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ANTIFERROMAGNETIC COMPLEXES WITH A METAL–METAL BOND

XIII *. TRANSFORMATION OF μ_3-SULPHIDE CLUSTERS CONTAINING CHROMIUM AND COBALT ATOMS BY TREATMENT WITH PIVALIC ACID. MOLECULAR STRUCTURES OF THE PSEUDOTETRAHEDRAL CLUSTER $Cp_3Cr_3(\mu_3\text{-}S)_3(\mu_3\text{-}O)Co(CO)_3 \cdot Me_3CCOOH \cdot 0.5C_6H_6$, AND THE HETEROMETALLIC "BOW-TIE" CLUSTER $(Cp_2Cr_2SCMe_3)_2(\mu_3\text{-}S)_4Co$

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Summary

The influence of pivalic acid on the triangular metal cluster $(Cp_2Cr_2SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ (II) and its unstable precursor with a probable structure $(Cp_2Cr_2SCMe_3)_2(\mu_3\text{-}S)_2Co(CO)_3$ (A) has been studied. An X-ray study has shown that A transforms into an antiferromagnetic ** pseudotetrahedral cluster $Cp_3Cr_3(\mu_3\text{-}S)_3(\mu_3\text{-}O)Co(CO)_3 \cdot Me_3CCOOH \cdot 0.5C_6H_6$(III). The base of the cluster is an isosceles metal triangle, Cp_3Cr_3, which is capped by the tridentate bridging sulphur atom (Cr–Cr 2.692(7), 2.868(8) and 2.884(8) Å, av. Cr–S 2.26(1) Å). The short Cr–Cr bond is bridged by an oxygen atom, and the long bonds have sulphide bridges which in their turn are weakly bonded to the $Co(CO)_3$ group (Co–O 2.16(2), Co–S 2.47(1) and 2.48(1) Å). In addition, the μ_3-O bridging atom forms a hydrogen bond with the $HOOCCMe_3$ molecule, while the Co atom is situated at weakly-bonding distances from the Cr^{III} atoms (Co–Cr 3.216(6), 3.238(6) and 2.892(6) Å). The transformation of cluster II in the reaction with Me_3CCOOH leads to the antiferromagnetic cluster $(Cp_2Cr_2SCMe_3)_2(\mu_3\text{-}S)_4Co$ (IV), which according to an X-ray structural study, has a distorted bow-tie framework Cr_4Co with the central Co^{II} atom surrounded also by four μ_3-bridging sulphide atoms. The angle formed by the

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* Part XII cf. ref. 1.

** Magnetic measurements taken by V.M. Novotortsev and O.G. Ellert to be published separately.

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planes of the Cr_2Co metal triangles is equal to 85.40°. The bond lengths between pairs of chromium atoms in different triangles are almost equal (2.679(2) and 2.665(2) Å) and close to the length of the Cr–Cr bond in the initial cluster II. At the same time, Co–Cr bonds in one of the triangles (2.776(2) and 2.774(2) Å) are noticeably shorter than in the other (2.809(2) and 2.959(2); all these values exceed, however, the length of the ordinary Co–Cr bond (2.59 Å) found in II.

The Co–S bonds are also elongated (up to 2.26 Å). It is proposed that elongation of Co–S and Co–Cr bonds in III and IV (as well as Co–O in III) results from an excessive number of electrons in the metal framework as compared to the number of corresponding bonding orbitals.

Introduction

Recently, in the study of transformations of heterometallic chromium-sulphide complexes, we have found that all ligands, besides one sulphide bridge, are cleaved off under the action of benzoic acid [2]:

$$(CpCrSCMe_3)_2S \cdot Cr(CO)_5 \xrightarrow{PhCOOH} Cr_3S(OOCPh)_6$$

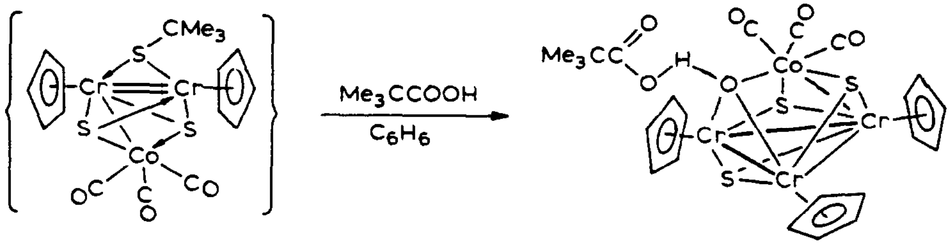
$$(CpCrSCMe_3)_2S \cdot Mn_2(CO)_9 \xrightarrow{PhCOOH} Mn_3S(OOCPh)_6$$

$$(Cp_2Cr_2SCMe_3)(\mu_3\text{-}S)_2Fe(CO)_3 \xrightarrow{PhCOOH} Fe_3S(OOCPh)_6$$

At the same time, in the reaction with the weaker trimethylacetic acid, cyclopentadienyl ligands are retained, and the tetrahedral cluster $Cp_3Cr_3(\mu_3\text{-}S)_4Fe(OOCCMe_3)$ with a terminal trimethylacetate group at the Fe atom and two unpaired electrons is formed [2]. Taking into account this peculiar reaction of Me_3CCOOH, it seemed interesting to study its reactions with the metallocyclic cluster $(Cp_2Cr_2SCMe_3)(\mu_3\text{-}S)_2 \cdot Co(CO)_2$ (II) and its unstable precursor $(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Co(CO)_3$ (A). Earlier, we had shown that II, on heating with tolane in toluene, loses some cobalt atoms, transforming into the heterometallic tetrahedral diamagnetic cluster $Cp_3Cr_3(\mu_3\text{-}S)_4Co(CO)$ [3].

