

All operations, including the syntheses of the starting compounds were carried out under dry oxygen-free nitrogen by standard Schlenk techniques. Benzene and toluene were purified by distillation from sodium/benzophenone ketyl. Hexane and heptane were dried by boiling over sodium. Dichloromethane (CH_2Cl_2) was purified by double distillation from P_2O_5. Thin layer chromatography (TLC) (Merck, 5 × 7.5 cm^2, Kieselgel 60 F_{254}) was used when possible to monitor the progress of the reaction under study. Column chromatography was on Kieselgel 60 (Merck, 70–230 mesh ASTM). The starting material $Cp_2Cr_2(SCMe_3)_2S$ (**1**) was prepared as described elsewhere [8]. Infrared spectra were obtained with a Bio-Rad FTS-45 spectrometer in KBr pellets. Mass spectra were measured on a Finnigan MAT 8320 (70 eV).

4.2. *Preparation of $WI(CO)_4(NO)$ (2)*

To a solution of 3.50 g (3.97 mmol) of $[^nBu_4N][WI(CO)_5]$ [6] in 30 ml of CH_2Cl_2 was added dry solid, $NOBF_4$ at room temperature, until all of the **2** had reacted (IR monitoring). Removal of solvent *in vacuo* left a yellow residue, which was recrystalized from hot hexane. The resulting yellow solid consists of *ca.* 80% of **2** and 20% of $W(CO)_6$. IR, ν cm^{-1}: (CH_2Cl_2 or THF) 2048 (vs), 1704 (m); (hexane) 2048 (vs), 1709 (m).

4.3. *Reaction of $(\eta^5\text{-}C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (1) with $WI(CO)_4(NO)$ (2) (ratio 1:2) at 40–50°C*

A violet solution of **1** (120 mg, 0.27 mmol) and **2** (230 mg, 0.46 mmol) in benzene (50 ml) was stirred at

TABLE 6. Data collection and processing parameters for **3**, **7**, $Fe_2S_2(CO)_3$ and $Fe_4S_4(NO)_4$

Compound	**3**	**7**
Formula	$C_{22}H_{28}Cr_2I_2N_2O_6S_3W_2$	$C_{22}H_{37}Cr_2NOS_5W$
Mol. wt	1238.1	779.7
Colour and habit	Brown-green prism	Green prism
Space group	*Pnma* (No 62)	*Pnma* (No 62)
a (Å)	21.039(11)	18.077(3)
b (Å)	13.439(10)	15.283(3)
c (Å)	11.890(8)	10.338(2)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å^3)	3362(4)	2856(1)
Z	4	4
ρ_{calcd} (g cm^{-1})	2.452	1.813
Radiation; λ (Å)	Graphite-monochromator, MoKα; 0.71073	Graphite-monochromator, MoKα; 0.71073
Temp (°C)	−60	−60
Abs. coeff (cm^{-1})	96.21	52.05
Cryst. size (mm)	0.25 × 0.25 × 0.25	0.45 × 0.35 × 0.30
Scan type	$\omega-2\theta$	$\omega-2\theta$
Scan speed	Variable; 2.49–14.65	Variable; 2.49–14.65
Scan width	1.60	1.40
Collen range	$+h, +k, +l$	$+h, +k, +l$
2θ range	5–52	5–52
Unique data	3066	2909
Refl. obsd	$2167(F \geq 4\sigma(F))$	$2459(F \geq 6\sigma(F))$
No of variables	211	157
Weighting scheme	Unit weight	$w^{-1} = \sigma^2(F) + 0.0000F^2$
R	0.039	0.029
R_W	0.045	0.034
Residual extrema in final diff. Map (e Å^{-3})	1.08 to −1.09	1.67 to −1.03
Compound	$Fe_2S_2(CO)_6$	$Fe_4S_4(NO)_4$
Formula	$C_6Fe_2O_6S_2$	$Fe_4N_4O_4S_4$
Mol. wt	343.9	471.7
Colour and habit	Orange prism	Black-brown prism
Space group	P-1 (No 2)	$P2_12_12_1$ (No 19)
a (Å)	6.561(2)	9.060(3)
b (Å)	7.773(2)	11.287(3)
c (Å)	11.414(3)	11.440(3)
α (°)	83.64(2)	90
β (°)	75.79(2)	90
γ (°)	78.59(2)	90
V (Å^3)	552.0(3)	1169.8(3)
Z	2	4
ρ_{calcd} (g cm^{-1})	2.069	2.678
Radiation; λ (Å)	Graphite-monochromator, MoKα; 0.71073	Graphite-monochromator, MoKα; 0.71073
Temp (°C)	−60	−60
Abs. coeff (cm^{-1})	29.97	55.55
Cryst. size (mm)	0.50 × 0.40 × 0.15	0.35 × 0.20 × 0.10
Scan type	$\omega - 2\theta$	$\omega - 2\theta$
Scan speed	Variable; 2.49–14.65	Variable; 2.49–14.65
Scan width	1.70	1.70
Collen range	$+h \pm k \pm l$	$+h, +k, +l$
2θ range	5–60	4–60
Unique data	3170	1797
Refl. obsd	$2463(F \geq 8\sigma(F))$	$1505(F \geq 4\sigma(F))$
No of variables	145	145

