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ANTIFERROMAGNETIC COMPLEXES WITH METAL–METAL BONDS

IX *. SYNTHESIS AND MOLECULAR STRUCTURES OF METHYLCYCLOPENTADIENYLCHROMIUM(III) SULFIDE DIAMAGNETIC TETRAMER AND THE ANTIFERROMAGNETIC COPPER(II) BROMIDE ADDUCT OF THE TETRANUCLEAR CLUSTER $(MeC_5H_4)_4Cr_4(\mu_3\text{-}O)(\mu_3\text{-}S)_3$

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Summary

Reaction of $(MeC_5H_4)_2Cr$ with $HSCMe_3$ gave $(MeC_5H_4)_2Cr_2S(SCMe_3)_2$ (I) in the form of violet antiferromagnetic crystals ($-2J = 478$ cm^{-1}). Pyrolysis of I in xylene and its reaction with a $CuBr_2$ solution in THF/Et_3N (1/1) leads to readily-soluble black diamagnetic crystals of $(MeC_5H_4)_4Cr_4S_4$ (II). An oxygen-containing antiferromagnetic analog of complex II, $(MeC_5H_4)_4Cr_4O_4$ (III) was isolated on oxidation of $(MeC_5H_4)_2Cr$ with traces of oxygen in the presence of Ar.

The reaction of I with $CuBr_2$ in the absence of Et_3N yielded black-green needle-like crystals of the antiferromagnetic adduct $(MeC_5H_4)_4Cr_4S_3O \cdot CuBr_2$ (IV) (μ_{eff} at room temperature is 3.91 BM). The structures of II and IV were established by X-ray crystallography. The molecule of II contains a metallotetrahedral Cr_4 skeleton (Cr–Cr 2.822(2) Å) with faces centered at the μ^3-bridged S atoms (Cr–S 2.248(2) Å). Each Cr atom is bonded to a η^5-MeC_5H_4 ligand (Cr–$C_{aver.}$ 2.241(9) Å). In IV the tetrahedral Cr_4 skeleton is distorted owing to the μ^3-O bridging ligand

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* For part VIII see ref. 17.

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(Cr–Cr 2.70(1)–2.78(1) Å, Cr–$S_{aver.}$ 2.25(2) Å, Cr–O 2.07(2)–2.12(2) Å) and to $CuBr_2$ coordination to a sulfur atom (Cu–Br 2.23(2) Å, BrCuBr 163.9(8)°, Cu··· S 3.02 Å).

Introduction

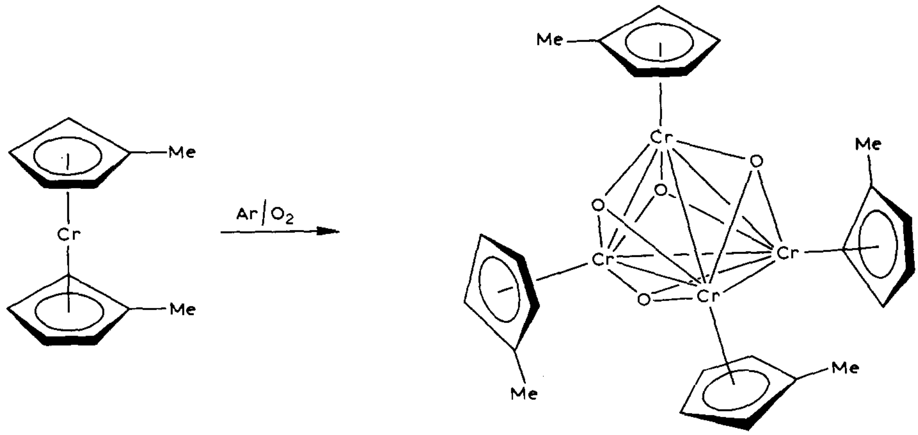
At present, the clusters $[CpMS]_4$, with a cubic metal-sulfide M_4S_4 skeleton (M = Cr [1,2], Fe [3], and Co [4]) have been isolated. The structure of the last two complexes was established by means of an X-ray analysis: the cobalt complex has no direct Co–Co bonds (Co · · · Co 3.296 Å, Co–S–Co 93–97°) while the iron complex contains only two direct Fe–Fe bonds (2.65 Å) with four Fe · · · Fe distances being nonbonding (3.36 Å). Dahl's et al. [5] qualitative MO diagram assigns 6 bonding (a_1,e,t_2) and 6 antibonding (t_1,t_2) orbitals to a metal skeleton. Occupied by 24 electrons of the four Co^{III} ions (d^6 electronic configuration) these orbitals provide no direct Co–Co bonds, whereas with 20 electrons of four Fe^{III} ions (d^5 electronic configuration) per 6 bonding orbitals there are only 4 antibonding orbitals; thus two Fe–Fe bonds are generated. It has been assumed [6] that the complex $[CpMnS]_4$ should contain 4 direct Mn–Mn bonds since 16 electrons of 4 Mn^{III} ions (d^4 electronic configuration) would occupy 6 bonding and only two antibonding orbitals. Finally, in the $[CpCrS]_4$ cluster 12 electrons of 4 chromium(III) atoms (d^3 electronic configuration) should occupy only 6 bonding orbitals leaving vacant antibonding orbitals and producing a tetrahedral metal skeleton. Accepting 12 electrons from the surrounding ligands (5 from π-C_5H_5, 4 from face-centered S atoms and 3 from Cr neighbours) each chromium atom acquires an inert gas shell and the cluster becomes generally diamagnetic. However, this is not the case when the bonding–antibonding orbital energy difference in the metal skeleton decreases on change of ligands, e.g. by replacing sulfur by oxygen atoms. Recently [7], the synthesis and X-ray study of $[CpCrO]_4$ showed broad variation of its Cr–Cr bond lengths which are pairwise equal to 2.71, 2.83 and 2.90 Å. The complex is antiferromagnetic with 2 unpaired electrons per cluster molecule at room temperature (unfortunately this brief communication gave no other details).