Results and discussion

In ref. 4 we proposed that formation of the trinuclear cluster $(Cp_2Cr_2SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ (II) from $(CpCrSCMe_3)_2S$ (I) and $Co_2(CO)_8$ proceeds through intermediate $(Cp_2Cr_2SCMe_3)(\mu_3\text{-}S)_2 \cdot Co(CO)_3$ (A), which is easily decarbonylated by concentration of the reaction mixture in vacuo. In the present work we have shown that if a reaction mixture of 2 moles of I and 1 mole of $Co_2(CO)_8$ in benzene is treated without concentrating with pivalic acid with subsequent boiling, it is possible to isolate large brown prisms of the antiferromagnetic cluster $Cp_3Cr_3(\mu_3\text{-}S)_3(\mu_3\text{-}O)Co(CO)_3 \cdot MeCCOOH$ (III) in a low yield, crystallizing with a half mole of benzene:



(A)

(III)

TABLE 1

ATOMIC COORDINATES ($\times 10^3$) (for Co, S, Cr $\times 10^4$) FOR THE STRUCTURE OF $Cp_3Cr_3S_3OCo(CO)_3 \cdot HOOCCMe_3 \cdot 0.5C_6H_6$

Atom	*x*	*y*	*z*
Co	−0.0050(2)	0.2256(2)	0.2091(1)
Cr(11)	−0.3354(6)	0.3257(6)	0.2837(4)
Cr(12)	−0.2761(7)	0.0761(6)	0.1527(4)
Cr(13)	−0.2728(7)	0.3239(6)	0.1179(4)
S(11)	−0.1179(10)	0.1438(10)	0.0636(7)
S(12)	−0.2047(11)	0.1452(9)	0.2906(7)
S(13)	−0.4689(10)	0.2177(10)	0.1634(7)
O	−0.166(3)	0.378(2)	0.221(2)
O(1)	0.214(3)	−0.011(2)	0.170(2)
O(2)	0.222(3)	0.390(2)	0.128(2)
O(3)	0.098(4)	0.345(3)	0.396(1)
$O_{ac.}(1)$	0.004(3)	0.572(2)	0.299(2)
$O_{ac.}(2)$	−0.151(3)	0.731(2)	0.302(2)
C(1)	0.135(4)	0.067(4)	0.176(2)
C(2)	0.135(4)	0.315(4)	0.157(3)
C(3)	0.050(4)	0.313(2)	0.432(1)
C_{ac} (1)	−0.026(3)	0.693(3)	0.311(3)
C_{ac} (2)	0.105(5)	0.779(4)	0.351(3)
$C_{ac.}(3)$	0.228(5)	0.752(4)	0.290(4)
C_{ac} (4)	0.154(4)	0.769(4)	0.443(3)
$C_{ac.}(5)$	0.044(5)	0.933(3)	0.362(4)
C(11)	−0.535(3)	0.445(4)	0.351(3)
C(12)	−0.532(4)	0.364(3)	0.387(2)
C(13)	−0.399(4)	0.367(4)	0.434(2)
C(14)	−0.310(4)	0.483(3)	0.407(3)
C(15)	−0.386(5)	0.524(4)	0.360(3)
C(21)	−0.386(5)	−0.101(3)	0.033(3)
C(22)	−0.422(5)	−0.082(4)	0.069(2)
C(23)	−0.429(4)	−0.084(3)	0.170(2)
C(24)	−0.271(5)	−0.124(5)	0.176(3)
C(25)	−0.202(4)	−1.140(5)	0.092(3)
C(31)	−0.375(5)	0.499(3)	0.107(3)
C(32)	−0.230(4)	0.510(3)	0.092(3)
C(33)	−0.188(4)	0.416(4)	0.027(3)
C(34)	−0.302(4)	0.343(3)	−0.020(2)
C(35)	−0.431(5)	0.387(4)	0.035(4)
$C_b(1)$	0.501(4)	0.043(4)	0.421(3)
$C_b(2)$	0.412(5)	0.112(4)	0.506(4)
$C_b(3)$	0.590(5)	−0.054(5)	0.422(3)

TABLE 2

BOND LENGTHS IN THE MOLECULE $Cp_3Cr_3S_3OCo(CO)_3 \cdot HOOCCMe_3 \cdot 0.5C_6H_6$

Bond	d(Å)	Bond	d(Å)	Bond	d(Å)
Co–Cr(12)	2.892(6)	Cr(11)–O	1.95(2)	Cr(13)–O	1.87(2)
Co–S(11)	2.48(1)	Cr(11)–C(Cp)	2.25(2)	Cr(13)–C(Cp)	2.21(2)
Co–S(12)	2.47(1)	Cr(12)–Cr(13)	2.884(8)	O–C(CO)$_{av}$	1.10(3)
Co–O	2.16(2)	Cr(12)–S(11)	2.24(3)	O$_{ac}$ (1)–C$_{ac}$ (1)	1.29(3)
Co–C(CO)$_{av}$	2.02(3)	Cr(12)–S(12)	2.22(1)	O$_{ac}$ (2)–C$_{ac}$ (1)	1.23(3)
Cr(11)–Cr(12)	2.868(8)	Cr(12)–S(13)	2.29(1)	C$_{ac}$ (1)–CMe$_3$	1.50(4)
Cr(11)–Cr(13)	2.692(7)	Cr(12)–C(Cp)	2.27(2)	C–C(Me)$_{av}$	1.56(4)
Cr(11)–S(12)	2.32(1)	Cr(13)–S(11)	2.32(1)	C–C(Cp)$_{av}$	1.40(4)
Cr(11)–S(13)	2.29(I)	Cr(13)–S(13)	2.29(1)	C–C(C$_6$H$_{av}$	1.44(5)
Non-bonding distances					
Co ··· Cr(11)	3.219(6)	Co ··· Cr(13)	3.238(6)	O$_{ac}$ (1) ··· O	2.56(3)

