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Journal of Organometallic Chemistry 612 (2000) 9–13

Antiferromagnetic complexes with metal–metal bonds[☆] Part XXIX. Synthesis and molecular structures of heterochalcogenide binuclear complex $[\pi\text{-}(CH_3C_5H_4)Cr(\mu\text{-}SPh)]_2Se$ and trinuclear mixed-metal cluster $[\pi\text{-}(CH_3C_5H_4)_2Cr_2(\mu\text{-}SPh)](\mu_3\text{-}S)(\mu_3\text{-}Se)Co(CO)_2$

A.A. Pasynskii [a],*, F.S. Denisov [a], Yu. V. Torubaev [a], N.I. Semenova [a], V.M. Novotortsev [a], O.G. Ellert [a], S.E. Nefedov [a], K.A. Lyssenko [b]

[a] *N.S. Kurnakov Institute of General and Inorganic Chemistry RAS, Leninsky prospect 31, Moscow V-71 117907, Russia*
[b] *A.N. Nesmeyanov Institute of Organoelement Compounds RAS, ul. Vavilova 28, Moscow V-334 117813, Russia*

Received 19 April 2000; received in revised form 26 May 2000

Abstract

$[Cp'Cr(CO)_2(\mu\text{-}SPh)]_2$ ($Cp' = \pi\text{-}CH_3C_5H_4$) obtained by the interaction of $[Cp'Cr(CO)_3]_2$ with Ph_2S_2 was decarbonylated to $[Cp'Cr(CO)(\mu\text{-}SPh)]_2$ which reacted with Se powder to give the antiferromagnetic complex $[Cp'Cr(\mu\text{-}SPh)]_2(\mu\text{-}Se)$ (μ_{eff} reduces from 0.79 down to 0.30 μB in the 290–80 K temperature range with exchange parameter $-2J = 552$ cm^{-1}), characterized by X-ray diffraction analysis (Cr–Cr 2.730, Cr–S 2.635, Cr–Se 2.401–2.396 Å, Cr–Se–Cr 69.4°). Another route to $[Cp'Cr(\mu\text{-}SPh)]_2(\mu\text{-}Se)$ was the interaction of $[Cp'Cr(CO)_3]_2(\mu\text{-}Se)$ with Ph_2S_2. Treatment of $[Cp'Cr(\mu\text{-}SPh)]_2(\mu\text{-}Se)$ with $Co_2(CO)_8$ results in the mixed-metal heterochalcogenide cluster $Cp'_2Cr_2(\mu\text{-}SPh)(\mu_3\text{-}S)(\mu_3\text{-}Se)Co(CO)_2$ characterized by X-ray analysis (Cr–Cr 2.624, Cr–Co 2.602–2.625, Cr-μ_3-S 2.32, Co-μ_3-S 2.23, Cr-μ_3-Se 2.43, Co-μ_3-Se 2.30, Cr-μ-S_{Ph} 2.32 Å). The cluster is antiferromagnetic (μ_{eff} reduced from 0.73 down to 0.45 μB in the 290–80 K temperature range with exchange parameter $-2J = 688$ cm^{-1}). © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Chromium; Cobalt; Chalcogenides; Cyclopentadienyl complexes; Metal carbonyls; Mixed-metal clusters; Magnetic properties; X-ray

1. Introduction

The study of the structure and magnetic properties of the mixed-metal chalcogenide-containing clusters is interesting for many reasons: for modeling of the action of natural metallo-enzymes such as the active center of nitrogenase MoFeS-cofactor [1], for the understanding of the nature of exchange interactions in the magnetic materials [2] and for the synthesis of precursors for the mixed-metal chalcogenide materials [3].

