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ANTIFERROMAGNETIC COMPLEXES WITH A METAL–METAL BOND

XIV *. SYNTHESIS AND MOLECULAR STRUCTURE OF THE ANTIFERROMAGNETIC CLUSTER $[Cp_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2]_2Mn$, CONTAINING A HETEROMETALLIC "BOW-TIE" Cr_4Mn FRAMEWORK **

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Summary

The antiferromagnetic cluster $[Cp_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2]_2Mn$ (II) was obtained by reaction of $(CpCrSCMe_3)_2S$ with $CpMn(CO)_3$ (reagent ratio 2 : 1) under UV irradiation in boiling toluene. The structure of II was established by an X-ray structural study. Crystals of II are orthorhombic, space group $Fdd2$, $a = 39.715(13)$, $b = 21.127(7)$, $c = 7.808(3)$ Å, $V = 6551.4$ Å^3, $Z = 8$. The molecule of II has a symmetrical bow-tie metal framework Cr_4Mn with short Cr–Cr bonds (2.690(4) Å) and elongated Cr–Mn bonds (2.936(3) and 2.947(3) Å). The angle between the planes of Cr_2Mn triangles is equal to 90°. The central Mn^{II} atom (d^5 electron configuration) is situated on a crystallographic two-fold axis and, besides Cr atoms, is surrounded by four μ^3-bridging sulphur atoms (Mn–S, 2.393(5) and 2.389(5) Å). Both Cr–Cr bonds are bridged by a tert-butylthiolate group (av. Cr–S 2.347(5) Å).

Introduction

Recently, we have described the first representatives of a new type of clusters, viz antiferromagnetic complexes $[Cp_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2]_2M$ with a metal bow-tie framework Cr_4M, where M = Cr^{II} [1] or Co^{II} [2]. It was noted that the geometry of

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* Part XIII cf. reference 2.

** Magnetochemical research by V.M. Novotortsev, O.G. Ellert and Z.M. Seifulina to be published separately.

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TABLE 1

ATOMIC COORDINATES MULTIPLIED BY 10^4 (for Mn, Cr and S by 10^5). ANISOTROPIC TEMPERATURE FACTORS ARE GIVEN IN THE FORM: $T = \exp[-1/4(B_{11}a^{\star}h + \ldots + 2B_{23}b^{\star}c^{\star}kl)]$