TABLE 3

BOND ANGLES IN THE MOLECULE $Cp_3Cr_3S_3OCo(CO)_3 \cdot HOOCCMe_3 \cdot 0.5C_6H_6$

Angle	ω (°)	Angle	ω(°)
Cr(11)CoCr(12)	55.7(2)	S(11)Cr(12)S(13)	99.3(4)
Cr(11)CoCr(13)	49.3(2)	S(12)Cr(12)S(13)	100.1(4)
Cr(12)CoCr(13)	55.8(2)	CoCr(13)Cr(11)	65.0(2)
CoCr(11)Cr(12)	56.4(2)	CoCr(13)Cr(12)	56.0(2)
CoCr(11)Cr(13)	65.7(2)	CoCr(13)S(11)	49.6(3)
CoCr(11)S(12)	49.7(3)	CoCr(13)S(13)	53.9(3)
CoCr(11)S(13)	99.7(3)	CoCr(13)O	39.7(8)
CoCr(11)O	40.8(8)	Cr(11)Cr(13)Cr(12)	61.8(2)
Cr(12)Cr(11)Cr(13)	62.4(2)	Cr(11)Cr(13)S(11)	102.2(3)
Cr(12)Cr(11)S(12)	49.3(3)	Cr(11)Cr(13)S(13)	53.9(3)
Cr(12)Cr(11)S(13)	51.3(3)	Cr(11)Cr(13)O	46.5(8)
Cr(12)Cr(11)O	81.0(8)	Cr(12)Cr(13)S(11)	49.5(3)
Cr(13)Cr(11)S(12)	102.7(3)	Cr(12)Cr(13)S(13)	51.1(3)
Cr(13)Or(11)O	44.1(8)	Cr(12)Cr(13)O	81.8(8)
S(12)Cr(11)S(13)	97.3(4)	S(11)Cr(13)S(13)	97.3(4)
S(12)Cr(11)O	90.5(9)	S(11)Cr(13)O	89.2(9)
S(13)Cr(11)O	97.2(9)	S(13)Cr(13)O	99.5(9)
CoCr(12)Cr(11)	67.9(2)	CoS(11)Cr(12)	75.5(4)
CoCr(12)Cr(13)	68.2(2)	CoS(11)Cr(13)	85.0(4)
CoOr(12)S(11)	56.0(3)	Cr(12)S(11)Cr(13)	78.6(4)
CoCr(12)S(12)	55.8(3)	CoS(12)Cr(11)	84.4(4)
CoCr(12)S(13)	109.6(3)	CoS(12)Cr(12)	76.0(4)
Cr(11)Cr(12)Cr(13)	55.8(2)	Cr(11)S(12)Cr(12)	78.3(4)
Cr(11)Cr(12)S(11)	99.0(3)	Cr(11)S(13)Cr(12)	77.6(4)
Cr(11)Cr(12)S(12)	52.5(3)	Cr(11)S(13)Cr(13)	72.2(4)
Cr(11)C(12)S(12)	92.5(3)	Cp(11)S(13)Cr(13)	72.2(4)
Cr(11)Cr(12)S(13)	51.1(3)	Cr(12)S(13)Cr(13)	78.1(4)
Cr(13)Cr(12)S(11)	19.9(3)	Cr(12)S(13)Cr(13)	78.1(4)
Cr(13)Cr(12S(12)	99.6(3)	CoOCr(11)	102.9(11)
Cr(13)Cr(12)S(13)	50.8(3)	CoCr(13)	106.6(11)
S(11)Cr(12)S(12)	111.8(4)	Cr(1)OCr(13)	89.5(11)

The IR spectrum of III has bands of the stretching modes of C_5H_5 rings at 790, 1000, 1420, 3080 cm^{-1}, CO group at 1880, 1910, 1930 and 1995 cm^{-1}, and also of the OCO group of the Me_3CCOOH molecule at 1380 and 1720 cm^{-1}. The structure of III was solved by an X-ray structural study. The basis of the molecule is an isosceles metal triangular frame, $(C_5H_5)_3Cr_3$ (Cr–Cr 2.692(7), 2.868(8) and 2.884(8) Å), under which there is a tridentate bridging S atom (Fig.1). On the opposite side, over the short Cr–Cr bond, there is a bridging oxygen atom and over the longer Cr–Cr bonds there are bridging sulphur atoms (Cr–O 1.95(2) and 1.87(2) Å, av. Cr–S 2.32(1) and 2.22(1) Å), forming a "crown" cap. The "crown" is capped by the $Co(CO)_3$ group, which is weakly bonded to the bridging oxygen and sulphur atoms (Co–O 2.16(2), Co–S 2.47(1) and 2.48(1) Å), and located at a distance of 3.216(6), 3.238 and 2.892 Å from the chromium atoms in the base of the cluster.

