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Antiferromagnetic complexes with metal–metal bonds. Part XXX. Synthesis and molecular structures of the antiferromagnetic adducts $[Cp'Cr(\mu\text{-}SPh)]_2(\mu_3\text{-}Se)\cdot ML$ ($Cp' = \eta^5\text{-}CH_3C_5H_4$, $ML = Fe_3(\mu_3\text{-}S)_2(CO)_8$, $Mn_2(CO)_9$, $Mn_2(CO)_8$), paramagnetic complexes $Cp'Cr(\mu\text{-}SPh)_3Mn(CO)_3$ and $[Cp'Cr(\mu\text{-}SPh)]_2Te$, diamagnetic cluster $Cp'_2Cr_2(\mu\text{-}SPh)(\mu_3\text{-}S)(\mu_3\text{-}Te)Co(CO)_2$☆

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Abstract

The photochemical reactions of antiferromagnetic heterochalcogenic complex $[Cp'Cr(\mu\text{-}SPh)]_2(\mu\text{-}Se)$ (**1**) ($Cp' = \eta^5\text{-}CH_3C_5H_4$) with $Fe_3(\mu_3\text{-}Se)_2(CO)_9$ or $Mn_2(CO)_{10}$ at room temperature gives new mixed-metal heterochalcogenic clusters $[Cp'Cr(\mu\text{-}SPh)]_2(\mu_3\text{-}Se)Fe_3(\mu_3\text{-}Se)_2(CO)_8$ (**2**), $[Cp'Cr(\mu\text{-}SPh)]_2(\mu_3\text{-}Se)Mn_2(CO)_9$ (**3**) and $[Cp'Cr(\mu\text{-}SPh)]_2(\mu_4\text{-}Se)Mn_2(CO)_8$ (**4**) which are antiferromagnetic ($-2J = 256$, 230 and 324 cm^{-1}, respectively) and characterized by X-ray diffraction analysis (**2**: Cr–Cr 2.763(1) Å; Fe–Fe 2.6184(9) and 2.706(1) Å; Cr–Se 2.447, 2.460 Å; **3**: Cr–Cr 2.762 Å; Mn–Mn 2.920 Å; Cr–Se 2.447, 2.460 Å; **4**: Cr–Cr 2.816 Å, Mn–Mn 2.835 Å, Cr–Se 2.464 Å). The photochemical reaction of **1** and $Mn_2(CO)_{10}$ at higher temperature gives the paramagnetic complex $Cp'Cr(\mu\text{-}SPh)_3Mn(CO)_3$ (**5**) with a weak Cr–Mn bond (3.0239 Å). The new heterochalcogenic complex $[Cp'Cr(\mu\text{-}SPh)]_2(\mu\text{-}Te)$ (**6**) which obtained at the interaction of $[Cp'Cr(CO)(\mu\text{-}SPh)]_2$ with Te and was studied by X-ray method (Cr–Cr 2.772 Å, Cr–S 2.359 Å, Cr–Te 2.601–2.607 Å, Cr–Te–Cr 64.3°), reacted with $Co_2(CO)_8$ with formation of the diamagnetic mixed-metal heterochalcogenic cluster $[Cp'_2Cr_2(SPh)](\mu_3\text{-}S)(\mu_3\text{-}Te)Co(CO)_2$ (**7**) (Cr–Cr 2. 646 Å, Cr–Co 2.627 Å–2.623 Å, Cr–μ_3-S 2.282–2.299 Å, Co–μ_3-S 2.199 Å, Cr–μ_3-Te 2.630–2.618 Å, Co–μ_3-Te 2.466 Å, Cr–μ-S_{Ph} 2.335 Å). The role of super-exchange spin–spin interaction through the chalcogen bridge atom is discussed.