Thus it is of interest to discuss the structure and magnetic properties of the tetrahedral chromium clusters the sulfide and oxygen bridges recently prepared by us from bis(methylcyclopentadienyl)chromium. Note that introducing the methyl group into the ring increases complex solubility and affects essentially its electronic structure in comparison to an unsubstituted ligand.

Results

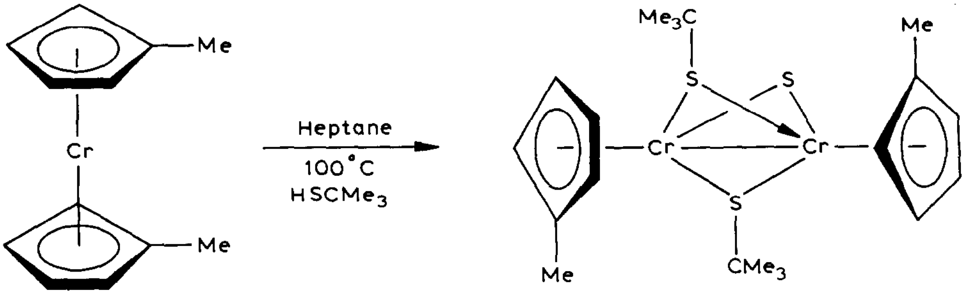
$(MeC_5H_4)_2Cr$ was synthesized analogously to Cp_2Cr [8] from $CrCl_3$ and MeC_5H_4Na in THF. It is sensitive to air: in the presence of even traces of oxygen in argon it converts into the crystalline $[(MeC_5H_4)CrO]_4$ complex isolated in the form of blue prisms.

The complex was identified by means of its elemental analysis and mass spectrum, showing the molecular ion peak (*m/e* 588) and its fragmentation products: $(P\text{–}MeC_5H_4)^+$ (*m/e* 509) $\rightarrow$ $(P - 2MeC_5H_4)^+$ (*m/e* 430) $\rightarrow$ $(P - 3MeC_5H_4)^+$ (*m/e* 351) $\rightarrow$ $(P - 4MeC_5H_4)^+$ (*m/e* 272).



The IR spectrum contains the bands assigned to ligand modes in π-MeC_5H_4 (782, 800, 1010, 1425, 3025 cm^{-1}) and an intense band at 590 cm^{-1} due to the Cr_3O group vibrations. In analogy to its unsubstituted species $[CpCrO]_4$ [7], the $[MeC_5H_4CrO]_4$ cluster is antiferromagnetic (μ_{eff} changes from 2.64 to 0.60 BM between 290–80 K).