Recently we have investigated antiferromagnetic complexes with metal–metal bonds and chalcogenide bridging ligands and estimated that the role of superexchange interactions through the chalcogenide bridges is comparable with the direct exchange through the metal–metal bond. For example in the binuclear complex $[CpCr(\mu\text{-}SCMe_3)]_2(\mu\text{-}S)$ (**1**) (Cr–Cr 2.69, Cr–(μ-S) 2.24 Å) the exchange parameter $-2J$ is equal to 430 cm^{-1} [4]; it remains almost unchanged ($-2J = 440$ cm^{-1}) in $[CpCr(\mu\text{-}SCMe_3)]_2(\mu\text{-}S)Mo(CO)_5$ when only one lone pair of the μ_3-sulfide bridge is involved in coordination to a new metal atom (Cr–Cr 2.73, Cr–(μ-S) 2.27 Å) [5]. When both electron pairs of sulfide bridge in **1** participate in the coordination to new metal atoms, for example in $[CpCr(\mu\text{-}SCMe_3)]_2(\mu_4\text{-}S)[W(CO)_2NO(\mu\text{-}I)]_2$ (**2**) [6,7] or $[CpCr(\mu\text{-}SCMe_3)]_2(\mu_4\text{-}S)[Me_3Pt(\mu\text{-}I)]_2$ (**3**) [8], slight elongation of Cr–Cr bond (to 2.764 in **2** and 2.761 Å in **3**) is accompanied by significant elongation of Cr–(μ-S) bonds (2.36 in **2** and

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[☆] For Part XXVIII, see Ref. [8]

* Corresponding author. Tel.: + 7-095-9543841; fax: + 7-095-9541279.

E-mail address: aapas@ionchran.rinet.ru (A.A. Pasynskii).

PII: S0022-328X(00)00341-7

2.34 Å in **3**) resulting in the considerable decreasing of the exchange parameter (to 338 and 202 cm^{-1}, respectively).

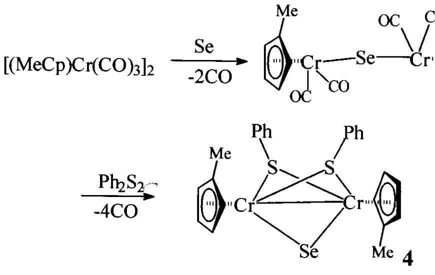
It was interesting to substitute the sulfur bridge in **1** by selenium atom and to investigate the effect of this substitution on magnetic properties, on one hand, and to prepare the mixed-metal heterochalcogenide, on the other hand.

A few years ago Goh et al. reported a structure of an analog of **1**, the antiferromagnetic binuclear complex $[CpCr(\mu\text{-}SPh)]_2S$ [9] which was obtained earlier by one of us from **1** and PhSH [10] and recently by Goh et al. from $[CpCr(CO)_3]_2$ and Ph_2S_2 with the intermediate formation of $[CpCr(CO)(\mu\text{-}SPh)]_2$ which possesses a double M=M bond [9]. The complex $[CpCr(CO)_2]_2(\mu\text{-}Se)$ containing a multiply bonded selenium bridge is also known, being prepared by the interaction of $[CpCr(CO)_3]_2$ and elemental Se under appropriate conditions [11].

Here we used the more soluble methylcyclopentadienyl analogs of $[CpCr(CO)_2]_2(\mu\text{-}Se)$ and $[CpCr(CO)_2(\mu\text{-}SPh)]_2$ as initial compounds for the synthesis of heterochalcogenide binuclear Cr(III) complexes of type **1** and their mixed-metal derivatives. Earlier it was shown [12] that the methylcyclopentadienyl analog of **1** $[Cp'Cr(SCMe_3)]_2(\mu\text{-}S)$ (**1′**) on treatment with $Co_2(CO)_8$ lost one *t*-Bu group with the formation of the trigonal mixed-metal cluster $[Cp'_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2]$ which has antiferromagnetic properties ($-2J = 578$ cm^{-1}).

2. Results and discussion

The interaction of selenium powder with $[Cp'Cr(CO)_3]_2$ ($Cp' = \pi\text{-}CH_3C_5H_4$) containing a rather weak Cr–Cr bond (3.247 Å) [13] gives the orange binuclear complex $[Cp'Cr(CO)_2]_2(\mu\text{-}Se)$ and then, after treatment by Ph_2S_2, violet crystals of binuclear heterochalcogenide complex $[Cp'Cr(\mu\text{-}SPh)]_2(\mu\text{-}Se)$ (**4**):