TABLE 6 (continued)

Compound	$Fe_2S_2(CO)_6$	$Fe_4S_4(NO)_4$
Weighting scheme	Unit weight	Unit weight
R	0.054	0.048
R_W	0.070	0.058
Residual extrema in final diff.		
Map (e Å^{-3})	1.33 to −2.30	1.27 to −0.89

40–50°C. After 30 min a brown green solution was formed. At this stage TLC(CH_2Cl_2) indicated the absence of all starting materials and the formation of a single brown green band. It was separated by use of column chromatography (5 × 30 cm^2, silica gel, CH_2Cl_2). The solution was concentrated to 15 ml and after addition of 5 ml of heptane cooling to −5°C gave brown green prismatic crystals of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu_4\text{-}S)W_2(\mu\text{-}I)_2(CO)_4(NO)_2$ (**3**) (280 mg, 0.226 mmol, 83.7%). MS (FAB), m/z: 1238, $Cp_2Cr_2(SCMe_3)_2SW_2I_2(CO)_4(NO)_2$. IR, ν cm^{-1}: 3112 (w), 2960 (m), 2918 (m), 2854 (w), 2000 (vs), 1909 (vs), 1638 (vs), 1468 (w), 1452 (m), 1432 (w), 1391 (w), 1152 (m), 1066 (w), 1017 (w), 843 (w), 822 (s), 581 (w), 479 (w), 462 (w).

4.4. Reaction of 3 and 1 (ratio 1:1) at 80°C

A deep violet solution of **3** (395 mg, 0.5 mmol) and **1** (220 mg, 0.5 mmol) in toluene (50 ml) was stirred at 80°C for 2 h during which the colour changed to deep green. This solution was concentrated and chromatographed on silica gel (5 × 30 cm^2, CH_2Cl_2) to afford a major green band, traces of initial **1** and a black green starting zone (not isolated). The green solution (50 ml) was concentrated to 15 ml, heptane (5 ml) was added and cooling to −5°C gave green plates of $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2W(SCMe_3)(NO)$ (**7**) (372 mg, 0.447 mmol, 47.7%). MS (EI or FAB), m/z: 780, $Cp_2Cr_2(S)_2(SCMe_3)_2W(SCMe_3)(NO)$; 723, $Cp_2Cr_2(S)_2(SCMe_3)_2WS(NO)$; 691, $Cp_2Cr_2(S)_2(SCMe_3)_2W(NO)$; 643, $Cp_2Cr_2(S)_3(SCMe_3)W(NO)$; 577, $Cp_2Cr_2(S)_4W(NO)$; 547, $Cp_2Cr_2(S)_4W$; 515, $Cp_2Cr_2(S)_3W$; 483, $Cp_2Cr_2(S)_2W$; 451, $Cp_2Cr_2(S)W$, 419, Cp_2Cr_2W; 182, Cp_2Cr; 117, CpCr. IR, ν cm^{-1}: 3078 (w), 2980 (w), 2949 (m), 2914 (m), 2884 (m), 2850 (m), 1588 (vs), 1445 (m), 1429 (m), 1386 (m), 1166 (w), 1144 (m), 1070 (w), 1010 (m), 849 (w), 842 (w), 830 (s), 810 (s), 788 (m), 602 (w), 567 (w).