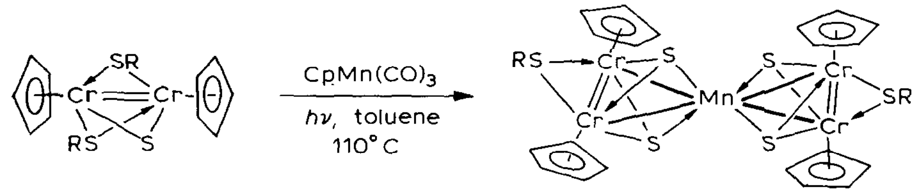
Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	1/4	3/4	26135(48)	1.0(1)	1.8(2)	1.4(1)	−0.1(1)	0	0
Cr(1)	19287(6)	66892(12)	16181(36)	1.18(9)	2.2(1)	1.02(9)	0.0(1)	0.0(1)	−0.1(1)
Cr(2)	23857(6)	61967(12)	37829(36)	1.22(9)	1.8(1)	1.35(9)	0.02(9)	0.0(1)	0.1(1)
S(1)	24920(11)	65353(20)	10074(51)	1.0(2)	2.3(2)	1.4(2)	0.0(2)	0.2(1)	−0.1(2)
S(2)	20519(10)	70786(20)	43068(53)	1.4(2)	1.8(2)	1.0(1)	0.0(2)	0.0(2)	0.0(2)
S(3)	19439(10)	56295(19)	24785(54)	1.0(2)	1.8(2)	1.5(2)	−0.3(1)	−0.2(2)	−0.3(2)
C_t(1)	1605(4)	5332(8)	3918(21)	2.5(8)	2 9(9)	1.3(7)	−1.6(7)	0.6(7)	0.5(7)
C_t(2)	1556(5)	5742(10)	5516(24)	4(1)	4(1)	1.7(8)	−3.2(9)	0.9(8)	−1.1(8)
C_t(3)	1728(5)	4650(9)	4464(27)	5(1)	2.2(9)	4(1)	−1.1(8)	1.3(9)	−0.1(9)
C_t(4)	1277(4)	5291(9)	2909(27)	2.5(9)	4(1)	4(1)	−0.6(8)	−0.3(9)	0.5(9)
Cp(11)	1512(4)	6529(8)	−283(19)	1.6(8)	4(1)	0.7(7)	0.4(7)	−0.3(7)	0.7(7)
Cp(12)	1388(4)	6932(8)	1088(20)	2.7(9)	3.8(9)	1.2(7)	0 4(8)	−0.7(7)	0.4(8)
Cp(13)	1588(4)	7523(9)	1068(21)	2.6(8)	3.0(9)	2.1(8)	0.8(7)	−0.4(8)	0.8(8)
Cp(14)	1826(4)	7466(8)	−311(19)	3.4(9)	2.2(8)	1.5(8)	0.5(7)	−1.8(7)	0.2(7)
Cp(15)	1790(4)	6858(8)	−1166(20)	4.0(9)	3.4(9)	1.0(7)	−1.7(8)	−2.3(8)	0.9(7)
Cp(21)	2826(4)	5559(8)	4174(27)	3.2(9)	1.9(8)	3.8(9)	1.9(7)	−1.4(9)	−0.2(9)
Cp(22)	2918(4)	6217(10)	4695(24)	1.5(8)	6(1)	4(1)	0.5(9)	−2.1(8)	2.4(9)
Cp(23)	2672(5)	6347(9)	6202(23)	5(1)	5(1)	1.2(7)	0.8(9)	−1.6(8)	0.4(8)
Cp(24)	2494(4)	5795(7)	6392(20)	0.9(6)	2.0(7)	2.4(8)	0.6(6)	−0.9(7)	0.7(7)
Cp(25)	2568(4)	5329(7)	5193(22)	0.6(7)	3.1(9)	2.0(7)	0.5(6)	0 2(7)	0.7(7)

the moieties $Cp_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2$ (Q) in both Q_2M molecules was in fact identical (average Cr–Cr 2.670, Cr–$SCMe_3$ 2.358, Cr–(μ_3-S) 2.305 Å). It also closely resembles the geometry of these moieties in complexes $Cp_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2 \cdot ML$, designated as QML, where ML = $Mn(CO)_3$ [3], $Fe(CO)_3$ [4] or $Co(CO)_2$ [5]. In fact, the moiety Q can be considered as a unique chelating tetradentate ligand, forming two M–(μ_3-S) and two M–Cr bonds with M. The nature of M–Q bonding depends to a large degree on the nature of M in Q_2M, as well as on the nature of ML in QML complexes. In particular, in the complex Q_2Cr all $Cr_{central}$–$Cr_{peripheral}$ bonds have almost the same length (av. 2.911 Å), corresponding to the normal Cr–Cr bond (2.950 Å) in the binuclear complex $(CpCrNO)_2(\mu\text{-}SPh)_2$ [6]. The Cr–(μ_3-S) bonds (av. 2.31 Å) with central and peripheral Cr atoms are also of almost equal length. On the contrary, in the complex Q_2Co, all Co–Cr bonds are much longer than ordinary Co–Cr bonds in $QCo(CO)_2$ (~ 2.6 Å). It is noteworthy that Co–Cr bonds in Q_2Co are of equal length only in one triangle (2.77 Å), while in the other their lengths are markedly different (2.81 and 2.96 Å).

These results suggested that the difference in Q–M bonding was governed by the difference in electron configuration of Cr^{II} (d^4) and Co^{II} (d^7). Therefore it appeared interesting to obtain other clusters of the Q_2M type, in particular Q_2Mn, where Mn^{II} would have a d^5 electron configuration.

