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Antiferromagnetic complexes with the metal–metal bond

XIX *. Influence of the nature of the bridging ligands on geometry and magnetic properties of the metallotetrahedral clusters $(MeC_5H_4)_4Cr_4(\mu_3\text{-}E)_4$ where E = O, S, Se

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Abstract

Interaction of $(MeC_5H_4)_2Cr$ with oxygen or selenium results in formation of 60-electron clusters $(MeC_5H_4)_4Cr_4(\mu_3\text{-O})_4$ (I) and $(MeC_5H_4)_4Cr_4(\mu_3\text{-Se})_4$ (III). Their structures were determined by X-ray diffraction study (I: space group $I\bar{4}$, $a = b = 13.0857(7)$, $c = 7.0538(4)$ Å, $V = 1207.9$ Å^3, $Z = 2$, $R_1 = 0.058$, $R_w = 0.066$; III: space group Pbca, $a = 18.456(2)$, $b = 17.164(1)$, $c = 16.227(2)$ Å, $V = 5140.4$ Å^3, $Z = 8$, $R_1 = 0.054$, $R_w = 0.047$). In contrast to the relatively symmetrical structure of sulfide $(MeC_5H_4)_4Cr_4(\mu_3\text{-S})_4$ (II) (Cr–Cr 2 × 2.848 and 4 × 2.822 Å) and selenide III, in I a pronounced tetrahedral distortion of the metal core is observed (Cr–Cr 2 × 2.896(3) and 4 × 2.759(3) Å). All the Cr–Cr bonds in III are elongated, compared with those in II (up to ~ 3.00–3.04 Å). The oxide cluster I is antiferromagnetic whereas the analogous sulfide and selenide clusters are diamagnetic.

Introduction

The cubane-like clusters $[Cp_4M_4S_4]^{n+}$, where Cp = π-C_5H_5, may serve as models for metal enzymes of the ferredoxine type and they attract considerable interest because they allow the number of electrons in the metal core to vary depending on

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* For part XVIII see ref. 17.

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the nature of metal and the value of n [1]. In the case of M = Co or Fe there is an excess of electrons in the metal core (72e and 68e respectively instead of 60e) which is considerably loosened [1], whereas in case of M = Cr [2,5] the metal core is formally electron saturated for $n = 0$ and changes readily to an electron deficient state for $n = 1$ (59e) [7]. The electron deficiency is enhanced up to 56e for M = V, and up to 52e for tetracation $(MeC_5H_4)_4V_4S_4^{4+}$, consequent on electrochemical oxidation [9–11], and for M = Ti [12]. Thus the capacity of this "electron reservoir" may vary from 72 to 52 electrons, i.e. the metal core may lose up to 20 electrons in the case of M = Ti ($n = 0$), while the geometry changes only slightly (from 3.3 to 2.8–2.9 Å). It is also noteworthy that introduction of a methyl group into each ring leaves the geometry of the metal core almost unchanged, e.g. the Cr–Cr bond lengths in $Cp'_4Cr_4S_4$ [4,6], where $Cp' = \pi$-MeC_5H_4, are only 0.03 Å shorter than in $Cp_4Cr_4S_4$ [5]. At the same time the nature of the bridging ligands E influences the structure and the properties of the cluster significantly. For instance in contrast to the diamagnetic symmetrical cluster $Cp_4Cr_4S_4$ (Cr–Cr 2.818–2.891 Å) [5] its oxygen analogue is antiferromagnetic and has a distorted core with the Cr–Cr bond lengths equal pairwise to 2.7, 2.8 and 2.9 Å, respectively [3].

It seems quite interesting to consider the influence of the nature of E bridges on the geometry and properties of the clusters using the $Cp'_4Cr_4E_4$ series with E = O, S, Se as a good example.

