Journal of Organometallic Chemistry, 165 (1979) 57—64

ANTIFERROMAGNETIC COMPLEXES INVOLVING METAL—METAL BONDS

I. SYNTHESIS AND MOLECULAR STRUCTURE OF AN ANTIFERROMAGNETIC DIMER WITH A Cr—Cr BOND

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(Received June 28th, 1978)

Summary

The binuclear complex $(C_5H_5)_2Cr_2(S)(SCMe_3)_2$ was prepared by refluxing a solution of chromocene and t-butylmercaptane in heptane. The structure of the product was determined by single crystal X-ray diffraction. The chromium atoms are linked by a sulphide bridge (S—Cr 2.24 Å, <CrSCr 74.1°) and two $SCMe_3$ bridges (Cr—S 2.38 Å, <CrSCr 68.3—69.3°). The two cyclopentadienyl ligands (C—C 1.41 Å, Cr—C 2.23 Å) are in apical positions, their ring planes being parallel to each other. The complex is an antiferromagnet ($-2J$ 430 cm^{-1}) despite the small Cr—S—Cr angles and short chromium—chromium distance (2.689 Å) indicative of strong Cr—Cr bonding.

Introduction

Studies of correlations between the structure and magnetic properties of transition metal polynuclear complexes are important in the understanding of the nature of exchange interactions between paramagnetic ions. In particular, the contribution from direct exchange through metal—metal bonds and from superexchange via bridge ligands may be estimated *.

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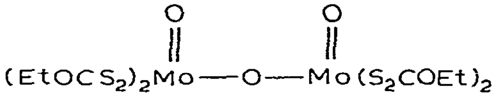
* According to Kepert and Vrieze [1], metal—metal bonds are defined as direct metal—metal interactions of no less than 15—20 kcal/mol energy.

Binuclear complexes containing equivalent exchange-coupled paramagnetic ions may be divided into four groups: (1) diamagnetic complexes involving metal—metal bonds; (2) diamagnetic complexes without metal—metal bonds; (3) antiferromagnetic complexes without metal—metal bonds; and (4) antiferromagnetic complexes involving metal—metal bonds.

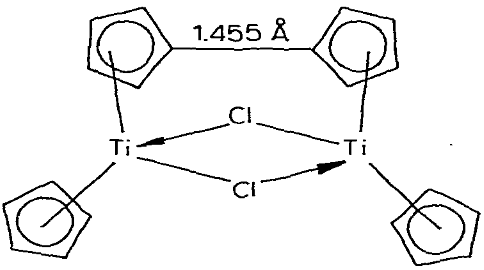
The first group includes the well known binuclear compounds of the metal carbonyl type, such as $Co_2(CO)_8$, and other organometallic compounds in which metals have rare gas electronic configurations [1].

The second group includes complexes exhibiting strong superexchange, e.g. via a ca. 180° oxygen bridge Mo^VOMo^V in I [2] or via the conjugated fulvalene ligand in the titanium complex II [3].



$$(EtOCS_2)_2\overset{\overset{O}{\|}}{Mo}—O—\overset{\overset{O}{\|}}{Mo}(S_2COEt)_2$$

(I)

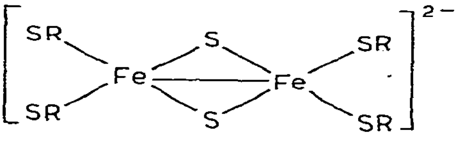


(II)

Ti----Ti 3.638 Å

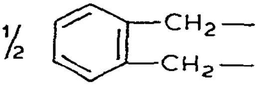
Copper acetate hydrate, $H_2O \cdot Cu(OOCCH_3)_4Cu \cdot H_2O$ [4], is the classic example of complexes of the third type. The complexes studied by us recently, $LM(OOCR)_4ML$ ($L = \pi\text{-}C_5H_5$, $M = Ti^{III}$ [5], V^{III} [6,7]; L = α-substituted pyridines, $M = Mn^{II}$, Fe^{II}, Co^{II}, Ni^{II} [8]) also belong to this group. Such complexes are known for all the first transition series metals except chromium which forms diamagnetic dimers of the first type probably containing Cr—Cr bonds. The X ray data for $C_5H_5Ti(OOCPh)_4TiC_5H_5$ [10], $C_5H_5V(OOCR)_4VC_5H_5$ ($R = CF_3$ [6], C_4H_3O [7]), $(quinoline)_2Co_2(OOCPh)_4$ [11], $(quinaldine)_2Ni_2(OOCCMe_3)_4$ [12], and $(acridine)_2Cu_2(OOCCMe_3)_4$ [12] show these complexes to contain no direct metal—metal bonds, the M···M distance for each complex being between 0.7 and 0.3 Å is larger than twice the covalent radius of the metal. Thus, in these compounds, the metal atoms are exchange coupled through carboxylate bridges only.