Results

Complex Q_2Mn (II) was synthesized by a photochemical reaction of $(CpCrSCMe_3)_2S$ (I) with $CpMn(CO)_3$ (reagent ratio 2 : 1) in boiling toluene:



(I, R = CMe_3) (II)

Dark green crystals of cluster II precipitate on cooling the reaction mixture. II is moderately soluble in heptane and benzene, and better so in THF, CH_2Cl_2 or $CHCl_3$. The IR spectrum of the complex has bands of the stretching modes of the C_5H_5 ring at 790, 995, 1410 and 3060 cm^{-1}, and of the CMe_3 group at 1140 and 2900 cm^{-1}. On the whole, the spectrum is similar to spectra of the bow-tie metal clusters Cr_4Cr [1] and Cr_4Co [2]. The mass spectrum of cluster II has no peak of the molecular ion, and the ion with the greatest mass results from the loss of tert-butylthiolate groups ($(Cp_2Cr_2S_2)_2Mn^+$, m/e 651). Further loss of Mn atoms leads to the ions $(C_5H_5)_4Cr_4S_4^+$ (m/e 596) and $(C_5H_5)_2Cr_2S_2^+$ (m/e 298). The structure of II was established by an X-ray structural study (Fig. 1). The molecule of II with the bow-tie Cr_4Mn metal framework involves two $Cr_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2$ fragments (Q) (Cr–Cr 2.690(4) Cr–S 2.323(5)–2.307(5) Å), which are coordinated to the Mn^{II} atom (d^5 electron configuration), situated on the crystallographic two-fold axis. The angle between the planes of Cr_2Mn triangles is 90°. On the whole, the cluster is symmetrical with a geometry that closely resembles that of the previously described bow-tie metal cluster Q_2Cr [1]. The distances Mn–Cr (2.936(3) and 2.947(3) Å) and Mn–S (2.393(5) and 2.389(5) Å) are only 0.02–0.06 Å longer than the corresponding distances from the central Cr^{II} ion in Q_2Cr. However, these distances significantly exceed the length of ordinary Mn–Cr (2.716(2) and 2.828(2) Å) and Mn–S (2.285(2) Å) bonds in $QMn(CO)_3$ [3].

Discussion

That the cluster Q_2Mn^{II} originates in the photochemical reaction of 2 mol of $(CpCrSCMe_3)_2S$ (I) and 1 mol $CpMn(CO)_3$ is essentially similar to formation of Q_2Cr from I and $C_6H_6Cr(CO)_3$ under UV irradiation [1]. As we have shown earlier, interaction of equimolar quantities of I and $CpMn(CO)_3$ under mild conditions (*hν*, 20 °C, THF) leads to the formation of the adduct $(CpCrSCMe_3)_2SMn(CO)_2Cp$ (IV), whose structure was solved by an X-ray study, and whose IR spectrum had two bands of stretching modes of CO at 1845 and 1912 cm^{-1}. Just this product was

TABLE 2

BOND LENGTHS *d* (Å)

Bond	*d*	Bond	*d*	Bond	*d*
Mn–Cr(1)	2.947(3)	Cr(1)–Cp(11)	2.25(2)	Cr(2)–Cp(21)	2.23(2)
Mn–Cr(2)	2.936(3)	Cr(1)–Cp(12)	2.25(2)	Cr(2)–Cp(22)	2.23(2)
Mn–S(1)	2.393(5)	Cr(1)–Cp(13)	2.26(2)	Cr(2)–Cp(23)	2.23(2)
Mn–S(2)	2.389(5)	Cr(1)–Cp(14)	2.27(2)	Cr(2)–Cp(24)	2.25(2)
Cr(1)–Cr(2)	2.690(4)	Cr(1)–Cp(15)	2.27(2)	Cr(2)–Cp(25)	2.26(2)
Cr(1)–S(1)	2.310(5)	Cr(2)–S(1)	2.321(5)	S(3)–C_t(1)	1.86(2)
Cr(1)–S(2)	2.307(5)	Cr(2)–S(2)	2.323(5)	C_t–C_t(av.)	1.54(2)
Cr(1)–S(3)	2.338(5)	Cr(2)–S(3)	2.356(5)	Cp–Cp(av.)	1.43(2)