Results and discussion

It has been shown that slow oxidation of $(MeC_5H_4)_2Cr$ by oxygen (1–3 vol.% in mixture with argon) results in formation of large black-blue prisms $(MeC_5H_4)_4Cr_4(\mu_3\text{-}O)_4$ (I) [4]. According to the X-ray diffraction data the highly symmetrical molecule I in the crystalline (space group $I\bar{4}$) occupies a special position, having the crystallographic $\bar{4}$ symmetry (only the MeC_5H_4CrO fragment is independent). As a result purely tetrahedral distortion of the metal core is observed (two long, 2.896(3) Å and four short 2.759(3) Å Cr–Cr distances) (Fig. 1, Table 1), while in the above-mentioned cyclopentadienyl analogue the metal–metal bonds can be divided into three pairs (2.7, 2.8, 2.9 Å) [3]. It may be noted that a slight distortion of this type (2 × 2.848 and 4 × 2.822 Å) has already been observed by us in $(MeC_5H_4)_4Cr_4(\mu_3\text{-}S)_4$ (II). The third cluster of this series $(MeC_5H_4)_4Cr_4(\mu_3\text{-}Se)_4$ (III) with the bridging Se atoms has been recently obtained from $(MeC_5H_4)_2Cr$ and H_2Se [8]. We have prepared it by direct interaction of $(MeC_5H_4)_2Cr$ and Se and isolated it in the form of brown-green prisms. In contrast to I (space group $I\bar{4}$) and II (space group $P\bar{4}3n$) III forms orthorhombic crystals (space group $Pbca$), with the cluster molecule in a general position.The metal core III is less symmetric and much more expanded than II (Cr–Cr (av.) 3.005 Å) (Fig. 2, Table 1). Thus the increase of the covalent radii of E in the series O, S, Se (0.66, 1.04, 1.17 Å [13]) results in systematic elongation of the Cr–Cr bonds in corresponding $(MeC_5H_4)_4Cr_4E_4$ complexes. It is noteworthy that the Cr–E bonds in I–III are markedly shortened in comparison with the sums of the covalent radii of Cr (1.46 Å [14]) and E, indicating the significant contribution of additional $\overleftarrow{\mathrm{Cr{-}\ddot{E}}}$ π-bonding which is very close for E = S and Se and relatively smaller for E = O. This differences in Cr–E bonding is reflected in the Cr–Cr bond lengths which are shortened to a greater extent in going from III to II than from II to I. Nevertheless the metal cores of all three clusters are

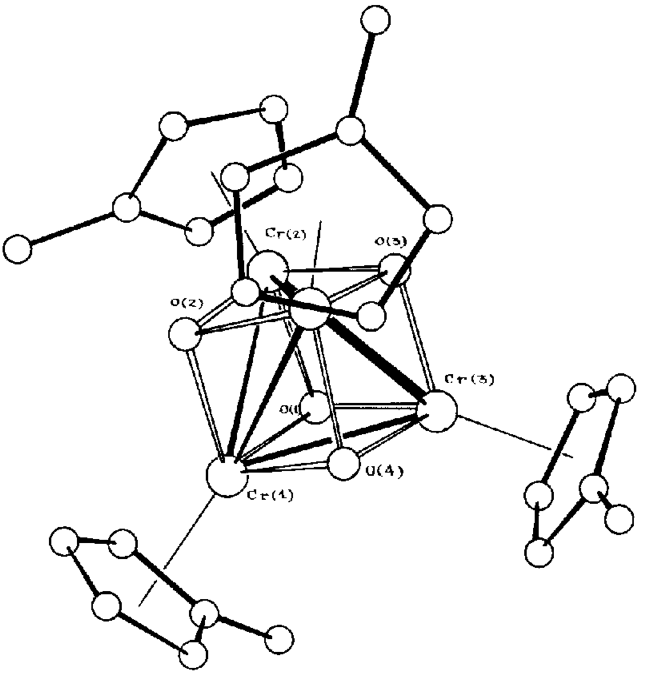

Fig. 1. The molecular structure of cluster $(MeC_5H_4)_4Cr_4(\mu_3\text{-}O)_4$ (I).

quite stable; mass-spectra show that under electron impact successive abstraction of four MeC_5H_4 ligands from molecular ion occurs, with formation of a $Cr_4E_4^+$ fragment.

Cluster I, just like $Cp_4Cr_4O_4$ [3] is antiferromagnetic, the effective magnetic moment decreasing from 2.64 to 0.60 BM in the temperature range of 296–77 K. It may possibly be due to the low energetic gap between HOMO and LUMO [15]; the observed enhancement of the covalent character of the Cr–S and Cr–Se bonds in comparison with Cr–O (i.e. the strengthening of the ligand field) leading to the increase of the energetic gap may explain the diamagnetic properties of clusters II and III.