As concerns complexes of the fourth type, the structures of only two iron(III) dimers are known which show antiferromagnetic properties (J —150 cm^{-1}) despite the presence of strong Fe—Fe bonds (III) [13,14]:



Fe —— Fe 2.69 Å , Fe —S— Fe 75°

R = $p\text{-}C_6H_4CH_3$;

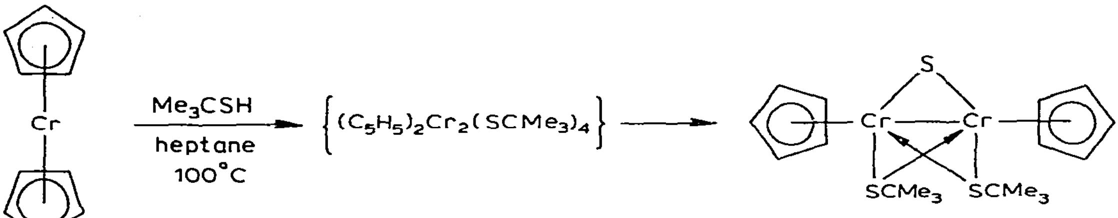


In these complexes, the Fe atoms are in the purely inorganic environment of the sulphide and thiolate sulphur atoms. At the same time all organometallic complexes that are known to contain metal—metal bonds are as a rule diamagnetic and belong to the first group of exchange coupled binuclear complexes.

In this paper, we report the synthesis and structure of the first antiferromagnetic organometallic binuclear complex, $(C_5H_5)_2(S)(SCMe_3)_2$ (III) containing a direct M—M bond (also see preliminary communication [15]).

Results and discussion

Chromocene reacts with t-butylmercaptan in heptane under reflux to give the three-bridge trivalent chromium bis(thiolate)sulphide III.



(III)

$(C_5H_5)_2Cr_2(S)(SCMe_3)_2$ (III) is probably formed in the decomposition of the $(C_5H_5)_2Cr_2(SCMe_3)_4$ intermediate analogous to the selenophenolate derivative, $(C_5H_5)_2Cr_2(SePh)_4$ [15]. The formation of metal—S bonds by this mechanism is typical of reactions between transition metal complexes and mercaptans; thus, $Co_2(CO)_8$ reacts with benzylmercaptan to give $Co_3(CO)_6S(SCH_2Ph)$ [16] and $Hg(SCMe_3)_2$ decomposes to HgS [17]).

III was obtained in the form of violet prisms, m.p. 189°C (dec.), which were stable in air and soluble in all organic solvents (crystallize from heptane). Its dimeric structure was proved by cryoscopic molecular weight measurements (found 436, calcd. 444), mass spectrometry (molecular ion M^+ 444), and single crystal X-ray diffraction (Fig. 1).

Two π-C_5H_5Cr fragments are linked through one S and two $SCMe_3$ bridges. The cyclopentadienyl ring planes are almost parallel and have a dihedral angle of 5°. These two ligands are in eclipsed configuration with respect to each other. The average Cr—C (C_5H_5) and C—C (C_5H_5) bond lengths, 2.23(4) and 1.41(5) Å, respectively, have the usual values for π-cyclopentadienylchromium derivatives [18]. The average Cr—$SCMe_3$ bond length, 2.38(1) Å (Cr—S distances range from 2.36 to 2.41 Å) is somewhat larger than that observed in $[C_5H_5Cr(NO)SPh]_2$, [19], which is 2.316 Å; it is however smaller than the sum of the covalent radii of Cr (1.46 Å [20]) and S (1.04 Å [21]). The Cr—S (sulphide) bond is even shorter, 2.24(1) Å. The latter value compares well with the Mo—S bond length in $(C_5H_5)_2Mo_2O_2(\mu\text{-}S)_2$, which is 2.33 Å [22] (the covalent radii of Cr and Mo (1.58 Å [20]) differ 0.12 Å).