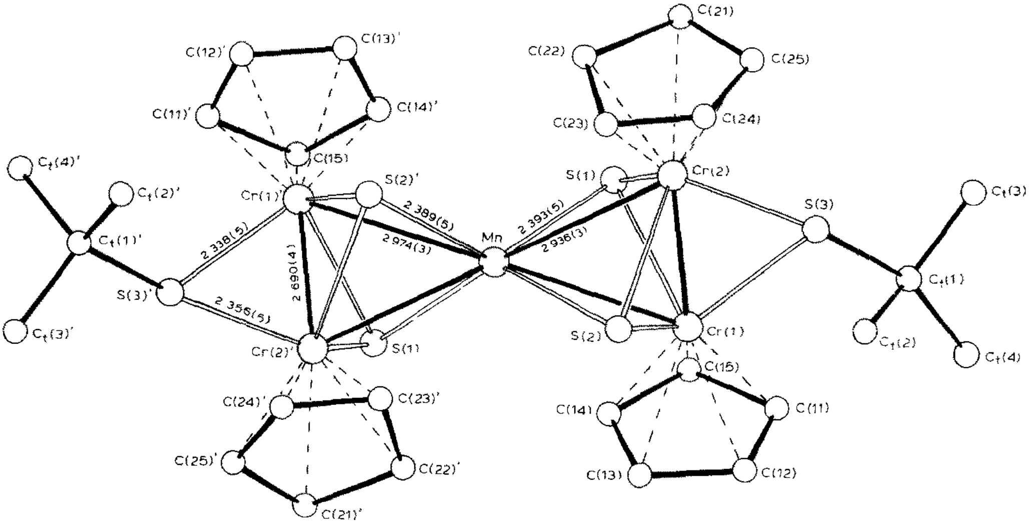


Fig 1. The structure of $[(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2Mn$.

TABLE 3

BOND ANGLES ω (degrees)

Angle	ω	Angle	ω	Angle	ω
Cr(1)MnCr(1)	149.4(1)	Cr(2)Cr(1)S(2)	54.8(1)	Cr(1)S(2)Cr(2)	71.0(1)
Cr(1)MnCr(2)	54.41(8)	Cr(2)Cr(1)S(3)	55.4(1)	Cr(1)S(3)Cr(2)	69.9(1)
Cr(1)MnCr(2)	138.3(1)	S(1)Cr(1)S(2)	91.9(2)	Cr(1)S(3)C_t(1)	118.5(5)
Cr(1)MnS(1)	50.0(1)	S(1)Cr(1)S(3)	84.2(2)	Cr(2)S(3)C_t(1)	116.7(5)
Cr(1)MnS(1)	111.5(1)	S(2)Cr(1)S(3)	94.3(2)	S(3)C_t(1)C_t(2)	113(1)
Cr(1)MnS(2)	49.9(1)	MnCr(2)Cr(1)	63.01(9)	S(3)C_t(1)C_t(3)	104(1)
Cr(1)MnS(2)	159.4(1)	MnCr(2)S(1)	52.6(1)	S(3)C_t(1)C_t(4)	109(1)
Cr(2)MnCr(2)	143.8(1)	MnCr(2)S(2)	52.5(1)	C_t(2)C_t(1)C_t(3)	110(1)
Cr(2)MnS(1)	50.4(1)	MnCr(2)S(3)	117.2(1)	C_t(2)C_t(1)C_t(4)	110(1)
Cr(2)MnS(1)	164.5(1)	Cr(1)Cr(2)S(1)	54.3(1)	C_t(3)C_t(1)C_t(4)	111(1)
Cr(2)MnS(2)	50.5(1)	Cr(1)Cr(2)S(2)	54.2(1)	Cp(12)Cp(11)Cp(15)	109(1)
Cr(2)MnS(2)	107.0(1)	S(1)Cr(2)S(2)	91.2(2)	Cp(11)Cp(12)Cp(13)	108(1)
S(1)MnS(1)	116.8(2)	Cr(1)Cr(2)S(3)	54.7(1)	Cp(12)Cp(13)Cp(14)	107(1)
S(1)MnS(2)	87.9(2)	S(1)Cr(2)S(3)	83.6(2)	Cp(13)Cp(14)Cp(15)	111(1)
S(1)MnS(2)	128.1(2)	S(2)Cr(2)S(3)	93.4(2)	Cp(11)Cp(15)Cp(14)	106(1)
S(2)MnS(2)	112.8(2)	MnS(1)Cr(2)	77.0(1)	Cp(22)Cp(21)Cp(25)	111(2)
MnCr(1)Cr(2)	62.59(9)	MnS(1)Cr(1)	77.6(1)	Cp(21)Cp(22)Cp(23)	103(1)
MnCr(1)S(1)	52.5(1)	Cr(1)S(1)Cr(2)	71.0(1)	Cp(22)Cp(23)Cp(24)	105(1)
MnCr(1)S(2)	52.4(1)	MnS(2)Cr(1)	77.7(1)	Cp(23)Cp(24)Cp(25)	115(1)
MnCr(1)S(3)	117.4(1)	MnS(2)Cr(2)	77.1(1)	Cp(21)Cp(25)Cp(24)	107(1)
Cr(2)Cr(1)S(1)	54.7(1)				