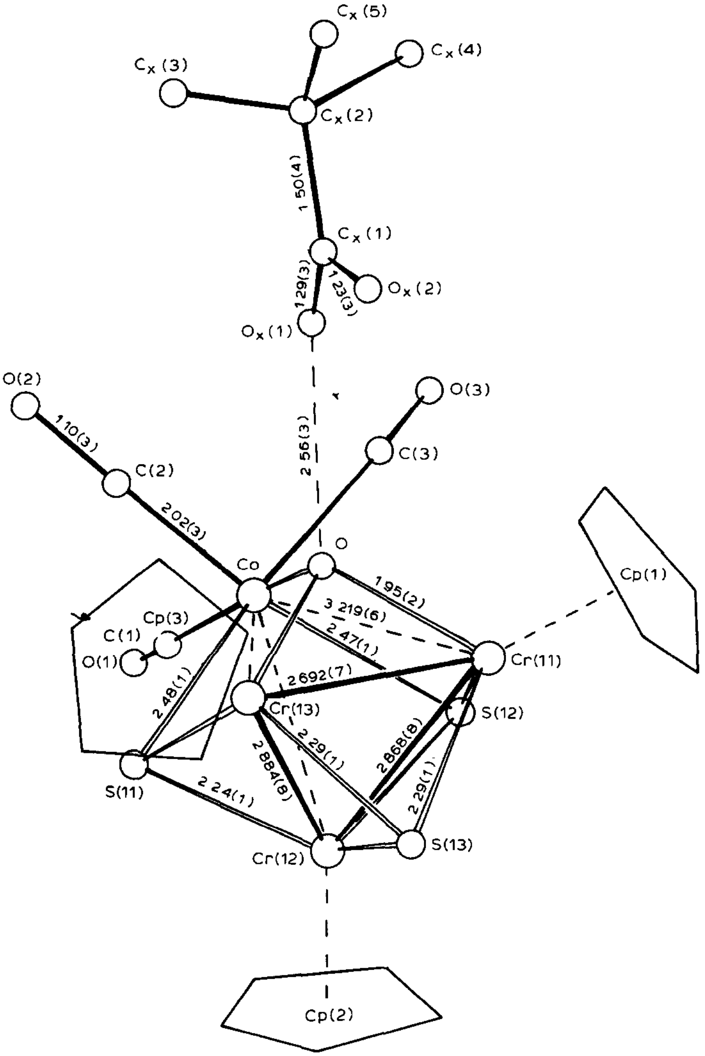
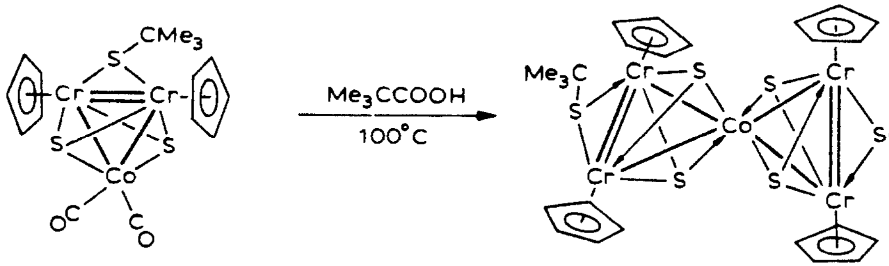


Fig. 1. The structure of $(C_5H_5)_3Cr_3(\mu_3\text{-}S)_3(\mu_3\text{-}O)Co(CO)_3 \cdot Me_3CCOOH$.

The mechanism of formation of III is as yet unclear. It seems that a possible source of bridging oxygen is trimethylacetic acid, one molecule of which forms a hydrogen bond with the μ_3-O atom. Although the H atom cannot be located in the Fourier series, nevertheless the average distance $O_{bridge} \cdots O_{acid}$ 2.56(2) Å and the non-equivalence of the C–O bonds (1.23(3) and 1.29(3) Å) indicate O – H – O interaction. Then nature of bonding in III can be described if the cluster is represented as a result of the joining of neutral fragments $Co(CO)_3$ and $(C_5H_5)_3Cr_3(S)_3O$ (A). The latter is probably similar to the isoelectronic paramagnetic cluster $Cp_3Mo_3S_4$, which has been structurally characterized [5]. As shown [6] this cluster is capable of addition of a C_5H_5Mo moiety, which results in the metal tetrahedron $(C_5H_5)_4Mo_4S_4$ [6] with equivalent ordinary Mo–Mo bonds. The latter is similar to the isoelectronic uncharged clusters of chromium $(MeC_5H_4)_4Cr_4S_4$ and $(MeC_5H_4)_4Cr_4OS_3 \cdot CuBr_2$ (IIIa), which we described previously [7]. In the case of cluster III, coordination of the $Co(CO)_3$ group introduces into the metal framework four electrons more than the C_5H_5Mo or $(MeC_5H_4)Cr$ groups. These additional electrons enter the antibonding orbitals of the metal framework, leading to drastic weakening of six Cr–Co, Co–O and Co–S bonds. As for the hydrogen bond μ_3-O $\cdots$ H-OOCCMe$_3$, its effect on the metal framework geometry is as insignificant as that of a weak coordination of $CuBr_2$ with μ_3-S in the abovementioned cluster IIIa. The difference in preferred coordination H $\cdots$ μ_3-O and $CuBr_2 \cdots \mu_3$-S is probably governed by the Pearson principle [8]. Proton, as a hard Lewis acid, is preferably bonded to μ_3-O, which is a hard Lewis base. On the other hand, $CuBr_2$, as a soft Lewis acid, is coordinated with μ_3-S, which is a softer base.