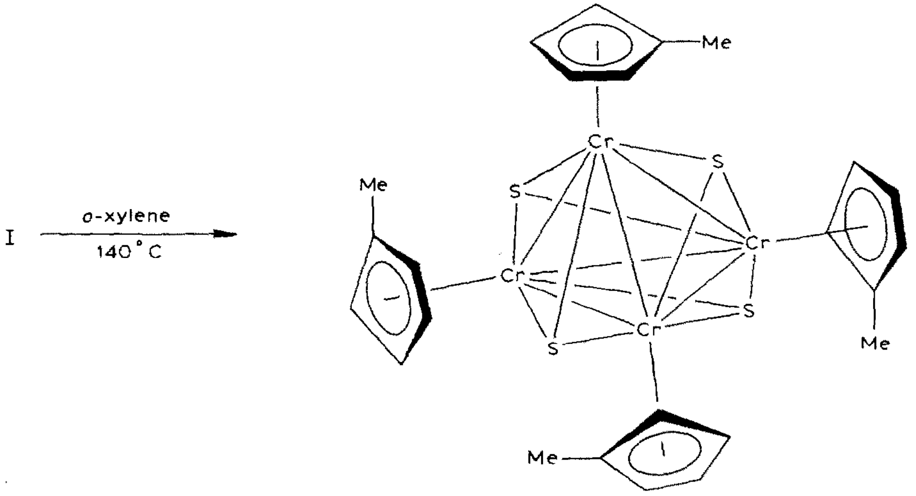
$(MeC_5H_4)_2Cr$ and tert-butylmercaptan refluxed in heptane give the binuclear $(MeC_5H_4CrSCMe_3)_2S$ (I) complex which, analogously to the unsubstituted $(CpCrSCMe_3)_2S$ complex, was isolated by chromatography on alumina and crystallized from pentane in the form of large violet prisms:



(I)

The IR spectrum of I contains stretching bands characteristic of CMe_3 (1140 cm^{-1}) and Me (1340 cm^{-1}) and coordinated cyclopentadienyl rings (795, 802 (split band), 1025, 1435 and 3040 cm^{-1}). The mass spectrum of I (at 150°C) shows the peaks of molecular ion P^+ (m/e 472) and its fragmentation products: $(MeC_5H_4)_2Cr_2S_3{}^+$ (m/e 358), $(MeC_5H_4)_2Cr_2S_2{}^+$ (m/e 326), $(MeC_5H_4)Cr_2S(SH)^+$ (m/e 249), $(MeC_5H_4)Cr_2S_2{}^+$(m/e 248), $Cr_2S_2(SH)^+$ (m/e 201) etc. I is antiferromagnetic, its μ_{eff} decreases from 1.00 to 0.31 BM at 294–81 K which is in accord with the HDVV model [9] for the coupling constant $-2J$ 478 cm^{-1} (0.7% monomer impurity, mean-square error 4.0%).

Analogously to the thermal transformation of $(CpCrSCMe_3)_2S$ into $(CpCrS)_4$ [10] pyrolysis of I in boiling *ortho*-xylene gives large multifaced black crystals corresponding to the formula of $(MeC_5H_4)_4Cr_4S_4$ (II):



(II)

II was isolated by chromatography of the black-green reaction solution on alumina and crystallized from pentane. The mass spectrum of II shows the peak of the molecular ion P^+(m/e 652) and the products of sequential elimination of MeC_5H_4 ligands: $(P - MeC_5H_4)^+$ (m/e 573) → $(P - 2MeC_5H_4)^+$(m/e 494) → $(P - 3MeC_5H_4)^+$ (m/e 415) → $(P - 4MeC_5H_4)^+$ (m/e 336), the ratio of the main peak intensities being almost the same for II and the similar $[CpCrS]_4$ (III) [10]. The IR spectrum of II is similar to that of III showing, however, the stretching bands of the CH_3 group at 1360 and 2860 cm^{-1}. Analogously to III [10], complex II is practically diamagnetic (μ_{eff} is about 0.2 BM at room temperature and it varies slightly for samples from different syntheses). The better solubility of II with respect to III enabled us to grow large crystals. Thus X-ray analysis was performed to establish the structure of II. Cluster II crystallizes into cubic symmetry (space group $P\ 43n$), unusual for organometallic complexes, the molecule having $2_12_12_1$ crystallographic symmetry. In the Cr_4 metaltetrahedral skeleton all Cr–Cr bonds are practically equivalent and close to those found for clusters with heterotetrahedral metal skeletons $Cp_3Cr_3Co(S)_4(CO)$ ($Cr-Cr_{aver.}$ 2.820(1) Å) [11] and $Cp_3Cr_3(S)_4Fe(OOCCMe_3)$ ($Cr-Cr_{aver.}$ 2.830(3) Å) [12]. The μ^3-bridged sulfur atom is located over each face of the Cr_4 tetrahedron in II with equivalent Cr–S bond lengths (2.248(2) Å). Generally, the structure of Cr_4S_4 is pseudocubic with each Cr^{III} atom bound to a η^5-MeC_5H_4 ring ($Cr-C_{aver.}$ 2.240(9), $C-C_{aver.}$ 1.43(1), $C-Me_{aver.}$ 1.49(1) Å).