Keywords: Chromium; Manganese; Cobalt; Iron; Chalcogenide; Cyclopentadienyl complexes; Metal carbonyls; Mixed-metal clusters; Magnetic properties; X-ray analyses

1. Introduction

In our preceding researches of antiferromagnetic homo- and heterochalcogenic complexes $[\eta^5\text{-}(RC_5H_4)_2Cr_2(\mu\text{-}SR')_2](\mu\text{-}X)$ where $R = CH_3$, $R' = Ph$, $X = Se$ [1] or $R = H$, $R' = CMe_3$, $X = S$ [2] and their mixed-metal derivatives [1,3,4] we observed the significant effect of the chalcogen bridge atom nature on the

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magnetic properties of clusters. In the investigated clusters the contribution of super-exchange interactions via chalcogenide bridge is comparable to the contributions of direct interactions through Cr–Cr bond [5]. Moreover the substitution of sulphur atom by a bigger selenium atom results in the significant increasing of exchange parameter $-2J$ from 430 cm^{-1} for [CpCr(μ-$SCMe_3$)]$_2$(μ-S) [2] to 578 cm^{-1} for [Cp′Cr(μ-SPh)]$_2$(μ-Se) (1) notwithstanding with the elongation of Cr–Cr bond from 2.689 to 2.730Å [1]. It was known too that the biggest elongation of the Cr–Cr bond took place at the substitution of sulphur by tellurium atoms: from 2.676 Å in [CpCr(μ-SPh)]$_2$(μ-S) [6] up to 2.935 Å in [CpCr(μ-TePh)]$_2$(μ-Te) [7] (the magnetic properties of the last complex were not learned-only a suggestion was done about its paramagnetic activity because of the signal broadening in ^{1}H- and ^{13}C-NMR spectra [7]).

In the case of Cp_2Cr_2(μ-$SCMe_3$)$_2$(μ-S)·ML the super-exchange interactions depend strongly upon the type of ML coordination [4,8–11] (see Table 1)

The greatest exchange parameter values were observed in the triangular metal clusters $Cp'_2Cr_2(SR)(\mu_3\text{-}S)(\mu_3\text{-}X)Co(CO)_2$ ($X = S$, $R = CMe_3$ $-2J = 578$ cm^{-1} [12]; $X = Se$, $R = Ph$, $-2J = 692$ cm^{-1} [1]).

So we prepared some ML- containing derivatives of 1 on one hand and tellurium-containing complexes [Cp′Cr(μ-SPh)]$_2$(μ-Te) and $Cp'_2Cr_2(SPh)(\mu_3\text{-}S)(\mu_3\text{-}Te)Co(CO)_2$ on the other hand to study the influence of ML and chalcogen atom nature on the structures and magnetic properties of clusters.

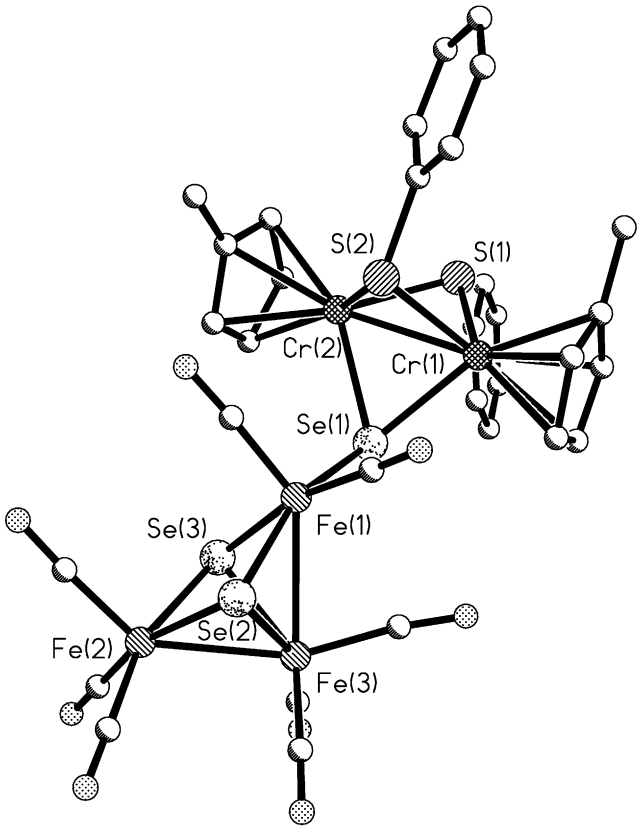
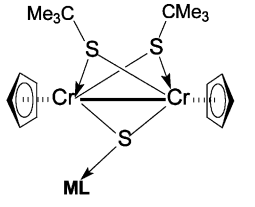