Under influence of Me_3CCOOH bonding of a part of cobalt atoms also occurs on an earlier prepared metal triangular cluster $(C_5H_5)_2Cr(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ (II). But in this case, tert-butylthiolate groups are retained, and after heating the reaction mixture in xylol at 100 °C for 4 h, the antiferromagnetic heterometallic bow-tie cluster $[(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2Co$ (IV) is unexpectedly obtained:



(II)

(IV)

Black-brown crystals of IV precipitate in analytically pure form upon cooling of the reaction mixture. The IR spectrum of IV contains intense bands of stretching modes of the C_5H_5 rings in the area of 790, 990, 1400 and 3060 cm^{-1} and of the CMe_3 group at 1140 and 2700–2980 cm^{-1}. The structure of IV is proved by an X-ray structural study (Fig.2). The metal skeleton of the cluster molecule is a "bow-tie" Cr_4Co fragment with an angle between the planes of Cr_2Co triangles of 85.40 °. A marked elongation of the Cr–Co bonds is to be noted (2.766(2) and 2.774(2) Å in one Cr_2Co triangle, and 2.809(2) and 2.959(2) Å in the other, as compared to ordinary bonds of 2.590 Å in the initial metallotriangular cluster II [4] or 2.618 Å in the tetrahedral cluster $(C_5H_5)_3Cr_3(\mu_3\text{-}S)_4Co(CO)$ (V) [3]. The Co–S bonds are also significantly elongated to 2.243(3)–2.275(3) Å in comparison with 2.190 Å in II, and 2.160 Å in V. At the same time the dichromium fragments $(Cp_2Cr_2SCMe_3)(\mu_2\text{-}S)_2$ retain, in fact, the same geometry as in the initial II with Cr=Cr bond lengths of 2.679(2) and 2.665(2) Å typical for this class of clusters. Relative elongation of Co–Cr and Co–S bonds in the spirane nucleus of the heteronuclear cluster IV is in contrast with the formation of ordinary $Cr_{central}$–$Cr_{peripheral}$ bonds (2.933 and 2.889

TABLE 4

ATOMIC COORDINATES MULTIPLIED BY 10^4 (for Co and by 10^5, for Cr and S by 10^5) FOR COMPOUNDS IV

Atom	*x*	*y*	*z*	Atom	*X*	*Y*	*z*
Co	79327(10)	1980(13)	37604(4)	Cr(1)	67717(12)	24439(15)	41528(5)
Cr(2)	54899(12)	1390(15)	40490(5)	Cr(3)	98937(12)	−14789(15)	38280(5)
Cr(4)	93750(11)	−2415(15)	30322(5)	S(1)	72103(18)	3173(24)	44743(8)
S(2)	63517(19)	13506(24)	34686(8)	S(3)	49312(20)	21047(24)	44635(8)
S(4)	98043(20)	8647(24)	37088(8)	S(5)	82220(18)	−18106(23)	33949(8)
S(6)	110850(19)	−14913(24)	31933(8)	C(1)	3647(8)	3058(10)	4207(3)
C(2)	3548(9)	2861(11)	3684(4)	C(3)	2579(9)	2519(12)	4447(4)
C(4)	3809(9)	4627(12)	4322(4)	C(5)	11235(8)	−3197(10)	2888(3)
C(6)	10061(8)	−3951(11)	2803(3)	C(7)	11815(8)	−2874(11)	2439(4)
C(8)	12069(8)	−4099(11)	3197(3)	C(9)	6839(8)	4668(10)	4393(3)
C(10)	7131(8)	4645(11)	3917(3)	C(11)	8156(8)	3836(11)	3884(3)
C(12)	8524(8)	3381(10)	4338(3)	C(13)	7714(8)	3903(10)	4650(3)
C(14)	3730(8)	−842(11)	3918(3)	C(15)	4459(12)	−1283(12)	3573(4)
C(16)	4171(80	−1283(11)	4345(4)	C(17)	5197(8)	−2051(11)	4275(4)
C(18)	5395(9)	−2046(12)	3795(4)	C(19)	10213(8)	−3474(10)	4204(3)
C(20)	11250(7)	−2648(10)	4256(3)	C(21)	10940(7)	−1418(10)	4498(3)
C(22)	9738(7)	−1494(10)	4596(3)	C(23)	9279(8)	−2761(10)	4414(3)
C(24)	8012(8)	249(I0)	2486(3)	C(25)	8469(8)	1508(10)	2664(3)
C(26)	9683(8)	1581(11)	2573(3)	C(27)	9972(8)	353(II)	2335(3)
C(28)	8961(8)	−474(10)	2282(3)				

TABLE 5

ANISOTROPIC TEMPERATURE FACTORS[a] FOR Co, Cr and S ATOMS IN THE FORM $T = \exp[-1/4B_{11}a^{\star 2}h^2 + B_{22}b^{\star 2}k^2 + B_{33}c^{\star 2}l^2 + 2B_{12}ab^{\star}hk + 2B_{13}a^{\star}c^{\star}hl + 2B_{23}b^{\star}c^{\star}kl)]$ FOR COMPOUND IV