Cluster II is generated also in the reaction of the binuclear complex I with $CuBr_2$ in THF in the presence of triethylamine:

$$\underset{(I)}{2(MeC_5H_4CrSCMe_3)_2S} \xrightarrow[\substack{THF\\Et_3N}]{CuBr_2} \underset{(II)}{[MeC_5H_4CrS]_4}$$

The same reaction in the absence of Et_3N gave unexpectedly a mixed ligand cluster

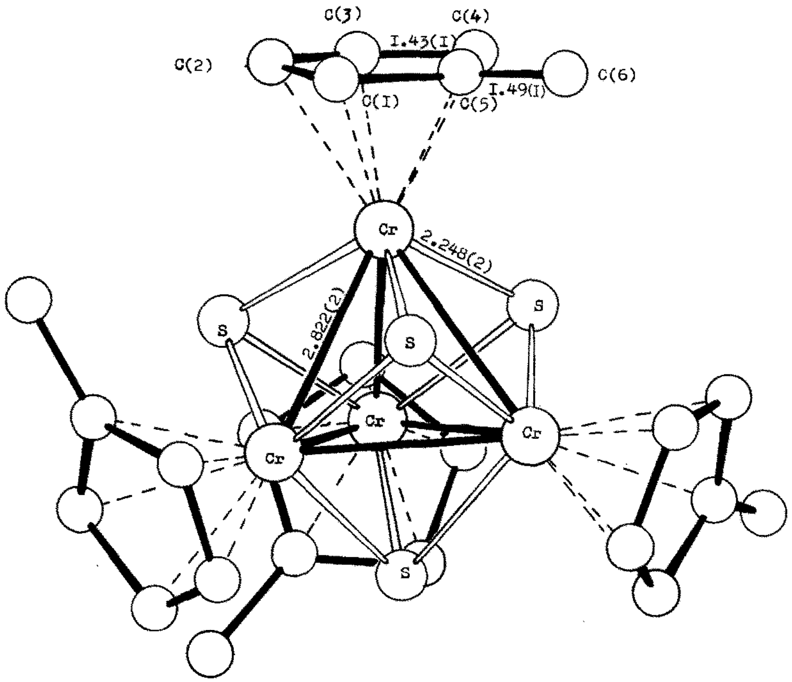
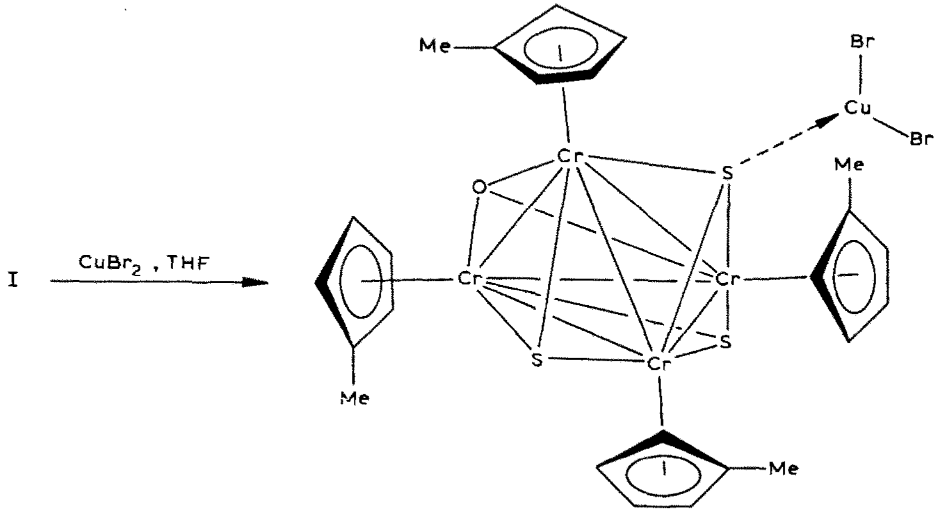


Fig. 1. The structure of complex $(MeC_5H_4)_4Cr_4(\mu^3\text{-}S)_4$.

$(MeC_5H_4Cr)_4(\mu^3\text{-}O)(\mu^3\text{-}S)_2(\mu^4\text{-}S)\cdot CuBr_2$(IV):



(IV)

In the 400–4000 cm^{-1} region the IR spectrum of IV is practically identical to that of II apart from the medium intensity band at 520 cm^{-1}, which is probably due to the Cr_3O vibrations. The mass spectrum of the complex (400°C) shows no molecular

(Continued on p. 316)

TABLE I

ATOMIC COORDINATES ($\times 10^4$, for Cr and $S \times 10^5$) AND ANISOTROPIC TEMPERATURE FACTORS FOR $(MeC_5H_4CrS)_4$ IN THE FORM $T = \exp - 1/4(B_{11}h^2a^{*2} + \ldots + 2B_{12}hka^*b^* + \ldots)$.