4.5. Reaction of 1 and 2 (ratio 3:2) at 80°C

A violet solution of **1** (750 mg, 1.65 mmol) and **2** (500 mg, 1.12 mmol) was stirred in toluene (60 ml) at 80°C for 3 h during which the colour changed to deep green. At this stage TLC (CH_2Cl_2) showed the presence of brown green and green bands and a green blue spot at the starting position. Both products were separated by column chromatography (5 × 30 cm^2, silica gel).

(i) Brown green solution in CH_2Cl_2/heptane (1:1) which gave brown green crystals of **3** (200 mg, 0.162 mmol, 14.4%).

(ii) Green solution in CH_2Cl_2 which gave green crystals of **7** (695 mg, 0.891 mmol, 79.6%).

4.6. Reaction of $Fe_3(\mu_3\text{-}S)_2(CO)_9$ (11) with 2 (ratio 1:2) at 80°C

A brown red solution of **11** (240 mg, 0.5 mmol) and **2** (450 mg, 1 mmol) was refluxed in benzene (50 ml) for 5.5 h. A deep brown precipitate, which displayed no ν(CO) and ν(NO) bands in the IR spectrum, was filtered off from a brown solution. The filtrate was concentrated and chromatographed on silica gel (5 × 30 cm^2) to give three fractions:

(i) A black brown solution in hexane which after concentration and cooling (−30°C), gave black brown prisms of $Fe_4S_4(NO)_4$ (80 mg, 0.169 mmol, 16.9%). MS (EI), m/z: 472, $Fe_4S_4(NO)_4$. IR, ν cm^{-1}: ν_{NO} 1762 (vs).

(ii) A yellow orange solution in hexane which gave yellow orange prismatic crystals of $Fe_2S_2(CO)_6$ (130 mg, 0.379 mmol, 37.9%). MS (EI), m/z: 344, $Fe_2S_2(CO)_6$. IR, ν cm^{-1}: ν_{CO} 2041 (vs), 2017 (vs), 1995 (vs), 1978 (vs).

(iii) A cherry brown solution in benzene/heptane (1:2) which gave cherry red crystals of inital **11** (80 mg, 0.165 mmol, 16.5%).

4.7. Magnetic measurements and calculations

The temperature dependence of the magnetic susceptibilities (χ_m) of compounds **3** and **7** were determined by the Faraday technique in the region 296–77 K, using an apparatus devised in the Institute of General and Inorganic Chemistry of the Russian Academy of Sciences [17]. Details of the calculations of the effective magnetic moment (Fig. 2) and exchange parameters (−2J) by use of Heisenberg–Dirac–Van Vleck (HDVV) model [18] were described earlier [2,19]. The values of magnetic moments, the calculated exchange parameters and least square errors are given in Table 2.

4.8. Crystal structure determinations

Green prisms of **7** were grown by slow cooling of a hot (70°C) benzene/heptane (1:1) solution to room temperature. Crystals of $Fe_2S_2(CO)_6$, **3** and $Fe_4S_4(NO)_4$ were obtained as described in the accounts of the syntheses. The crystals were all mounted in air on glass fibers using 5 min epoxy resin. The unit cells were determined and refined from 24 equivalent reflections with $2\theta \geq 22$–$26°$ and obtained from a Siemens R3/m four-circle diffractometer. Intensity data were corrected for Lorentz and polarization effects. Backgrounds were scanned for 25% of the peak widths on each end of the scan. Three reflections were monitored periodically for each compound as a check for crystal decomposition or movement. No significant variation in these standards was observed, and so no correction was applied. Details of crystal parameters, data collection and structure refinement are given in Table 6.

All structures were solved by use of direct methods to locate the transition metals and the sulfur atoms. The other atoms were located in subsequent difference Fourier maps. The DIFABS method [20] was used for the absorption correction of **3** and **7** at the stage of the isotropic approximation. An anisotropic refinement was applied to all non-hydrogen atoms. A disordering of the CMe_3 group bonded to the S(2) atom in **3** was observed. Two positions of this fragment were revealed and refinement of their population parameters gave a value close to 0.5. In **3** disordering of the W(CO)(NO) fragment, located in the crystallographic mirror plane was also found and so this unit was refined as a $W(NO)_2$ group. However, in Fig. 1 we have labelled one group as NO and the other one as CO. The H atoms of **3** and **7** were generated geometrically (C–H bond fixed at 0.96 A) and all were assigned the same isotropic temperature factor of U = 0.08 A^2. Computations were performed using the SHELXTL PLUS program package [21] on a VAXstation 3100 computer. Selected bond lengths and angles for **3** and **7** are given in Tables 1 and 2 and the positional parameters and the equivalent isotropic thermal parameters are listed in Tables 7 and 8. Full lists of bond lengths and angles and tables of thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