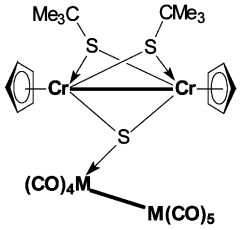
Fig. 1. Molecular structure of complex **2**.

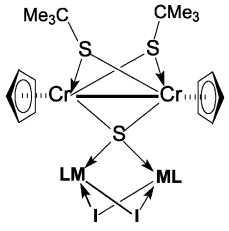
2. Results and discussion

The photochemical interaction between [Cp'_2Cr_2(μ-$SPh)_2$](μ-Se) (**1**) and $Fe_3(\mu_3\text{-}Se)_2(CO)_9$ at the room temperature gives the adduct [Cp′Cr(μ-SPh)]$_2$(μ_3-Se)·$Fe_3(\mu_3\text{-}Se)_2(CO)_8$ (**2**) which was structurally characterized by means of single-crystal X-ray diffraction analysis (Fig. 1, Tables 2 and 3):

Table 1
Types of complexes and $-2J$ values







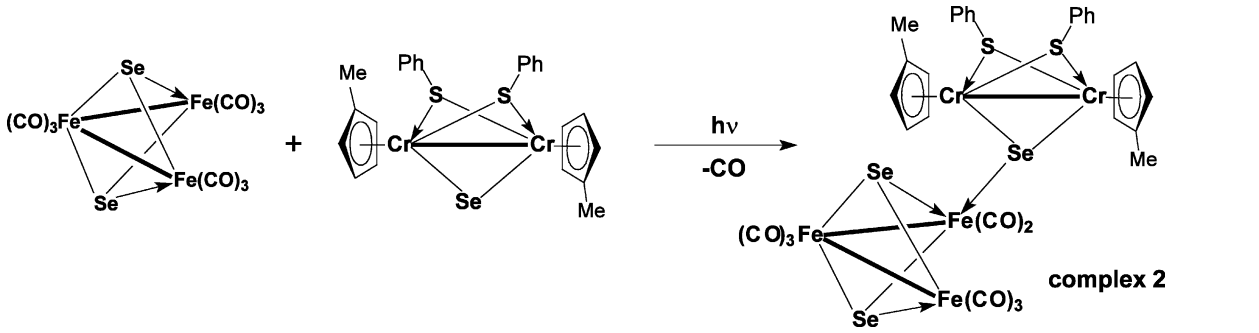
ML	-2*J*	ML	-2*J*	ML	-2*J*
$Mo(CO)_5$ [8]	440 cm^{-1}	$Mn_2(CO)_9$ [9]	400 cm^{-1}	$[Me_3Pt(\mu\text{-}I)]_2$ [4]	202 cm^{-1}
$W(CO)_5$ [8]	440 cm^{-1}	$Re_2(CO)_9$ [10]	424 cm^{-1}	$[W(CO)_2(NO)I]_2$ [11]	338 cm^{-1}