The chromium—chromium distance in III (2.689 Å) is significantly smaller than twice the metal radius (2.92 Å) and than the Cr—Cr ordinary bond length in the diamagnetic $[C_5H_5Cr(NO)SPh]_2$ (2.950 Å) [19].

In view of the latter observation, the antiferromagnetic properties of III are of particular interest. The effective magnetic moment ($\mu_{eff.}$) decreases with tem-

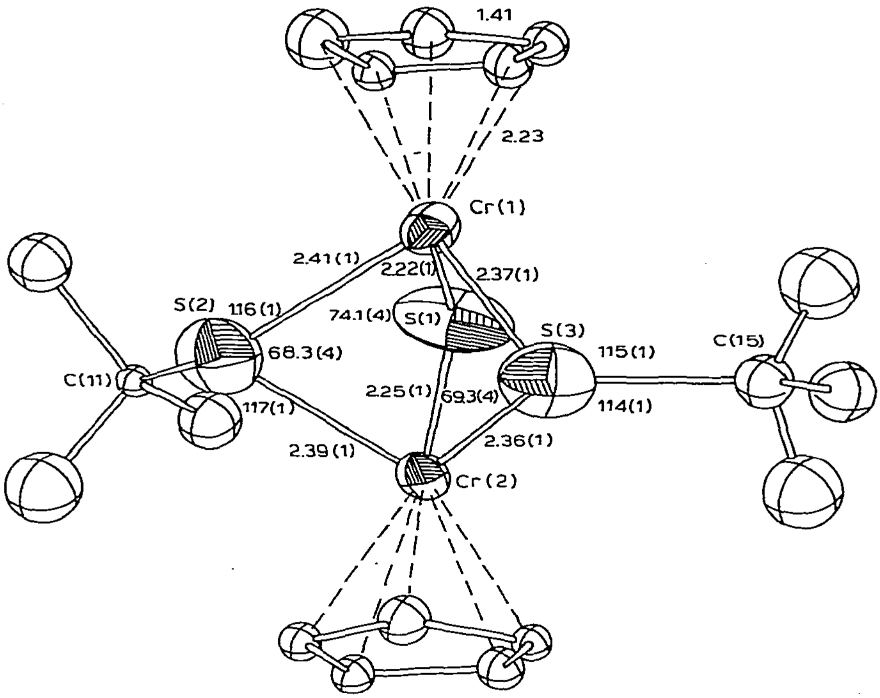
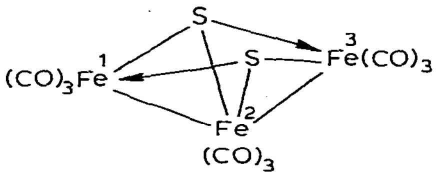


Fig. 1. Structure of $(\pi\text{-}C_5H_5)_2Cr_2(\mu\text{-}S)(\mu\text{-}SCMe_3)_2$.

perature from 0.98 to 0.02 BM in the range 297 to 79 K. The temperature dependence follows the Heisenberg—Dirac—Van Vleck model [23] for two paramagnetic ions having spins $S_1 = S_2 = 3/2$ with exchange integral between them, $2J$, of -430 cm^{-1}.

The presence of short Cr—S$_{(sulphide)}$ and Cr—S$_{(thiolate)}$ bonds might be interpreted as indicative of the absence of direct Cr—Cr interactions, thus the exchange, as with the adamantane-like complex $(Me_4N)_2[Co_4(SPh)_4(\mu_2\text{-}SPh)_6]$, which contains no Co—Co bonds (Co···Co 3.85 Å, <CoSCo 113°, J — 17 cm^{-1}) [24] should be only through the bridge ligands. The analysis of the Cr—S—Cr angle values however, shows this interpretation to be incorrect. In fact, the Cr—S(1)—Cr angle in III (74.1° Fig. 1) is far smaller than the angle Fe(1) SFe(3) in complex IV (98.4°, the corresponding Fe···Fe distance is equal to 3.37 Å) [25]:



(IV)

On the other hand, the CrS(1)Cr angle has a similar value to that observed for the FeSFe angle in the dimer $[(RS)_2FeS]_2^{2-}$ (R = p-$C_6H_4CH_3$), which contains a 2.69 Å Fe—Fe bond and the FeSFe angle is equal to 75°. A similar angle is also

TABLE 1

MEAN BOND LENGTHS AND VALENCE ANGLES IN COMPOUND III

Bond	d (Å)	Angle	ω°
Cr=Cr	2.689(8)	S(1)—Cr—S(2)	81.0(5)
Cr—S	2.24(1)	S(1)—Cr—S(3)	96.7(5)
Cr—SCMe$_3$	2.38(1)	S(2)—Cr—S(3)	91.0(5)
Cr—C(Cp)	2.23(4)	Cr—S(1)—Cr	74.1(5)
S—CMe$_3$	1.81(4)	Cr—S(2)—Cr	68.3(4)
C—C(Cp)	1.41(5)	Cr—S(3)—Cr	69.3(4)
C—C(Me)	1.45(6)	Cr—S—C	117(1)
		C—C—C(Cp)	108(3)

observed in the diamagnetic dimer $(C_5H_5)_2Mo_2O_2S_2$, this contains a 2.894 Å Mo—Mo bond and the MoSMo angle is equal to 77.3° [22].

Similarly, the $CrS_{(thiolate)}Cr$ angles in III (68.3 and 69.3°) are far smaller than in $(C_5H_5)_2Fe_2(\mu\text{-}SEt)_2(\mu\text{-}S_2)$ (92.95°) [26] and $[C_5H_5Fe(CO)SPh]_2$ (98°) [27] (the Fe···Fe distances are equal to 3.307 and 3.39 Å, respectively). One-electron oxidation of the former Fe derivative and of $[C_5H_5Fe(CO)SMe]_2$ leads to the formation of one-electron Fe—Fe bonds (3.06 and 2.925 Å, respectively), which are associated with a significant decrease of the FeSFe angles to 84.4 and 81.8° [28], respectively. The formation of ordinary two-electron Fe—Fe bonds in $Fe_2(CO)_6(SEt)_2$ [29], $[C_5H_5Fe(CN)SEt]_2$ [28], and $[C_5H_5Fe(MeCN)SEt_2{}^{2+}$ [28], where the Fe—Fe distance are equal to 2.537, 2.625, and 2.649 Å, respectively, leads to angles of 68, 73.3, and 73.9° which are near to those observed in III for the $CrS_{(thiolate)}Cr$ angles. It should be noted that these angles in compound III are smaller than that (79.1°) in the aforementioned dimer $[C_5H_5Cr(NO)SPh]_2$. This contains an ordinary Cr—Cr bond of 2.950 Å [17]. Further narrowing of the CrSCr angles in III appears to be hindered by S···C (C_5H_5) nonbonded interactions, and the corresponding distances are shorter (3.2—3.4 Å) than those typical for Van der Waals interactions (3.55 Å [30]). A similar situation occurs in $C_5H_5V(OOCR)_4VC_5H_5$ [6,7] where short O(OOCR)···C(C_5H_5) nonbonded interactions prevent approach of vanadium atoms to each other. With the vanadium complex, shortening of the O···C distances is due to repulsion between the oxygen atoms of neighbouring OOCR groups (the O(OOCR)···O(OOCR) distances are equal to 2.6—2.7 Å in that compound). The S···S distances in III (3.5—3.6 Å) are typical for Van der Waals interactions and do not affect the complex geometry. The only reason for the steric strain, therefore, may be the formation of strong Cr—Cr bonds. Thus complex III is the first example of an antiferromagnetic binuclear organometallic compound containing direct metal—metal bonds. metal bonds.

The mean bond lengths and valence angles in compound III are listed in Table 1.