observed in the present study in the reaction mixture in the first stage (according to IR spectra and TLC on Al_2O_3), but disappeared when the reaction was continued for 5 hours. This fact does not disagree with our previous conclusion indicating stability of I · ML adducts with coordination number of M equal to 6 [7]. In fact, under severe conditions (prolonged UV irradiation in boiling toluene) further decarbonylation of adduct III is possible with reduction of the Mn coordination number to 5. According to ref. 5, this is accompanied by the loss of tert-butyl group and probably intermediate formation of the complex QMnCp *. Reaction of the latter with I leads to the formation of cluster Q_2Mn (II):

$$\mathrm{I} \xrightarrow[h\nu]{\mathrm{CpMn(CO)_3}} \underset{\mathrm{(III)}}{\mathrm{I\cdot Mn(CO)_2Cp}} \xrightarrow[\substack{-2\mathrm{CO}\\ -\mathrm{CMe_3}}]{h\nu} \{\mathrm{QMnCp}\} \xrightarrow[\substack{h\nu,\ 110^\circ\mathrm{C}\\ \mathrm{toluene}}]{\mathrm{I}} \underset{\mathrm{(II)}}{\mathrm{Q_2Mn}}$$

Structure II is notable for a relative increase in length of the Mn–Cr and Mn–S bonds as compared to the corresponding ordinary bonds in $QMn(CO)_3$ (IV), although, as mentioned above, the geometry of cluster II is on the whole similar to that found for Q_2Cr [1]. The above mentioned fragment $Cp_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2$ (Q) remains intact on transition from QML to Q_2M, and this allows us to use the same model of Q–Mn bonding in II, which we have discussed previously in the case of $QMn(CO)_3$ [3]. Namely, it is proposed that the binuclear moiety Q involves a short

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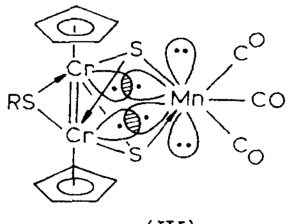
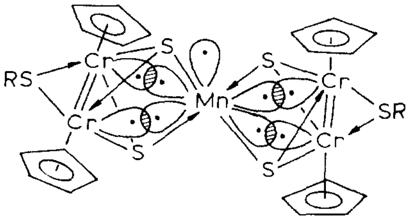
* We have recently observed a similar transformation in the photochemical reaction of I with $Mn_2(CO)_{10}$, where the first stage yields the adduct I · $Mn_2(CO)_9$ (characterized by an X-ray study [5]), which is then transformed into the metallocyclic cluster $QMn(CO)_3$ (IV) [3].