Table 2
Crystal data and structure refinement for **2**–**4**

	2	**3**	**4**
Empirical formula	$C_{32}H_{24}Cr_2Fe_3O_8S_2Se_3$	$C_{33}H_{24}Cr_2Mn_2O_9S_2Se1/2(C_4H_{10}O)$	$C_{32}H_{24}Cr_2Mn_2O_8S_2Se$
Formula weight	1109.06	958.54	893.47
Diffractometer	Smart 1000 CCD	Smart 1000 CCD	Siemens P3
Temperature (K)	110(2)	293(2)	293(2)
Radiation, λ(Mo–K_α) (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	Cc
Unit cell dimensions			
a (Å)	10.532(3)	11.0719(7)	16.032(3)
b (Å)	25.344(1)	15.712(1)	13.766(3)
c (Å)	13.581(5)	21.601(1)	16.377(3)
β (°)	94.72(2)	96.943(1)	104.72(1)
V (Å^3)	3613(2)	3730.2(4)	3496(1)
Z	4	4	4
ρ_{calc} (g cm^{-3})	2.039	1.707	1.698
Linear absorption, μ (cm^{-1})	49.45	23.70	25.19
Absorption correction	Semiempirical from equivalents	Semiempirical from equivalents	ψ-curve
F(000)	2160	1916	1776
T_{max}/T_{min}	0.752/0.443	0.838/0.753	0.852/0.673
Scan type	ω-scan 0.3°/10 s exposure per frame	ω-scan 0.3°/10 s exposure per frame	$\theta/2\theta$
θ Range (°)	1.61–30.05	1.61–28.95	1.98–25.05
Measured	42203	23121	3167
Unique	10445 [$R_{int} = 0.0524$]	9027 ($R_{int} = 0.0323$)	3167 ($R_{int} = 0.0215$)
With [$I > 2\sigma(I)$]	6686	5871	2442
Parameters	453	571	427
Final $R(F_{hkl})$: R_1	0.0358	0.0406	0.0647
wR_2	0.0675	0.1007	0.1517
GOF	0.972	0.810	0.974
ρ_{max}/ρ_{min} (e Å^{-3})	0.881/−0.632	1.505/−0.415	1.623/−1.437

Table 3
Selected bond lengths (Å) and bond angles (°) for **2**–**4**

2	**3**		**4**		
Bond lengths					
Cr(1)–Cr(2)	2.763(1)	Cr(1)–Cr(2)	2.7620(7)	Cr(1)–Cr(2)	2.816(3)
Cr(1)–Se(1)	2.4483(9)	Se(1)–Cr(1)	2.4593(6)	Cr(1)–Se(1)	2.463(2)
Cr(2)–Se(1)	2.4560(8)	Se(1)–Cr(2)	2.4469(6)	Cr(2)–Se(1)	2.464(3)
Fe(1)–Se(2)	2.320(1)	Cr(1)–S(1)	2.360(1)	Cr(1)–S(1)	2.375(4)
Fe(1)–Se(3)	2.3493(8)	Cr(1)–S(2)	2.359(1)	Cr(2)–S(1)	2.379(5)
Fe(1)–Se(1)	2.4648(9)	Se(1)–Mn(1)	2.5506(6)	Cr(1)–S(2)	2.343(4)
Fe(2)–Se(2)	2.3595(8)	Mn(1)–Mn(2)	2.9502(7)	Cr(2)–S(2)	2.344(4)
Fe(2)–Se(3)	2.374(1)			Se(1)–Mn(2)	2.413(2)
Fe(3)–Se(2)	2.366(1)			Se(1)–Mn(1)	2.425(3)
Fe(3)–Se(3)	2.3758(8)			Mn(1)–Mn(2)	2.835(3)
Fe(2)–Fe(3)	2.6184(9)				
Fe(1)–Fe(3)	2.706(1)				
Bond angles					
Cr(1)–Se(1)–Cr(2)	68.58(3)	Cr(2)–Se(1)–Cr(1)	68.52(2)	Mn(2)–Se(1)–Mn(1)	71.75(9)
Cr(1)–Se(1)–Fe(1)	114.56(3)	Cr(2)–S(1)–Cr(1)	71.82(3)	Mn(2)–Se(1)–Cr(1)	136.05(9)
Cr(2)–Se(1)–Fe(1)	112.53(3)	Cr(1)–S(2)–Cr(2)	71.54(3)	Mn(1)–Se(1)–Cr(1)	126.72(1)
Fe(1)–Se(2)–Fe(2)	97.84(3)	Cr(1)–S(2)–Cr(2)	71.54(3)	Mn(2)–Se(1)–Cr(2)	139.5(1)
Fe(1)–Se(2)–Fe(3)	70.53(2)			Mn(1)–Se(1)–Cr(2)	122.61(8)
Fe(2)–Se(2)–Fe(3)	67.29(3)			Cr(1)–Se(1)–Cr(2)	69.71(7)
Fe(1)–Se(3)–Fe(2)	96.66(3)			Cr(1)–S(2)–Cr(2)	73.9(1)
Fe(1)–Se(3)–Fe(3)	69.88(3)				
Fe(2)–Se(3)–Fe(3)	66.92(2)				