4

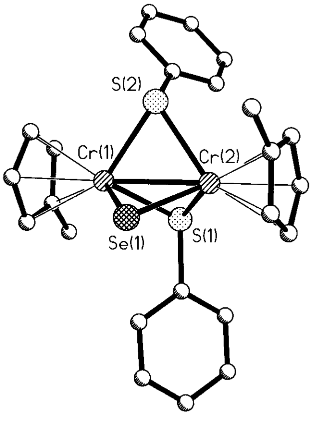
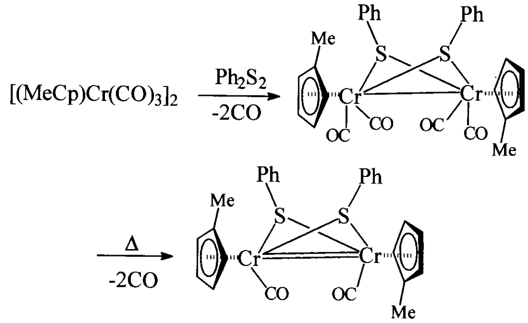


Fig. 1. The molecular structure of binuclear complex **4**.

Another approach to the synthesis of **4** utilizes the reaction of elemental selenium with $[Cp'Cr(CO)(\mu\text{-}SPh)]_2$, product of $[Cp'Cr(CO)_2(\mu\text{-}SPh)]_2$ decarbonylation:



Compound **4** is characterized by X-ray analysis (Fig. 1). The structure contains a direct Cr–Cr bond (Cr–Cr 2.730 Å) linked by two thiolate bridge groups (Cr–S av. 2.635 Å) and a selenium bridge atom (Cr–Se 2.401 and 2.396 Å, Cr–Se–Cr 69.4°). The compound **4** is antiferromagnetic (μ_{eff} reduces from 0.73 down to 0.45 m_B in the 290–80 K temperature range). The exchange interaction in **4** is described in terms of Heisenberg–Dirack–Van–Flek model with exchange parameter, $-2J = 552$ cm^{-1} (at spin value 3/2 for each Cr^{3+} ion). It is noteworthy that the $-2J$ value for **4** is considerably increased in comparison with the value of 430 cm^{-1} for **1**, despite having a longer Cr–Cr bond. Probably this could be explained on the base of the more diffuse orbitals at Se in comparison with sulfur causing a more effective superexchange through the selenium bridge atom.

The thermal decomposition of **4**, studied by differential scanning calorimetry (DSC) method, starts with the exothermic effect ($\Delta H = 67 \pm 5$ J g^{-1}) of two phenyl groups elimination in the range of 180–280°C and finishes with the endothermic effect ($\Delta H = 17$ J g^{-1}) of chalcogen elimination in the range 287–322°C. The change of mass is related to the equal probability of sulfur or selenium atom elimination from the intermediate $[Cp'_2Cr_2S_2Se]$ with the formation of stable cubane clusters, $[Cp'_4Cr_4S_4]$ and $[Cp'_4Cr_4S_2Se_2]$, of which the former one is well-documented [14].

Compound **4** reacts with $Co_2(CO)_8$ to give brown crystals of mixed-metal heterochalcogenide cluster $[Cp'_2Cr_2(\mu\text{-}SPh)(\mu_3\text{-}S)(\mu_3\text{-}Se)Co(CO)_2]$ (**5**):

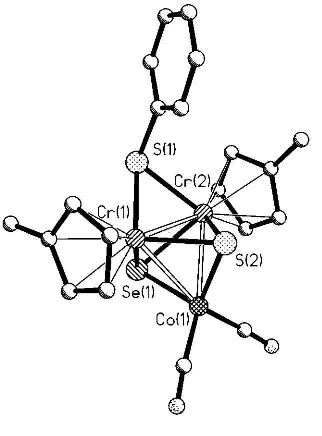
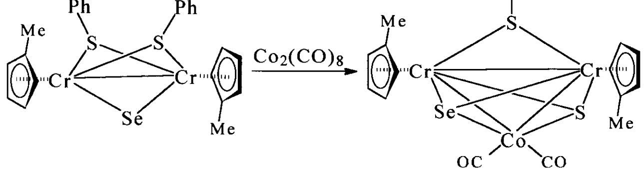


Fig. 2. The molecular structure of the cluster **5**.