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	31112(7)	43219(7)	5613(7)	0.88(4)	1.13(5)	0.93(4)	0.24(3)	−0.03(3)	−0.01(3)
S	17347(11)	41801(12)	6789(12)	1.17(6)	1.11(6)	1.51(7)	−0.02(5)	0.08(5)	0.22(5)
C(1)	3205(6)	3522(5)	1699(5)	3.0(4)	2.3(3)	1.9(3)	1.0(3)	−0.5(3)	0.6(3)
C(3)	4376(6)	3947(5)	952(5)	1.9(3)	2.2(3)	2.5(3)	1.0(3)	−0.6(3)	0(3)
C(4)	4004(5)	3271(5)	523(6)	1.4(3)	1.7(3)	2.6(3)	0.8(3)	−0.1(2)	0.2(3)
C(2)	3892(6)	4083(6)	1679(6)	2.7(4)	2.4(4)	2.1(3)	1.1(3)	−1.2(3)	0(3)
C(5)	3279(5)	3007(5)	985(6)	2.0(3)	1.7(3)	2.3(3)	1.1(3)	−0.2(3)	0.7(3)
C(6)	2734(6)	2300(5)	756(7)	2.2(3)	1.6(3)	4.5(5)	0.2(2)	0.2(4)	0.3(3)

TABLE 2

BOND LENGTHS d(Å) IN $(MeC_5H_4CrS)_4$

Bond	d	Bond	d	Bond	d
Cr–Cr′	2.848(2)	Cr–C(1)	2.255(9)	C(1)–C(5)	1.43(1)
Cr–Cr″	2.822(2)	Cr–C(2)	2.239(9)	C(2)–C(3)	1.43(1)
Cr–Cr‴	2.822(2)	Cr–C(3)	2.225(9)	C(3)–C(4)	1.43(1)
Cr–S	2.247(2)	Cr–C(4)	2.232(8)	C(4)–C(5)	1.45(1)
Cr–S′	2.248(2)	Cr–C(5)	2.251(8)	C(5)–C(6)	1.49(1)
Cr–S″	2.248(2)	C(1)–C(2)	1.44(1)		