double Cr=Cr bond (2.6–2.7 Å) and that for coordination with the Mn atom this moiety uses two orbitals of the μ_3-sulphide bridges and one half-filled orbital of each Cr^{III} atom



(IV)



(II)

As seen in the scheme, the Mn^I atom (d^6 electron configuration) in structure IV forms only an ordinary (i.e. single-orbital two-electron) bond (2.72–2.83 Å in length) with each Cr^{III} atom. Similar bonding is realized in Q_2Cr, where the central Cr^{II} ion (d^4 electron configuration) forms four ordinary Cr–Cr bonds (2.9 Å long) with peripheral Cr atoms. Four more orbitals of Cr^{II} are used for ordinary Cr–S bonds, with one out of nine orbitals being evidently unfilled. In the case of Q_2Mn, the Mn^{II} ion has a d^5 electron configuration, i.e. there is one unpaired electron in this orbital. If this orbital is antibonding relative to Mn–Cr and Mn–S bonds, this can explain their marked weakness. On the other hand, it is the stability of the spherical d^5-electron shell of the Mn^{II} ion that can serve as a cause of weakening of the covalent Mn–Cr and Mn–S bonds in Q_2Mn, similarly to the weakening of Cp–Mn bonds in Cp_2Mn, which is known to be an ionic complex with 5 unpaired electrons [8]. Weakening of Q–M bonds is also observed in Q_2Co [2], where the Co^{II} ion with a d^7 electron configuration introduces into the metal framework three additional electrons as compared to Cr^{II}. Thus, not only is the vacant ninth orbital filled, but one electron also goes directly to the non-bonding orbitals of the metal framework. It is to be noted that at the same time the geometry of the Q fragments is not changed, while the Co–Cr bonds in one of the Cr_2Co triangles are strongly and not uniformly elongated (2.81 and 2.96 Å) as compared to the other bonds (2.77 Å). However, all Co–Cr bonds are longer than ordinary Co–Cr bonds (2.6 Å) in $QCo(CO)_2$ (cf. Introduction). It seems that the almost orthogonal arrangement of the planes of Cr_2Co triangles blocks electron delocalization over the entire bow-tie metal framework.

Experimental

All manipulations were carried out under a pure argon stream. Absolute solvents were prepared by distillation over Na suspension under a pure argon counterflow. Initial I, $C_5H_5Mn(CO)_3$ and $(C_5H_5)_2Mn$ were prepared according to reported methods [9,10]. IR spectra were measured with a Specord IR-75 spectrometer in KBr pellets. Mass spectra were obtained with a DS-50 apparatus. Intensities of X-ray reflections were measured with Syntex P 2_1 autodiffractometer (Mo-K_α, $\lambda = 0.7104$ Å, θ–2θ scan, $2 \leqslant \theta \leqslant 52°$, $T = -120\,°C$). Crystals of complex II are orthorhombic (space group $Fdd2$), $a = 39.715(13)$, $b = 21.127(7)$, $c = 7.808(3)$ Å, $V = 6551.4$ Å^3, $Z = 8$. The structure of II was solved by the direct method according to the modified

MULTAN [11] programm and refined in a full-matrix anisotropic approximation for all non-hydrogen atoms to $R = 0.066$, $R_W = 0.053$ (1166 reflections with $I \geqslant 2\sigma$).

$[(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2Mn(II)$

A violet solution of 1.2 g (2.7 mmol) of I and 0.3 g (1.4 mmol) of $CpMn(CO)_3$ in 35 ml of toluene was boiled for 8 hours in a quartz Schlenk vessel under UV irradiation (PRK-4 lamp) until ν_{CO} bands disappeared in the IR spectrum. After keeping the resulting black-green solution for 8–10 hours at room temperature, the precipitated black-green prisms were separated, washed with heptane and pentane and dried in vacuo. Yield 0.3 g (26.7%). IR spectrum (ν, cm^{-1}): 790s, 890w, 995m, 1045w, 1110w, 1140m, 1245w, 1340w, 1410m, 1460w, 1490w, 2900(br)w, 3060w.

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