Table 1
Crystal data and structure refinement for **4** and **5**

Empirical formula	$C_{24}H_{24}Cr_2S_2Se$	$C_{20}H_{19}CoCr_2O_2S_2Se$
Formula weight	559.51	597.36
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Temperature (K)	293	293
Wavelength (Mo–K_α, Å)	0.71073	0.71073
Unit cell dimensions		
a (Å)	12.070(3)	11.171(4)
b (Å)	13.924(4)	16.301(6)
c (Å)	13.684(4)	13.060(4)
β (°)	92.57(2)	114.18(2)
Volume (Å^3)	2297.5(12)	2169.8(13)
Z	4	4
D_{calc} (g cm^{-3})	1.618	1.829
$F(000)$	1128	1184
Theta range for data collection (°)	2.09–50.00	2.00–52.12
Independent reflections	4047	4264
R	0.0706 (for 2627 reflections $I>2\sigma I$)	0.0508 (for 3264 reflections $I>2\sigma I$)
R_w	0.2104 (for 3997 reflections)	0.1651 (for 4233 reflections)
Largest difference peak and hole (e Å^{-3})	1.362 and −1.164	2.123 and −1.238



As was mentioned above, **1′** reacts in the same manner with elimination of one t-Bu group and formation of a trigonal cluster $[Cp'_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2]$ (**6**) (Cr–Cr 2.590(2), Co–Cr 2.530(2) and 2.569(2), Cr–S 2.282(3), Co–S 2.213(3) Å). X-ray diffraction analysis demonstrates the similarity of the molecular structures of **5** (Fig. 2) and **6** where the Co atom has a distorted tetrahedral environment of one Se, one S atoms and two carbonyl groups (not taking into consideration two Cr–Co bonds). In **5** the lengths of the Cr–Cr bond (2.624 Å), the two Cr–Co bonds (2.602 and 2.625 Å) and the Cr-μ_3-S bonds (Cr–S 2.32 Å) are increased, probably due to the presence of the μ_3-Se bridge over the Cr_2Co triangle (Co–S 2.23, Cr–Se 2.43, Co–Se 2.30 Å) compared to the second μ_3-S bridge in **6**.

Cluster **5** is antiferromagnetic (μ_{eff} reduces from 0.73 down to 0.45 μB in the 290–80 K temperature range). The exchange parameter $-2J = 688$ cm^{-1} (Co^+ ion is diamagnetic) considerably exceeds the value of 578 cm^{-1} for **6** in spite of the Cr–Cr and Cr–Co bonds lengthening. It demonstrates that the big contribution of the superexchange interaction through Se bridge atom takes place in **5** as well as in **4**.

According to the DSC data, heating of **5** eliminates of two CO groups in the 60–180°C range with exothermic effects at 110 and 136°C. Then in the 170–320°C interval the loss of phenyl group occurs. The further heating up to 450°C does not produce any effects. So we assume that low-temperature pyrolysis of **5** gave the residue with the bulk formula $[Cp'_2Cr_2CoS_2Se]$.

3. Experimental

All manipulations were carried out in the pure argon atmosphere. IR-spectra were recorded at Specord-75 IR in KBr pellets.

X-ray investigation of complexes **4** and **5** was performed on an automatic four-circle diffractometer Siemens P3. The important crystallographic data and parameters of the refinement for **4** and **5** are presented in Table 1. Crystal structures were solved by direct method and refined in full-matrix anisotropic–isotropic (H-atoms) approximation. The positions of the hydrogen atoms were geometrically calculated. All calculations were carried out with the package of programs SHELXTL-PLUS-5 [15]. Atomic coordinates for **4** and **5** have been deposited with the Cambridge Crystal Structure Data Bank (Section 4). The most important bond lengths and angle values for the molecules of **4** and **5** are presented in Table 2.

*3.1. Preparation of $[Cp'Cr(\mu\text{-}SPh)]_2(\mu\text{-}Se)$ (**4**)*

3.1.1. Method 1

To a solution of 2.7 g (6.3 mmol) of $[Cp'Cr(CO)_3]_2$ in 40 ml of hexane 0.5 g (6.3 mmol) of Se powder was added. The reaction mixture was stirred at 50°C for 45 min. The dark red–brown solution was filtered and the solvent was evaporated to the one half of initial volume, then 30% excess of Ph_2S_2 (1.8 g, 8.2 mmol) was added. The mixture was refluxed for 4 h, whereupon a fine violet crystalline precipitate of **4** was formed and filtered, washed by hexane and dried in vacuum. Yield 1.0 g (1.8 mmol, 28%). Anal. Calc. for $C_{24}H_{24}Cr_2S_2Se$: C, 51.52; H, 4.32; S, 11.46. Found: C, 51.34; H, 4.81; S, 12.10%.