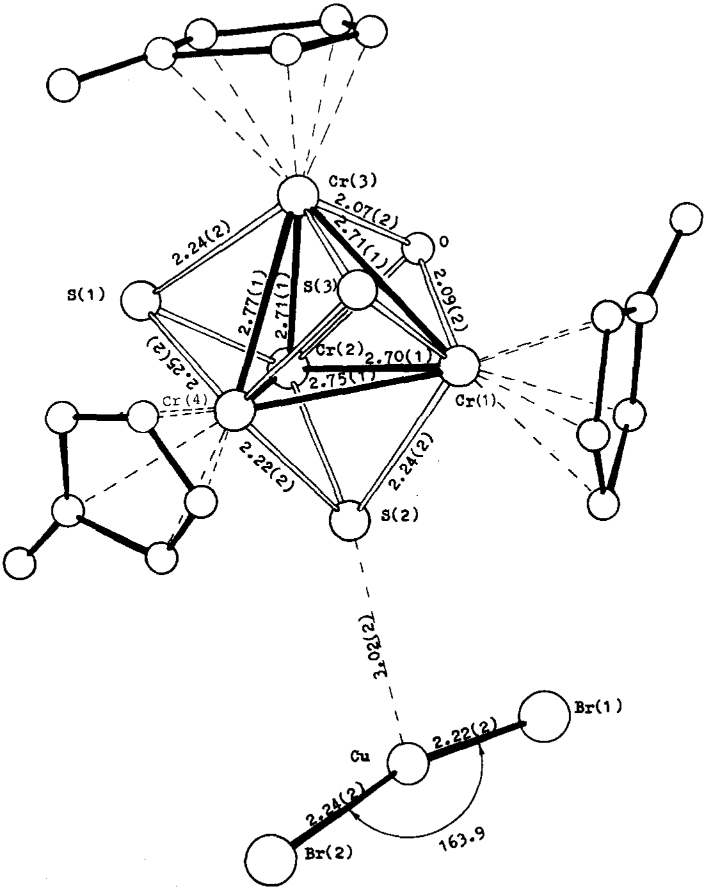


Fig. 2. The structure of $(MeC_5H_4)_4Cr_4(\mu^3\text{-O})(\mu^3\text{-S})_2(\mu^4\text{-S})\cdot CuBr_2$. The position of the MeC_5H_4 ring at the Cr(2) atom is not shown for clarity. Cr(1)–Cr(2) 2.70(1), Cr(1)–Cr(3) 2.71(1), Cr(1)–Cr(4) 2.75(1), Cr(2)–Cr(3) 2.71(1), Cr(2)–Cr(4) 2.78(1), Cr(3)–Cr(4) 2.77(1), Cr–S_{aver} 2.25(2), Cr(1)–O 2.09(2), Cr(2)–O 2.12(2), Cr(3)–O 2.07(2), S(2)···Cu 3.02(2), Cu–Br(1) 2.22(2), Cu–Br(2) 2.24(2) Å, CrCrCr 58.6(3)–61.2(3)°, CrSCr 73.9(6)–76.6(6)°, CrOCr 79.9(9)–81.0(9)°, S(2)Cu-Br(1) 96.9(6)°, S(2)CuBr(2) 99.1(6)°, Br(1)CuBr(2) 163.9(6)°.

TABLE 3

BOND ANGLES ω(°) IN $(MeC_5H_4CrS)_4$

Angle	ω	Angle	ω
CrCrCr	60.00(4)	C(1)C(2)C(3)	110.2(8)
CrCrS	51.84(6)	C(2)C(3)C(4)	106.7(8)
CrCrS	97.95(6)	C(3)C(4)C(5)	108.3(7)
SCrS	101.18(8)	C(1)C(5)C(4)	108.2(7)
CrSCr	78.06(7)	C(1)C(5)C(6)	126.8(8)
C(2)C(1)C(5)	106.6(8)	C(4)C(5)C(6)	125.0(8)

ion, the ion of maximum mass (*m/e* 636) corresponds to a cluster $(MeC_5H_4)_4Cr_4S_3O^+$. The complex is antiferromagnetic and its μ_{eff} decreases from 3.98 to 3.14 BM between 298 and 80 K.

The structure of IV is established unequivocally by X-ray analysis, although the accuracy of the Cr–C and C–C bond lengths determined is rather low owing to the poor quality of the crystals. The total molecular geometry and the main structural characteristics of the $Cr_4S_3O \cdot CuBr_2$ system are shown in Fig. 2. The Cu, Cr, Br and S atoms were iterated using anisotropic approximation. As in the case of II, the molecule of IV contains a Cr_4 metal tetrahedron in which the Cr–Cr bond lengths vary significantly (from 2.70 to 2.78(1) Å) (Fig. 2). The tridentate sulfide bridges reside over three Cr_3 faces (Cr–S 2.22(2)–2.26(2) Å); an oxygen atom is locates over one face as well (Cr–O 2.07–2.12(3) Å). Moreover, the S(2) atom generates a weak coordination bond to the $CuBr_2$ molecule (S–Cu 3.02(2) Å), the $CuBr_2$ geometry differing negligibly from a linear one (BrCuBr 163.9°, Cu–Br 2.22(2) and 2.23(2) Å). Significant variation is observed with temperature. Finally, the coordination sphere of each Cr atom in the metal tetrahedron is supplemented by the MeC_5H_4 π-bonded ligand.

Discussion

The elimination of the methylcyclopentadienyl ligand giving rise to $[MeC_5H_4CrO]_4$ observed in reaction of $(MeC_5H_4)_2Cr$ with molecular oxygen or its donors under Ar atmosphere is typical for the sandwich compounds. Thus the reaction of Cp_2Cr with N_2O [7] yielded the tetrahedral $(CpCrO)_4$ cluster. The trigonal-bipyramidal cluster $Cp_5V_5O_6$ was obtained by treating Cp_2V with N_2O [13], while the octahedral cluster $Cp_6Ti_6O_8$ was produced by treating $Cp_2Ti(CO)_2$ with a mixture of CO_2 and H_2 [14].

Similar conditions of formation of $(MeC_5H_4CrO)_4$ and $(CpCrO)_4$ and the similarity of their fragmentation under mass spectroscopy suggest the same structures and bond types. The magnetic properties of this complexes are similar too: for $(MeC_5H_4CrO)_4$, the effective magnetic moment changes from 2.64 to 0.60 BM and for the $(CpCrO)_4$ from 2.85 to 1.08 BM between 290–80 K.

The same enhancing exchange interactions are observed on going from $(CpCrSCMe_3)_2S$ ($-2J = 430$ cm^{-1}) [15] to $(MeC_5H_4CrSCMe_3)_2S$ ($-2J = 478$ cm^{-1}) although the similar chemical and spectral properties of the complexes suggest their structural similarity. The evident cause of this fenomenon is the increase of the electron-donor properties of the ligands upon replacement of hydrogen by the methyl group in cyclopentadienyl ring.