The geometry of $Fe_3(\mu_3\text{-}Se)_2(CO)_8$ fragment does not undergoes significant changes in comparison with the initial $Fe_3(\mu_3\text{-}Se)_2(CO)_9$ [13]. The length of Cr(1)–Cr(2) bond (2.763(1) Å) and the value of angle Cr(1)–Se(1)–Cr(2) (68.58(3)°) are close to those for complex **1** but Cr–Se bonds (2.4483(9) and 2.4560(8) Å) are elongated in comparison with **1** (Cr–Se 2.401 and 2.396 Å) and this elongation could be the reason of the decreasing of the exchange parameter of **2** ($-2J = 256$ cm^{-1}): μ_{eff} reduced from 1.8μ_B (287 K) to 0.42μ_B (79 K) with respect to 578 cm^{-1} for **1**.

The photochemical interaction between **1** and $Mn_2(CO)_{10}$ at the room temperature gives black crystals of $[Cp'Cr(\mu\text{-}SPh)]_2(\mu_3\text{-}Se)Mn_2(CO)_9$ (**3**) studied by X-ray analysis (Fig. 2, Tables 2 and 3).

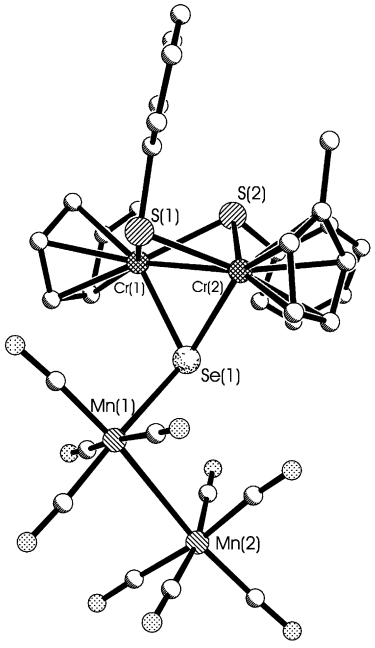
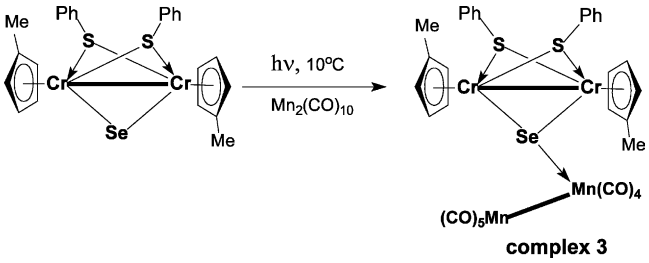
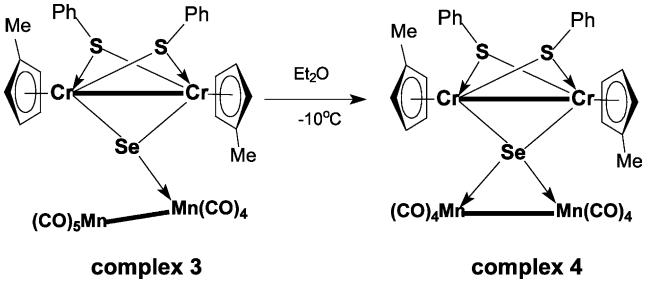


Fig. 2. Molecular structure of complex **3**.