TABLE 7. Atom coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) of **3**

	x	y	z	U_{eq} [a]
W(1)	497(1)	2500	557(1)	31(1)
W(2)	2165(1)	2500	62(1)	28(1)
I(1)	1425(1)	1055(1)	1291(1)	39(1)
Cr(1)	1191(1)	3528(2)	−2820(2)	28(1)
S(1)	1181(2)	2500	−1214(4)	23(1)
S(2)	524(3)	2500	−3900(5)	44(2)
S(3)	2061(2)	2500	−3294(4)	27(1)
O(1)	−106(11)	2500	2975(16)	86(9)
O(2)	3194(8)	2500	1980(14)	55(6)
O(3)	−469(5)	4082(8)	−195(10)	57(4)
O(4)	2907(5)	4135(8)	−1165(10)	59(4)
N(1)	−99(6)	3489(10)	102(11)	43(4)
N(2)	2621(6)	3486(10)	−700(11)	46(4)
C(1)	113(12)	2500	2121(19)	45(8)
C(2)	2811(9)	2500	1298(17)	29(6)
C(3)	2336(9)	2500	−4775(19)	36(7)
C(4)	1874(15)	2500	−5626(22)	79(13)
C(5)	2768(8)	3407(13)	−4895(15)	61(6)
C(6)	−350(10)	2500	−3628(24)	61(11)
C(7)	−522(37)	2500	−2298(52)	132(47)
C(8)	−603(16)	3386(47)	−4111(68)	240(50)
C(9)	−527(24)	2996(63)	−2905(59)	419(74)
C(10)	−738(24)	2500	−4550(52)	58(20)
C(11)	727(11)	4916(14)	−3437(19)	80(9)
C(12)	709(9)	4917(11)	−2276(18)	63(7)
C(13)	1346(10)	4931(10)	−1858(16)	58(7)
C(14)	1766(11)	4930(12)	−2819(20)	70(8)
C(15)	1378(11)	4919(12)	−3784(18)	68(8)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 8. Atom coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) of **5** [a]

	x	y	z	U_{eq}
W(1)	1927(1)	2500	128(1)	15(1)
Cr(1)	3309(1)	3490(1)	1105(1)	17(1)
S(1)	2189(1)	4078(1)	260(1)	19(1)
S(2)	3290(1)	2500	−619(2)	17(1)
S(4)	1634(1)	2500	−2059(2)	23(1)
S(3)	2634(1)	2500	2307(2)	19(1)
O(1)	423(4)	2500	1330(7)	35(2)
N(1)	1030(4)	2500	827(7)	19(2)
C(1)	1593(3)	4715(4)	1410(6)	25(2)
C(2)	1566(4)	4322(5)	2765(6)	36(2)
C(3)	823(3)	4727(4)	836(6)	28(2)
C(4)	1902(4)	5638(4)	1453(7)	40(2)
C(5)	648(5)	2500	−2515(9)	26(3)
C(6)	645(6)	2500	−3983(9)	41(4)
C(7)	261(3)	3305(4)	−1997(7)	34(2)
C(11)	3673(4)	4571(4)	2400(7)	33(2)
C(12)	3801(4)	4834(4)	1123(6)	30(2)
C(13)	4319(3)	4282(4)	589(7)	32(2)
C(14)	4522(3)	3654(4)	1534(7)	33(2)
C(15)	4129(3)	3849(4)	2662(6)	29(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Acknowledgements

We thank the Swiss National Science Foundation and the Russian Fundamental Science Foundation (93-03-5394) for financial support.

References and notes

1 A.A. Pasynskii and I.L. Eremenko, *Sov. Sci. Rev. B. Chem.*, *10* (1987) 443 and references cited therein.

2 I.L. Eremenko, H. Berke, B.I. Kolobkov and V.M. Novotortsev, *Organometallics*, *13* (1994) 244.

3 (a) C.G. Barraclough, L.A. Bowden, R. Colton and C.J. Commons, *Aust. J. Chem.*, *26* (1973) 241; (b) E.E. Isaacs and W.A.G. Graham, *J. Organomet. Chem.*, *99* (1975) 119.