Table 1

Geometric parameters of clusters I, II and III

	$(MeC_5H_4)_4Cr_4(\mu_3\text{-}O)_4$ (I)	$(MeC_5H_4)_4Cr_4(\mu_3\text{-}S)_4$ (II)	$(MeC_5H_4)_4Cr_4(\mu_3\text{-}Se)_4$ (III)
Cr–Cr (Å)	2×2.896 4×2.759	2×2.848 4×2.822	2.977; 2.995; 2.998 3.019; 3.037; 3.043
Cr–E (Å)	1.940–1.960	2.247–2.248	2.389–2.397
Cr–E–Cr (°)	90.1–90.6 95.8	78.06	76.85–78.95

Experimental

All operations necessary for preparation of both initial complex $(MeC_5H_4)_2Cr$ [16] and complex III were carried out under a pure argon flow; absolute solvents were used. IR spectra were measured with a "Specord 75IR" instrument in KBr pellets. Magnetic susceptibility was measured by the Faraday method using the equipment designed in the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences. The cell parameters for I: space group $I\bar{4}$, $a = b =$ 13.0857(7), $c = 7.0538(4)$ Å, $V = 1207.9$ Å^3, $Z = 2$; and III: space group $Pbca$, $a = 18.456(2)$, $b = 17.164(1)$, $c = 16.227(2)$ Å, $V = 5140.4$ Å^3, $Z = 8$ were measured with a Hilger & Watts diffractometer (λ(Mo-K_α), $\theta/2\theta$ scan, $2\theta_{max}$ 60°, T 20°C). The structures were solved by the direct method and refined in block-diagonal anisotropic approximation (for all non-hydrogen atoms) up to $R_I = 0.058$ ($R_w = 0.066$) for I and $R_I = 0.054$ ($R_w = 0.047$) for III.

Synthesis of $(MeC_5H_4)_4Cr_4Se_4$ (III)

A 20-fold excess of selenium metal was added to the red-brown solution of 0.7 g (33 mmol) of $(MeC_5H_4)_2Cr$ in 20 ml of toluene. The reaction mixture was refluxed

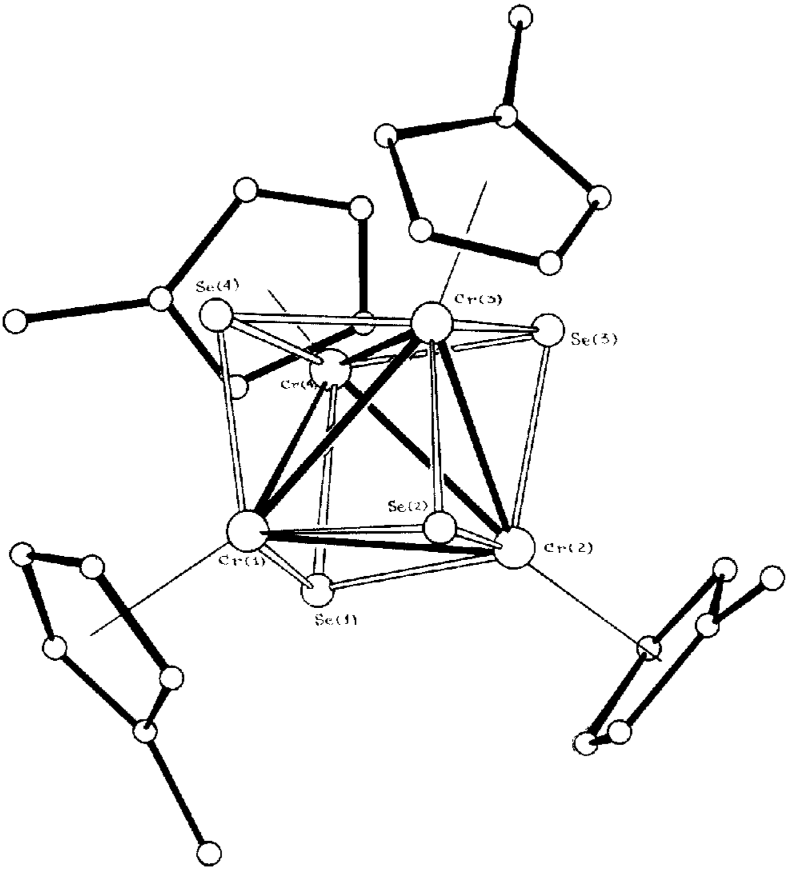

Fig. 2. The molecular structure of cluster $(MeC_5H_4)_4Cr(\mu_3\text{-}Se)_4$ (II).