Atom	B_{11}	B_{22}	B_{35}	B_{12}	B_{13}	B_{23}
Co	1.66(5)	0.90(5)	1.49(6)	0.10(5)	−0.02(4)	−0.13(5)
Cr(1)	1.69(6)	0.70(6)	1.51(7)	−0.01(5)	−0.03(5)	−0.04(5)
Cr(2)	1.37(6)	0.73(6)	1.74(7)	−0.07(5)	−0.02(5)	0.04(5)
Cr(3)	1.18(6)	1.11(6)	1.38(7)	−0.02(5)	−0.13(5)	0.00(5)
Cr(4)	1.29(6)	1.09(6)	1.45(7)	0.09(5)	0.04(5)	0.14(5)
S(1)	1.56(9)	1.09(9)	1.50(10)	0.04(8)	−0.11(8)	0.11(8)
S(2)	1.58(9)	1.29(10)	1.47(10)	0.00(8)	−0.08(8)	−0.01(8)
S(3)	1.91(10)	1.35(10)	1.61(11)	0.31(8)	0.23(8)	0.06(8)
S(4)	1.76(10)	1.03(9)	2.10(12)	−0.26(8)	0.08(9)	−0.20(8)
S(5)	1.32(9)	0.94(9)	1.56(11)	0.01(8)	−0.06(8)	−0.19(8)
S(6)	1.30(9)	1.38(10)	1.85(11)	0.13(8)	0.08(8)	−0.06(9)

[a] Carbon atoms are refined with isotropic temperature factors and their B_{iso} values vary in the range 1.7–3.1(2) Å^2.

Å) in the previously described homonuclear analogue $[(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2Cr$. This is probably explained by the fact that the Co^{II} atom (d^7 electron configuration) brings into the metal framework 3 electrons more than are needed to fill only the bonding orbitals of Co–Cr and Co–S. If these 3 electrons fill orbitals which are antibonding relative to the Co–Cr and Co–S bonds, the situation becomes

TABLE 6

BOND LENGTHS d(Å) FOR COMPOUND IV

Bond	*d*	Bond	*d*	Bond	*d*
Co–Cr(1)	2.809(2)	Cr(4)–Cr(3)	2.665(2)	C(5)–C(6)	1.55(1)
Co–Cr(2)	2.959(2)	Cr(4)–S(4)	2.288(3)	C(5)–C(7)	1.52(1)
Co–Cr(3)	2.766(2)	Cr(4)–S(5)	2.294(3)	C(5–C(8)	2.56(1)
Co–Cr(4)	2.774(2)	Cr(4)–S(6)	2.341(3)	C(9)–C(10)	1.44(1)
Co–S(1)	2.275(3)	Cr(4)–C(24)	2.251(9)	C(9)–C(13)	1.44(1)
Co–S(2)	2.273(3)	Cr(4)–C(25)	2.240(9)	C(10)–C(11)	1.42(1)
Co–S(4)	2.255(3)	Cr(4)–C(26)	2.25(1)	C(11)–C(12)	1.45(1)
Co–S(5)	2.243(3)	Cr(4)–C(27)	2.247(9)	C(12)–C(13)	1.42(1)
Cr(2)–Cr(1)	2.679(2)	Cr(4)–C(28)	2.242(9)	C(14)–C(15)	1.40(1)
Cr(2)–S(1)	2.308(3)	Cr(3)–S(4)	2.289(3)	C(14)–C(18)	1.40(1)
Cr(2)–S(2)	2.310(3)	Cr(3)–S(5)	2.289(3)	C(15)–C(16)	1.44(1)
Cr(2)–S(3)	2.351(3)	Cr(3)–S(6)	2.342(3)	C(16)–C(17)	1.41(4)
Cr(2)–C(14)	2.255(9)	Cr(3)–C(19)	2.240(9)	C(17)–C(18)	1.43(1)
Cr(2)–C(15)	2.26(1)	Cr(3)–C(20)	2.267(9)	C(19)–C(20)	1.44(1)
Cr(2)–C(16)	2.24(1)	Cr(3)–C(21)	2.266(9)	C(19)–C(23)	1.43(1)
Cr(2)–C(17)	2.24(1)	Cr(3)–C(22)	2.257(9)	C(20)–C(21)	1.43(1)
Cr(2)–C(18)	2.24(1)	Cr(3)–C(23)	2.246(9)	C(21)–C(22)	1.42-(1)
Cr(1)–S(1)	2.306(3)	Cr(1)–C(13)	2.273(9)	C(22)–C(23)	1.43(1)
Cr(1)–S(2)	2.299(3)	S(3)–C(1)	1.875(9)	C(24)–C(25)	1.42(1)
Cr(1)–S(3)	2.353(3)	S(6)–C(5)	1.88(1)	C(24)–C(28)	1.44(1)
Cr(1)–C(9)	2.258(9)	C(1)–C(2)	1.54(1)	C(25)–C(26)	1.43(1)
Cr(1)–C(10)	2.27(1)	C(1)–C(3)	1.53(f)	C(26)–C(27)	1.42(1)
Cr(1)–C(11)	2.244(9)	C(1)–C(4)	1.56(1)	C(27)–C(28)	1.41(1)

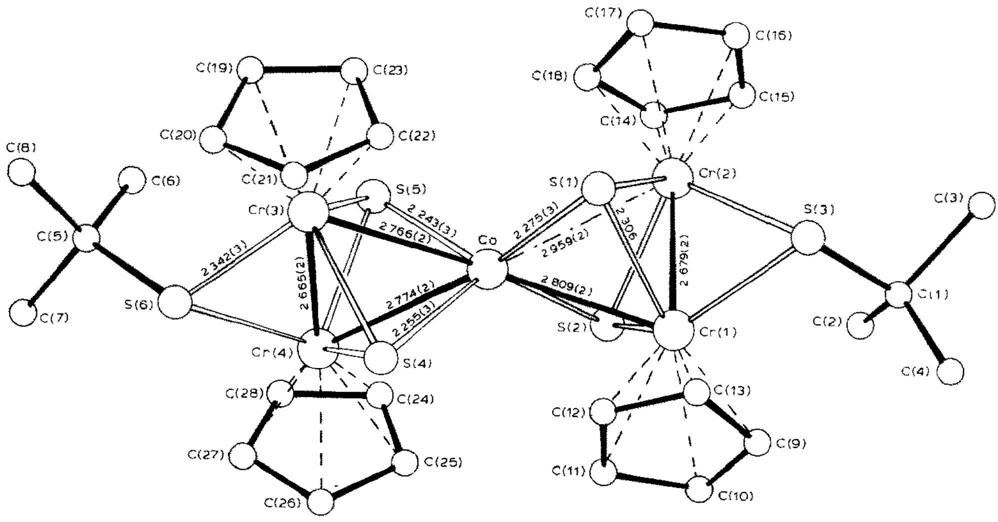


Fig. 2. The structure of $[(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2Co$.