IR spectrum (KBr, cm^{-1}): 2920 w, 1560 w, 1060 m, 1020 m, 810 s, 735 s, 680 m.

The single crystals of **4** suitable for X-ray diffraction analysis were obtained by recrystallization from CH_2Cl_2–hexane 1:3 mixture.

3.2. Method 2

A solution of Ph_2S_2 (1.3 g, 6.0 mmol) in 25 ml of hexane was slowly dropped to a green solution of 2.4 g (5.5 mmol) of $[CpCr(CO)_3]_2$ in 35 ml of hexane stirred for 3 h at 40°C. The resulting dark–brown reaction solution containing $[CpCr(CO)_2(SPh)]_2$ [9] was heated at 65°C for 4.5 h resulting a dark precipitation which was filtered and solved in 50 ml of THF. To the brown–green solution 0.4 g (5.5 mmol) of Se powder was added and reaction mixture was stirred at 50°C for 1 h. Then the dark-violet solution was filtered and concentrated in vacuum to one third of volume and finally 30 ml of hexane was added. The formed dark-violet crystals were filtered and dried in vacuum. Yield 1.5 g (2.7 mmol, 48%). IR spectral data are the same as for **4** obtained by method 1.

Table 2
Selected bond lengths (Å) and angles (°) in **4** and **5**

	4	**5**
Cr(1)–S(1)	2.375(2)	2.324(2)
Cr(1)–S(2)	2.363(2)	2.321(2)
Cr(1)–Cr(2)	2.733(2)	2.624(2)
Cr(1)–Se(1)	2.397(2)	2.413(1)
Cr(2)–S(1)	2.358(2)	2.334(2)
Cr(2)–S(2)	2.368(2)	2.317(2)
Cr(2)–Se(1)	2.404(2)	2.426(1)
Se(1)–Co(1)		2.298(1)
Co(1)–S(2)		2.227(1)
Co(1)–Cr(1)		2.625(1)
Co(1)–Cr(2)		2.602(1)
Cr(1)–Se(1)–Cr(2)	69.39(5)	
Cr(2)–S(1)–Cr(1)	70.52(7)	
Cr(1)–S(2)–Cr(2)	70.57(7)	
Cr(2)–S(2)–Cr(1)		68.89(5)
Cr(2)–Cr(1)–Co(1)		59.43(3)
Co(1)–Se(1)–Cr(1)		67.68(4)
Co(1)–Se(1)–Cr(2)		66.77(4)
Co(1)–Cr(2)–Cr(1)		60.31(3)
Co(1)–S(2)–Cr(1)		70.47(4)
Co(1)–S(2)–Cr(2)		69.83(4)

3.3. Preparation of $Cp'_2Cr_2(\mu\text{-}PhS)(\mu_3\text{-}S)(\mu_3\text{-}Se)Co(CO)_2$ (5)

A yellow–brown solution of 0.2 g (0.52 mmol) $Co_2(CO)_8$ in 40 ml of CH_2Cl_2 was added to the violet solution of 0.30 g (0. 52 mmol) of **4** in 10 ml CH_2Cl_2. The reaction mixture was stirred at room temperature for 20 min (the reaction monitored by TLC until the violet spot of **4** had disappeared). The solvent was evaporated in vacuum and the residue was extracted by 50 ml of hexane. The resulting dark red–brown extract was concentrated in vacuum to solution crystallization and then kept at −20°C. Yield: 0.26 g (0.44 mmol) Anal. Calc. for $C_{20}H_{19}Cr_2S_2SeO_2Co$: CO 9.4; Ph 12.9. DSC Anal. Found: CO 10 ± 1; Ph 12.2%. IR spectrum (KBr, cm^{-1}): 2900 w, 1950 vs, 1900 vs, 1560 w, 790 m, 710 m, 630 w.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 142351 and 142350. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank INTAS (grant 96-1256) and Russian Foundation of Fundamental Research (grants 97-03-33027, 96-03-33172 and 00-15-97359) for financial support.

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