On the other hand, on going from oxygen bridges to sulfides the clusters $[CpCrS]_4$ and $(MeC_5H_4)_4Cr_4S_4$ (II) become diamagnetic (the slight paramagnetism of II with μ_{eff} 0.2 BM is probably due to impurities). The 60-electron cluster II has a symmetrical tetrahedral metal skeleton with normal Cr–Cr bonds (average length 2.822(1) Å) and sulfide bridges symmetrically located over the Cr_3 face centers (Cr–S 2.248(2) Å). As mentioned above, these distances are close to those found in the heterometallic tetrahedral clusters $Cp_3Cr_3Co(\mu^3\text{-}S)_4(CO)$ [11] and $Cp_3Cr_3Fe(\mu^3\text{-}S)_4(OOCCMe_3)$ [12]. In spite of the distorted heterometallic tetrahedra (squeezed along the $M\text{–}Cr_3$ axis) the intracluster exchange interactions are sufficiently strong in all these sulfide-bridged complexes. The first of these, the 60-electron cluster, is diamagnetic, the second, 58-electron cluster, has μ_{eff} 2.81 BM which is temperature independent between 295 and 77 K (2 unpaired electrons localized at the iron atom). In the heteronuclear cluster $Cp_4Cr_3V(\mu^3\text{-}S)_4$ [1] the effective magnetic moment (1.62 BM per cluster molecule) is also temperature independent and its unpaired electron is localized at the vanadium atom.

Thus the metal tetrahedron distortion, e.g. due to the metal heteroatom, is not the reason for its antiferromagnetism. At the same time, replacing the sulfide bridges by oxygen in the homonuclear chromium clusters caused the metal skeleton distortion along with antiferromagnetism in $(CpCrO)_4$ and $(MeC_5H_4CrO)_4$.

In this light it is interesting to discuss the structure and magnetic properties of the tetrahedral cluster $(MeC_5H_4)_4Cr_4(\mu^3\text{-}O)(\mu^3\text{-}S)_2(\mu^4\text{-}S)\cdot CuBr_2$ (IV) generated in the reaction of $(MeC_5H_4CrSCMe_3)_2S$ with $CuBr_2$ in THF, and having three sulfide and one oxygen bridges over the faces. In this complex the Cr_4 tetrahedron is somewhat distorted since the bonds between chromium atoms coordinated to the bridged oxygen atoms ($Cr\text{–}Cr_{aver.}$ 2.71 Å) are significantly shorter than those between chromiums bonded only to the sulfide bridges ($Cr\text{–}Cr_{aver.}$ 2.76 Å). This is natural since the bridged Cr–O bonds (aver. 2.08 Å) are significantly shorter than Cr–S (aver. 2.24 Å). It is quite unexpected, however, that although weak the coordination of one sulfur atom (S(2)) to the $CuBr_2$ molecule ($S\cdots Cu$ 3.02 Å) produces practically no effect on its bonding to chromium atoms. The electron density withdrawal from the S(2) atom may, along with replacement of a sulfide bridge by oxygen, change the relative location of the bonding and antibonding orbitals in the metal tetrahedron with respect to the diamagnetic cluster $(MeC_5H_4CrS)_4$ and cause antiferromagnetism. It is quite obvious that the high μ_{eff} in IV (3.98 BM at room temperature) in comparison to $(MeC_5H_4CrO)_4$ and even $(CpCrO)_4$ is partially due to the unpaired electron in the coordinated $CuBr_2$ molecule (d^9 electronic configuration of Cu^{II}). Unfortunately, a detailed analysis of all exchange interactions in cluster IV is as yet very difficult. There is also no evidence to the nature of the oxygen atom in IV and the mechanism of formation of this cluster; as it was mentioned above the same reaction gave $(MeC_5H_4CrS)_4$ in the presence of Et_3N.

Experimental

All operations were carried out under a pure argon atmosphere. The starting $(MeCp)_2Cr$ was prepared by the reported method [8]. The commercial $HSCMe_3$ was purified by fractional distillation under a pure argon stream. Heptane, pentane and triethylamine were distilled from sodium amalgam under an argon stream. THF was purified by distilling from benzophenoneketylsodium under an argon stream. The IR spectra were recorded on a Specord IR-75 instrument. The mass spectra were recorded on an automatic DS-50 unit. The magnetic susceptibility was measured by Faraday's method on a unit designed at Inst. Gen. Inorg. Chem. Acad. Sci. USSR [16].

The X-ray experiment was performed on an Syntex $P2_1$ autodiffractometer (λ Mo-K_α) at $-100°C$ (θ–2θ scanning within $2 \leqslant 2\theta \leqslant 60°$). The crystals of II are cubic, space group $P43n$ with cell parameters: $a = 16.176(6)$ Å, $Z = 6$. The structure was decoded by the direct method using a modified MULTAN [*] program and iterated using full-matrix anisotropic approximation for nonhydrogen atoms to $R_1 = 0.045$, $R_w = 0.042$ for 926 reflections.