4 Y. Sulfab, F. Basolo and A.L. Rheingold, *Organometallics*, *8* (1989) 2139.

5 H.-U. Hund, U. Ruppli and H. Berke, *Helv. Chim. Acta*, *76* (1993) 963.

6 E.W. Abel, I.S. Butler and J.G. Reid, *J. Chem. Soc.*, (1963) 2068.

7 A.A. Pasynskii, I.L. Eremenko, Yu.V. Rakitin, V.M. Novotortsev, V.T. Kalinnikov, G.G. Aleksandrov and Yu.T. Struchkov, *J. Organomet. Chem.*, *165* (1979) 57.

8 A.A. Pasynskii, I.L. Eremenko, Yu.V. Rakitin, B. Orazsakhatov, V.M. Novotortsev, O.G. Ellert, V.T. Kalinnikov, G.G. Aleksandrov and Yu.T. Struchkov, *J. Organomet. Chem.*, *210* (1981) 377.

9 A.A. Pasynskii, I.L. Eremenko, S.E. Nefedov, B. Orazsakhatov, A.A. Zharkikh, O.G. Ellert, V.M. Novotortsev, A.I. Yanovsky and Yu.T. Struchkov, *J. Organomet. Chem.*, *444* (1993) 101.

10 V.G. Andrianov, B.P. Birjukov, Yu.T. Struchkov, *Zh. Strukt. Khim.* *10* (1969) 1129 (in Russian).

11 I.L. Eremenko, A.A. Pasynskii, B. Orazsakhatov, A.F. Shestakov, G.Sh. Gasanov, A.S. Katugin, Yu.T. Struchkov and V.E. Shklover, *J. Organomet. Chem.*, *338* (1988) 369.

12 C.H. Wei and L.F. Dahl, *Inorg. Chem.*, *4* (1965) 493.

13 A.A. Pasynskii, B.I. Kolobkov, I.L. Eremenko, S.E. Nefedov, S.B. Katser and M.A. Porai-Koshits, *Rus. J. Inorg. Chem.*, *37* (1992) 563 (in Russian).

14 (a) D. Seyferth, R.S. Henderson and L.-C. Song, *Organometallics*, *1* (1982) 125; (b) V.W. Day, D.A. Lesch and T.B. Rauchfuss, *J. Am. Chem. Soc.*, *104* (1982) 1290; (c) R.L. DeKock, T.R. Wagenmaker, D. Seyferth, R.S. Henderson and M.K. Gallagher, *Organometallics*, *8* (1989) 119.

15 (a) A.R. Butler, C. Glidewell, A.R. Hyde, J. McGinnis and J.E. Seymour, *Polyhedron*, *2* (1983) 1045; (b) C.T.-W. Chu, F.Y.-K. Lo and L.F. Dahl, *J. Am. Chem. Soc.*, *104* (1982) 3409.

16 The main geometric parameters are: $Fe_2S_2(CO)_6$, Fe–Fe 2.555(1) Å, Fe–S 2.228(2)–2.243(2) Å, Fe–C 1.785(8)–1.821(7) Å, S–S 2.021(3) Å, C–O 1.130(9)–1.149(11) Å, Fe–S–Fe 62.8(1)–70.0(1)°; $Fe_4S_4(NO)_4$, Fe–Fe 2.634(3)–2.664(3) Å, Fe–S 2.215(4)–2.230(4) Å, Fe–N 1.662(12)–1.681(12) Å, N–O 1.164(16)–1.170(17) Å, Fe–S–Fe 72.5(1)–73.9(1)°.

17 V.M. Novotortsev, *Ph.D. Thesis*, Institute of General and Inorg. Chem. Moscow, 1974.

18 J.H. Van Vleck, *The Theory of Electronic and Magnetic Susceptibilities*, Oxford University Press, London, 1932.

19 Yu.V. Rakitin, V.M. Novotortsev, V.T. Kalinnikov, A.A. Pasynskii, G.M. Larin, A.V. Philatov and T.Ch. Idrisov, *Koordinatsionnaya Khimiya*, *3* (1977) 807 (in Russian).

20 N. Walker and D. Stuart, *Acta Crystallogr.*, *A39* (1983) 158.

21 G.M. Sheldrick, in *Crystallographic Computering 3: Data Collection, Structure Determination, Proteins, and Databases*, New York, 1985, p. 175.