Table 2

Atomic coordinates multiplied by 10^4 (for Cr by 10^5) for the cluster $(MeC_5H_4)_4Cr_4O_4$ (I)

Atom	x	y	z	B_{eq}/B_{iso}
Cr	54040(15)	10303(15)	11892(30)	1.41(5)
O	4069(6)	355(6)	1068(11)	1.7(2)
C(1)	2506(12)	4946(13)	443(24)	3.5(5)
C(2)	1861(11)	4339(12)	1598(21)	3.0(4)
C(3)	1747(11)	3381(11)	666(21)	2.9(4)
C(4)	2710(9)	1579(11)	3875(28)	3.1(4)
C(5)	2215(9)	598(11)	3713(27)	3.1(4)
C(6)	1558(12)	233(16)	2088(28)	5.5(6)

Table 3

Bond lengths (d) in the cluster $(MeC_5H_4)_4Cr_4O_4$ (I)

Cr–Cr′	2.896(3)	Cr–C(4)	2.25(1)
Cr–Cr″	2.759(3)	Cr–C(5)	2.31(1)
Cr′–Cr″	2.759(3)	C(1)–C(2)	1.42(2)
Cr–O	1.960(8)	C(1)–C(5)	1.46(2)
Cr–O′	1.942(8)	C(2)–C(3)	1.42(2)
Cr–O″	1.940(8)	C(3)–C(4)	1.45(2)
Cr–C(1)	2.29(2)	C(4)–C(5)	1.44(2)
Cr–C(2)	2.27(1)	C(5)–C(6)	1.51(3)
Cr–C(3)	2.26(1)		

Table 4

Bond angles (ω) in the cluster $(MeC_5H_4)_4Cr_4O_4$ (I)

Angle	ω(°)	Angle	ω(°)
Cr′CrCr″	58.34(7)	CrCr″O′	44.7(2)
Cr′CrO	41.8(2)	CrCr″O	45.3(2)
Cr′CrO′	42.3(2)	OCrO′	83.9(3)
Cr′CrO″	85.8(2)	OCrO″	89.1(3)
CrCr′Cr″	63.31(7)	O′CrO″	89.6(3)
CrCr′O	44.7(2)	CrOCr′	95.8(3)
CrCr′O″	89.7(2)	CrO′Cr′	90.1(3)
CrCr″O″	189.3(2)	Cr′OCr″	90.6(3)

for 4 h. The solvent was evaporated to dryness in the argon flow at 120 °C. The solid residue thus obtained was washed by 20 ml of cold (−70 °C) pentane (to separate the unreacted $(MeC_5H_4)_2Cr$) and extracted in 30 ml of ether. The transparent brown extract was concentrated at 22 °C/0.1 torr to 5–8 ml and cooled to −18 °C. The large brown prisms which precipitated from the solution after two days were isolated by decantation, washed with cold (−70 °) pentane and dried in an argon flow at 22 °C. Yield: 0.63 g (91.4%). IR spectrum (ν, cm^{-1}): 800s, 900w,br, 1000m,br, 1420w,br.