TABLE 7

BOND ANGLES FOR COMPOUND IV

Angle	ω (Å)	Angle	ω (°)	Angle	ω (Å)
Cr(1)CoCr(2)	55.28(5)	CoCr(2)S(2)	49.24(7)	Cr(4)S(4)Cr(3)	71.23(9)
Cr(1)CoCr(3)	144.66(6)	CoCr(2)S(3)	114.16(8)	CoS(5)Cr(3)	75.55(8)
Cr(1)CoCr(4)	137.33(6)	Cr(1)Cr(2)S(1)	54.45(7)	CoS(5)Cr(4)	75.35(8)
Cr(1)CoS(1)	52.67(7)	Cr(1)Cr(2)S(2)	54.26(7)	Cr(4)S(5)Cr(3)	71.11(8)
Cr(1)CoS(2)	52.51(7)	Cr(1)Cr(2)S(3)	55.30(7)	Cr(4)S(6)Cr(3)	69.39(8)
Cr(1)CoS(4)	105.92(8)	S(1)Cr(2)S(2)	88.72(9)	Cr(4)S(6)C(5)	116.4(3)
Cr(1)CoS(5)	160.17(8)	S(1)Cr(2)S(3)	84.59(9)	Cr(3)S(6)C(5)	116.4(3)
Cr(2)CoCr(3)	138.10(6)	S(2)Cr(2)S(3)	95.83(9)	S(3)C(1)C(3)	106.5(7)
Cr(2)CoCr(4)	144.36(6)	CoCr(3)Cr(4)	61.24(5)	S(3)C(1)C(2)	111.6(7)
Cr(2)CoS(1)	50.28(7)	CoCr(3)S(4)	51.79(7)	S(3)C(1)C(4)	107.6(7)
Cr(2)CoS(2)	50.34(7)	CoCr(3)S(5)	51.47(7)	C(2)C(1)C(3)	112.4(8)
Cr(2)CoS(4)	160.19(8)	CoCr(3)S(6)	116.17(8)	C(2)C(1)C(4)	109.7(8)
Cr(2)CoS(5)	160.03(8)	Cr(4)Cr(3)S(4)	54.35(7)	C(3)C(1)C(4)	108.9(8)
Cr(3)CoCr(4)	57.40(5)	Cr(4)Cr(3)S(5)	54.54(7)	S(6)C(5)C(6)	113.3(6)
Cr(3)CoS(1)	106.50(8)	Cr(4)Cr(3)S(6)	55.29(7)	S(6)C(5)C(7)	106.2(7)
Cr(3)CoS(2)	161.65(9)	S(5)Cr(3)S(6)	93.61(9)	S(6)C(5)C(8)	106.1(6)
Cr(3)CoS(4)	52.90(7)	S(4)Cr(3)S(5)	91.21(9)	C(6)C(5)C(7)	111.2(8)
Cr(3)CoS(5)	52.98(7)	S(4)Cr(3)S(6)	84.78(9)	C(6)C(5)C(8)	110.3(8)
Cr(4)CoS(1)	163.25(8)	CoCr(4)Cr(3)	61.35(5)	C(7)C(5)C(8)	109.5(8)
Cr(4)CoS(2)	106.10(8)	CoCr(4)S(4)	51.85(7)	C(10)C(9)C(13)	108.4(8)
Cr(4)CoS(4)	52.90(7)	CoCr(4)S(5)	51.48(7)	C(9)C(10)C(11)	107.1(8)
Cr(4)CoS(5)	53.17(7)	CoCr(4)S(6)	116.32(8)	C(10)C(11)C(12)	108.8(8)
S(1)CoS(2)	90.48(9)	Cr(3)Cr(4)S(4)	54.41(7)	C(11)C(12)C(13)	107.7(8)
S(1)CoS(4)	115.12(9)	Cr(3)Cr(4)S(5)	54.35(7)	C(9)C(13)C(12)	107.9(8)
S(1)CoS(5)	123.04(9)	Cr(3)Cr(4)S(6)	55.33(7)	C(15)C(14)C(18)	110.0(9)
S(2)CoS(4)	126.04(9)	S(4)Cr(4)S(5)	91.12(9)	C(14)C(15)C(16)	106.8(9)
S(2)CoS(5)	111.90(9)	S(4)Cr(4)S(6)	84.84(9)	C(15)C(16)C(17)	107.6(9)
S(4)CoS(5)	93.32(9)	S(5)Cr(4)S(6)	93.51(9)	C(16)C(17)C(18)	107.6(9)
CoCr(1)Cr(2)	65.20(5)	CoS(1)Cr(2)	80.44(9)	C(14)C(18)C(17)	108.2(9)
CoCr(1)S(1)	51.67(7)	CoS(1)Cr(1)	75.66(7)	C(20)C(19)C(23)	108.6(8)
CoCr(1)S(2)	51.67(7)	Cr(1)S(1)Cr(2)	71.08(8)	C(19)C(20)C(21)	107.0(8)
CoCr(1)S(3)	119.72(8)	CoS(2)Cr(1)	75.83(8)	C(20)C(21)C(22)	108.4(8)
Cr(2)Cr(1)S(1)	54.54(7)	Cos(2)Cr(2)	80.42(9)	C(21)C(22)C(23)	108.6(8)
Cr(2)Cr(1)S(2)	54.66(7)	Cr(1)S(2)Cr(2)	71.08(8)	C(19)C(23)C(22)	107.3(8)
Cr(2)Cr(1)S(3)	55.26(7)	Cr(1)S(3)Cr(2)	69.44(8)	C(25)C(24)C(28)	106.9(8)
S(1)Cr(1)S(2)	89.05(9)	Cr(1)S(3)C(1)	118.9(3)	C(24)C(25)C(26)	109.0(8)
S(1)Cr(1)S(3)	84.62(9)	Cr(2)S(3)C(1)	114.4(3)	C(25)C(26)C(27)	107.3(8)
S(2)Cr(1)S(3)	96.10(9)	CoS(4)Cr(3)	75.31(9)	C(26)C(27)C(28)	108.7(8)
CoCr(2)Cr(1)	59.52(5)	CoS(4)Cr(4)	75.25(9)	C(24)C(28)C(27)	108.2(8)
CoCr(2)S(1)	49.29(7)				