The crystals of IV are monoclinic (space group Cc) with the cell parameters: $a = 17.77(2)$, $b = 9.742(9)$, $c = 16.36(2)$ Å; $\beta = 122.06(7)°$. The structure was decoded by the direct method and iterated using the anisotropic block-diagonal approximation for Cu, Br, Cr, S and the isotropic approach for O and C atoms to $R_1 = 0.089$ and $R_2 = 0.092$ for 1206 reflections $\geqslant 2\sigma$.

$(MeC_5H_4)_2Cr_2(SCMe_3)_2S$ (I)

2.3 g of $HSCMe_3$ was added to a red solution of 4.2 g of $(MeC_5H_4)_2Cr$ in 50 ml of heptane. The mixture was refluxed for 1 hour until stable black-violet colour was observed. The solution obtained was chromatographed over an alumina column (3 × 15 cm), eluted with heptane and the frontal black-brown zone (A) was separated from the violet zone (B). The violet solution (B) was concentrated to an oil, which was dissolved in a minimum quantity of pentane and cooled to $-5°C$. The violet prisms precipitated were separated from the mother liquid, washed with cold pentane ($-30°C$) and dried under vacuum. Yield 3.92 g, IR spectrum (ν cm^{-1}): 602w, 795s, 802s, 840w, 915w, 1025m, 1065w, 1140s, 1340s, 1435s, 1460m, 1480m, 2880m(br), 3040w.

$[MeC_5H_4CrS]_4$ (II)

a) The solution (A) was concentrated to an oil which was then extracted with warm pentane (30°C). The solution obtained was cooled to $-5°C$. The precipitated multi-faced crystals were separated from the solution, washed with cold pentane ($-30°C$) and dried under vacuum. Yield 0.54 g.

b) The reaction of I with $CuBr_2$ in the presence of Et_3N. A solution of 0.55 g of $CuBr_2$ in 10 ml of THF and 5 ml of Et_3N was added to a violet solution of I (0.7 g) in 10 ml of THF. The colour changed from violet to brown and black. The solution obtained was concentrated to an oil which was dissolved in heptane. The resultant black solution was chromatographed on an alumina column (3 × 15 cm); the black zone was eluted. The black heptane solution was concentrated to an oil which was dissolved in pentane and cooled to $-5°C$ The black crystals precipitated were separated from the solution, washed with cold pentane ($-30°C$) and dried under vacuum. Yield 0.35 g.

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[*] MULTAN program was modified by R.G. Gerr and A.I. Yanovskii.

c) Pyrolysis of I in o-xylene. A violet solution of I in 45 ml of *o*-xylene was refluxed for 2 hours. The resultant black solution was chromatographed on an alumina column (3 × 15 cm), the black zone was eluted with heptane. The solution was concentrated to an oil, which was dissolved in a minimum quantity of pentane and cooled to $-5°C$. The crystals precipitated were washed with cold pentane and dried under vacuum. Yield 0.39 g. IR spectrum (ν, cm^{-1}): 450w, 600w, 790s, 870m, 1015m, 1225w, 1360m, 1435m, 1475w, 2860m(br), 3050w.

$[MeC_5H_4CrO]_4$ (III)

A double-necked flask with 1.0 g of $(MeC_5H_4)_2Cr$ (dark-red oily substance) was evacuated (0.1 Torr) and was filled with argon with traces of O_2 (no more than 0.1%). Blue prisms formed on the flask walls, these were separated after addition of heptane and decanting. The crystals were washed with heptane and dried under vacuum. Yield 0.08 g. IR spectrum (ν, cm^{-1}): 525s, 590vs, 782s, 800s, 840w, 1010m, 1050w, 1350m, 1425m, 2850m(br), 2880m, 3025.

$(MeC_5H_4)_4Cr_4(\mu^3\text{-}O)(\mu^3\text{-}S)_2(\mu^4\text{-}S)\cdot CuBr_2$ (IV)

A filtered solution of 0.2 g of $CuBr_2$ in 10 ml THF was added to a violet solution of 0.3 g of I in 10 ml THF. After 10–15 min, the reaction mixture became black. The solvent was evaporated to dryness at 40°C/1 Torr, and the product was extracted with boiling pentane. The resultant black-green solution was concentrated to 10 ml and cooled to $-5°C$. The black-green needle-like crystals precipitated were separated from the mother liquid, washed with pentane and dried under vacuum. Yield 0.15 g. IR spectrum (ν, cm^{-1}): 520m, 655w, 810s, 1020m, 1145w, 1360m, 1435m, 1470m, 2860m(br), 3050w.

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