Table 5. Atomic coordinates (for Se and Cr × 10^5, C × 10^4) for a molecule of cluster $(MeC_5H_4)_4Cr_4Se_4$ (III)

	x	*y*	*z*
Se(1)	57444(6)	20799(7)	21233(8)
Se(2)	73885(6)	8454(8)	21169(8)
Se(3)	59734(7)	4984(8)	5832(8)
Se(4)	70556(6)	22947(7)	4502(8)
Cr(1)	60957(9)	7407(11)	20308(12)
Cr(2)	70241(10)	21701(12)	19189(12)
Cr(3)	58309(10)	18813(11)	6665(12)
Cr(4)	72046(10)	9261(12)	6567(13)
C(11)	5079(7)	122(7)	2398(8)
C(12)	5299(7)	589(7)	3047(8)
C(13)	5996(7)	297(7)	3323(8)
C(14)	6190(7)	−349(7)	2815(8)
C(15)	5629(7)	−461(8)	2211(8)
C(16)	4348(7)	203(9)	1898(10)
C(21)	8082(6)	2720(7)	2267(8)
C(22)	7681(7)	3289(7)	1929(8)
C(23)	7064(7)	3395(8)	2390(10)
C(24)	7085(7)	2875(9)	3049(9)
C(25)	7777(7)	2433(9)	2980(9)
C(26)	8834(7)	2446(10)	1906(12)
C(31)	5152(6)	2946(8)	394(8)
C(32)	4694(6)	2318(9)	584(9)
C(33)	4784(7)	1726(9)	−24(9)
C(34)	5320(7)	1960(8)	−592(8)
C(35)	5519(6)	2718(8)	364(9)
C(36)	5198(8)	3719(8)	809(10)
C(41)	7508(9)	−97(9)	−187(9)
C(42)	8008(6)	−61(8)	509(9)
C(43)	8372(6)	688(10)	367(11)
C(44)	8063(8)	1085(10)	−353(10)
C(45)	7533(9)	603(8)	−635(8)
C(46)	7063(8)	−802(10)	−416(11)

Table 6. The bond lengths *d* (Å) in the cluster $(MeC_5H_4)_4Cr_4Se_4$ (III)

Bond	*d* (Å)	Bond	*d* (Å)
Cr(1)–Cr(2)	2.988(3)	Cr(1)–C(12)	2.225(13)
Cr(1)–Cr(3)	2.995(3)	Cr(1)–C(13)	2.239(13)
Cr(1)–Cr(4)	3.043(3)	Cr(1)–C(14)	2.269(13)
Cr(2)–Cr(3)	3.037(3)	Cr(1)–C(15)	2.255(13)
Cr(2)–Cr(4)	2.977(3)	Cr(2)–C(21)	2.241(12)
Cr(3)–Cr(4)	3.019(3)	Cr(2)–C(22)	2.271(12)
Cr(1)–Se(1)	2.393(2)	Cr(2)–C(23)	2.238(14)
Cr(1)–Se(2)	2.397(2)	Cr(2)–C(24)	2.200(15)
Cr(1)–Se(3)	2.396(2)	Cr(2)–C(25)	2.258(14)
Cr(2)–Se(1)	2.390(2)	Cr(30–C(31)	2.259(13)
Cr(2)–Se(2)	2.393(2)	Cr(3)–C(32)	2.238(11)
Cr(2)–Se(4)	2.393(2)	Cr(3)–C(33)	2.250(13)
Cr(3)–Se(1)	2.394(2)	Cr(3)–C(34)	2.253(13)
Cr(3)–Se(3)	2.392(2)	Cr(3)–C(35)	2.278(14)
Cr(3)–Se(4)	2.395(2)	Cr(4)–C(41)	2.295(15)
Cr(4)–Se(2)	2.398(2)	Cr(4)–C(42)	2.265(13)
Cr(4)–Se(3)	2.391(2)	Cr(4)–C(43)	2.243(12)
Cr(4)–Se(4)	2.389(2)	Cr(4)–C(44)	2.295(16)
Cr(1)–C(11)	2.236(13)	Cr(4)–C(45)	2.251(14)

Table 7

Bond angles (ω) in cluster $(MeC_5H_4)_4Cr_4Se_4$ (III)