similar to that considered for the pseudometallotetrahedral cluster III, leading to elongation of these bonds.

Experimental

All manipulations were carried out under a pure argon flow. Absolute solvents were prepared by distillation over Na suspension under a pure argon counterflow. Initial $(C_5H_5)_2Cr_2(\mu\text{-}S)(\mu\text{-}SCMe_3)_2$, $Co_2(CO)_8$ and $(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ were prepared according to reported methods [9,10,4]. IR spectra were measured with a Specord UR-75 spectrometer in KBr pellets. X-ray reflection intensities were measured with a Synthex $P2_1$ autodiffractometer (Mo-K_α, $\lambda = 0.7104$ Å, θ–2θ scan, $2 \leqslant \theta \leqslant 52°$, $T = -120\,°C$). Crystals of complex III are triclinic (sp.gr. $P\bar{1}$), $a = 8.961(1)$, $b = 10.719(2)$, $c = 16.075(3)$ Å, $\alpha = 108.72(1)$, $\beta = 87.26(1)$, $\gamma = 91.52(1)°$ $V = 1460.6$ Å^3, $Z = 2$. Crystals of complex IV are monoclinic (sp.gr. $P2_1/n$), $a = 11.496(4)$, $b = 9.647(4)$, $c = 29.240(15)$ Å, $\beta = 91.87(4)°$, $V = 3240.9$ Å^3, $Z = 4$. Both structures were solved by the direct method using the modified MULTAN program [11]. The structure III was refined in a full-matrix anisotropic approximation for all non-hydrogen atoms to $R = 0.091$ and $R_w = 0.115$ for 1967 reflections with $I \geqslant 2\sigma$. The structure IV was refined in a block-diagonal anisotropic approximation for Co, Cr and S atoms, and in an isotropic approximation for C atoms to $R = 0.070$ and $R_w = 0.059$ for 2689 reflections with $I \geqslant 2\sigma$.

$(C_5H_5)_3Cr_3(\mu_3\text{-}S)_3(\mu_3\text{-}O) \cdot Co(CO)_3 \cdot HOOCCMe_3 \cdot 0.5C_6H_6$ (III)

To 20 ml of a violet benzene solution of 2 g of $(C_5H_5)_2Cr_2 \cdot (\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (I), a red solution of 1.5 g of $Co_2(CO)_8$ in 20 ml of benzene was added. A brown solution immediately resulted. To this reaction mixture 1 ml of Me_3CCOOH was added and boiled for 2 h. The dark brown solution formed was subjected to chromatography on Al_2O_3(5 × 10 cm, benzene), separating the brown area with $R_f \sim 0.6$. The obtained solution was evaporated to dryness, and resulting solid substance was washed with toluene and then dissolved in CH_2Cl_2. This brownish green solution was repeatedly chromatographed on Al_2O_3 (5 × 15 cm, CH_2Cl_2/THF 1/1), and the greenish brown area with $R_f \sim 0.8$ was separated. The greenish brown solution obtained was concentrated at 0.1 Torr to a quarter of volume and cooled to $-5\,°C$. Large dark prisms that precipitated were separated from solution, washed with pentane and dried in vacuo. Yield 0.12 g, IR spectrum (ν, cm^{-1}): 570w, 690w, 700w, 790m, 1000m, 1040m, 1380w, 1420m, 1620m, 1680m, 1720m, 1880s, 1910m, 1930m, 1995s, 2760–2960(br)w, 3080w, 3150w.

$[(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2Co$ (IV)

To a brown solution of 0.28 g of $(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2 \cdot Co(CO)_2$ in 10 ml of toluene, 2 ml of Me_3CCOOH was added. The resulting solution was refluxed for 2 h. The brown solution obtained was concentrated to 5 ml and cooled to $-5\,°C$. Precipitated brown prisms were separated from solution, washed with heptane and dried in vacuo. Yield 0.2 g. IR spectrum (ν, cm^{-1}): 589w, 715w, 790s, 990m, 1035w, 1140m, 1200w, 1320w, 1400m, 1460w, 1790w, 2700–2960(br)m, 3060w.

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