Experimental

Chromocene was synthesized by a published procedure [31]. t-Butylmercaptan obtained from a commercial source, was purified by fractional distillation

TABLE 2a

ATOMIC COORDINATES (X 10^4) AND TEMPERATURE FACTORS (e.s.d. in parentheses)

Atom	*X*	*Y*	*Z*	*B*	Atom	*X*	*Y*	*Z*	*B*
Cr(1)	163(7)	1446(2)	9754(7)		C(7)	−3354(42)	125(12)	8633(41)	3,1(9)
Cr(2)	−2411(7)	821(2)	8553(7)		C(8)	−3050(50)	165(14)	7306(49)	5,3(10)
S(1)	109(14)	900(4)	8107(14)		C(9)	−4325(44)	501(12)	6464(40)	3,1(10)
S(2)	−438(14)	795(4)	11106(14)		C(10)	−5241(46)	663(12)	7342(44)	4,1(9)
S(3)	−2904(15)	1611(4)	8769(14)		C(11)	−1145(41)	925(12)	12609(36)	2,4(8)
C(1)	1464(55)	1957(12)	11574(43)	3,1(9)	C(12)	−1842(69)	502(20)	12908(65)	11,7(18)
C(2)	2863(58)	1628(16)	11461(55)	7,4(13)	C(13)	−2561(33)	1200(16)	12359(50)	6,9(13)
C(3)	3007(50)	1636(14)	9973(49)	5,2(11)	C(14)	563(56)	1042(15)	14019(52)	7,2(14)
C(4)	1906(45)	1986(13)	9295(41)	3,7(9)	C(15)	−368(63)	1910(16)	6992(55)	6,6(12)
C(5)	1029(49)	2179(13)	10311(47)	4,6(10)	C(16)	−3229(68)	2389(22)	6931(72)	11,5(20)
C(6)	−4665(45)	398(12)	8680(42)	3,4(9)	C(17)	−5598(72)	1951(20)	6116(67)	11,9(19)
					C(18)	−3185(71)	1756(21)	5727(68)	8,4(14)

TABLE 2b

ANISOTROPIC TEMPERATURE FACTORS FOR Cr AND S
$T = \exp[-1/4(B_{11}h^2a^{*2} + \ldots + 2B_{12}hka^*b^* + \ldots)]$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr(1)	1.6(3)	3.0(3)	2.5(3)	0.1(3)	0.6(3)	0.0(3)
Cr(2)	2.4(3)	1.2(3)	3.1(4)	0.1(3)	0.8(3)	0.3(3)
S(1)	5.0(7)	4.9(7)	10.2(10)	−0.9(6)	5.2(7)	−2.3(8)
S(2)	5.8(7)	3.8(7)	7.1(8)	0.6(6)	2.1(7)	0.2(7)
S(3)	6.0(8)	5.9(8)	6.2(8)	−0.5(6)	2.6(7)	−1.2(7)

and heptane was distilled over sodium metal powder in an argon flow.

Preparation of $(C_5H_5)_2Cr_2(S)(SCMe_3)_2$. Me_3CSH (1 ml) was added to a filtered red solution of $(C_5H_5)_2Cr$ (0.50 g, 2.7 m*M*) in 30 ml of heptane and the mixture was refluxed for 4 h. After cooling the dark-violet reaction mixture, needle-like violet crystals precipitated. These were isolated, washed with pentane, and dried under vacuum at 20°C to give III in a 73% yield based on initial $(C_5H_5)_2Cr$. Found; C, 48.73; H, 6.35; Cr, 23.80. $C_{18}H_{28}S_3Cr_2$ calcd.: C, 48.64; H, 6.30; Cr, 23.42%. IR spectrum (ν, cm^{-1}): 570w, 600w, 810s, 848w, 1025m, 1070w, 1135m, 1165s, 1360m, 1395w, 1440m, 1460m, 2870w, 2910w, 2930m, 2990m, 3115w.

The X-ray structure determination was performed with a Syntex-P2$_1$ diffractometer, Mo-K_α, 968 reflections with $F^2 \geqslant 2\sigma$. The structure was solved by the least squares method in isotropic approximation (anisotropic factors for S and Cr were used), $R = 0.11$. The crystals are monoclinic, a 8.114(2), b 29.197(7), c 9.473(4) Å; β 111.53(3)°; $D_{\text{exptl.}}$ 1.41, $D_{\text{calcd.}}$ 1.42 g/cm^2; $Z = 4$; space group $P2_1/c$. The atomic coordinates and their temperature factors are given in Tables 2a and 2b.

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