Angle	ω (°)	Angle	ω (°)
Cr(1)Cr(2)Cr(3)	59.51(6)	Cr(2)Cr(3)Se(3)	96.89(8)
Cr(1)Cr(2)Cr(4)	61.23(6)	Cr(2)Cr(3)Se(4)	50.61(6)
Cr(1)Cr(3)Cr(2)	59.59(6)	Cr(2)Cr(4)Se(2)	51.50(6)
Cr(1)Cr(3)Cr(4)	60.79(6)	Cr(2)Cr(4)Se(3)	98.52(6)
Cr(1)Cr(4)Cr(2)	59.72(6)	Cr(2)Cr(4)Se(4)	51.57(6)
Cr(1)Cr(4)Cr(3)	59.22(6)	Cr(3)Cr(1)Se(1)	51.27(6)
Cr(2)Cr(4)Cr(3)	60.86(6)	Cr(3)Cr(1)Se(2)	99.00(8)
Cr(2)Cr(3)Cr(4)	58.89(6)	Cr(3)Cr(1)Se(3)	51.21(6)
Cr(3)Cr(1)Cr(2)	60.90(6)	Cr(3)Cr(2)Se(1)	50.64(6)
Cr(3)Cr(2)Cr(4)	60.25(6)	Cr(3)Cr(2)Se(2)	97.97(8)
Cr(4)Cr(1)Cr(2)	59.05(6)	Cr(3)Cr(2)Se(4)	50.65(6)
Cr(4)Cr(1)Cr(3)	59.99(6)	Cr(3)Cr(4)Se(2)	98.34(8)
Cr(1)Se(1)Cr(2)	77.63(7)	Cr(3)Cr(4)Se(3)	50.87(6)
Cr(1)Se(1)Cr(3)	77.48(7)	Cr(3)Cr(4)Se(4)	50.96(6)
Cr(1)Se(2)Cr(2)	77.50(8)	Cr(4)Cr(1)Se(1)	97.34(8)
Cr(1)Se(2)Cr(4)	78.80(8)	Cr(4)Cr(1)Se(2)	50.61(6)
Cr(1)Se(3)Cr(3)	77.45(7)	Cr(4)Cr(1)Se(3)	50.45(6)
Cr(1)Se(3)Cr(4)	78.95(8)	Cr(4)Cr(2)Se(1)	99.19(8)
Cr(2)Se(1)Cr(3)	78.83(8)	Cr(4)Cr(2)Se(2)	51.65(6)
Cr(2)Se(2)Cr(4)	76.85(8)	Cr(4)Cr(2)Se(4)	51.42(6)
Cr(2)Se(4)Cr(3)	78.74(8)	Cr(4)Cr(3)Se(1)	97.96(8)
Cr(2)Se(4)Cr(4)	77.01(8)	Cr(4)Cr(3)Se(3)	50.84(6)
Cr(3)Se(3)Cr(4)	78.29(8)	Cr(4)Cr(3)Se(4)	50.77(6)
Cr(1)Cr(2)Se(1)	51.23(6)	Se(1)Cr(1)Se(2)	101.19(8)
Cr(1)Cr(2)Se(2)	51.31(6)	Se(1)Cr(1)Se(3)	101.69(8)
Cr(1)Cr(2)Se(4)	98.47(8)	Se(1)Cr(2)Se(2)	101.40(8)
Cr(1)Cr(3)Se(1)	51.25(6)	Se(1)Cr(2)Se(4)	99.67(8)
Cr(1)Cr(3)Se(3)	51.34(6)	Se(1)Cr(3)Se(3)	101.80(8)
Cr(1)Cr(3)Se(4)	98.51(8)	Se(1)Cr(3)Se(4)	99.52(8)
Cr(1)Cr(4)Se(2)	50.59(6)	Se(2)Cr(1)Se(3)	99.43(8)
Cr(1)Cr(4)Se(4)	50.60(6)	Se(2)Cr(2)Se(4)	102.23(8)
Cr(1)Cr(4)Se(4)	97.37(8)	Se(2)Cr(4)Se(3)	99.56(9)
Cr(2)Cr(1)Se(1)	51.14(6)	Se(2)Cr(4)Se(4)	102.22(9)
Cr(2)Cr(1)Se(2)	51.19(6)	Se(3)Cr(3)Se(4)	100.48(8)
Cr(2)Cr(1)Se(3)	97.84(8)	Se(3)Cr(4)Se(4)	100.69(9)
Cr(2)Cr(3)Se(1)	50.53(6)		

In Tables 2–4 the atomic coordinates, bond lengths and bond angles are given for cluster I and in Tables 5–7 those for cluster III.

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