Selenium atom is coordinated to only one of manganese atoms (Mn–Se 2.5506(6) Å). The Mn–Mn and Cr–Cr bond lengths (2.920 and 2.762 Å, respectively) remain almost unchanged in comparison with initial compounds, while significant elongation of Cr–Se bonds up to 2.447 and 2.460 Å takes place. The similar elongation of Cr–Se bonds was observed in **2** and in the known cluster $Cp_2Cr_2(SePh)_2SeCr(CO)_5$ [14]. This Cr–Se bond elongation in **3** is accompanied by decreasing of its $-2J$ value to 230 cm^{-1} (μ_{eff} reduced from 1.68 down to 0.56μ_B in the 295–80 K temperature range) with respect to 578 cm^{-1} for **1**. It is noteworthy that $-2J$ values for all adducts $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)\cdot ML$ (Table 1) are near 400–440 cm^{-1} [3], e.g. very close to 430 cm^{-1} for the initial $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ [2]. It means that antiferromagnetic exchange interactions in selenide-bridged complexes are more sensitive to the nature of chalcogen atom than in the case of sulfide-bridged complexes.



Keeping of the ether solution of **3** at −10 °C for 48 h favours the further decarbonylation with the formation

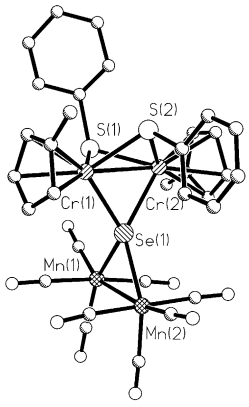


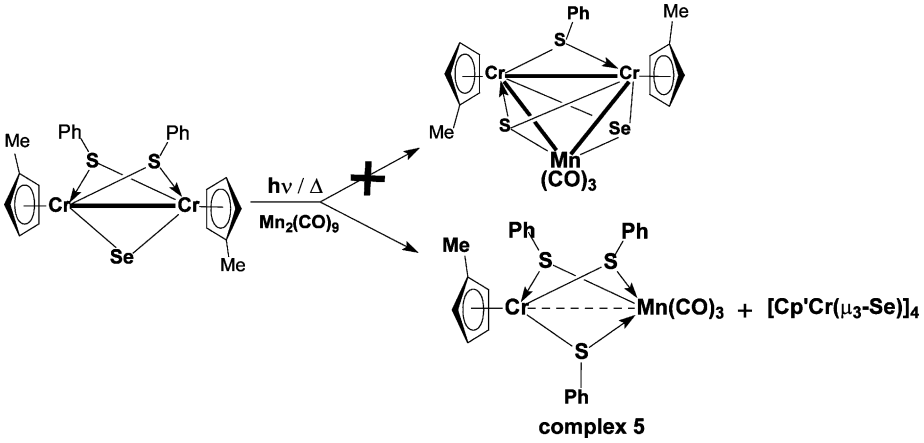
Fig. 3. Molecular structure of complex **4**.

of a new cluster $[Cp'Cr(\mu\text{-}SPh)]_2(\mu_4\text{-}Se)Mn_2(CO)_8$ (**4**) which was characterized by X-ray analyses (Fig. 3, Tables 2 and 3) and has a spirane-like metal–chalcogenide core where μ_4-Se atom is coordinated with two chromium (Cr–Cr 2.816(3) Å, Cr–Se av. 2.464 Å) and two manganese atoms (Mn–Mn 2.835(3) Å, Mn–Se av. 2.419 Å).

Due to an elongation of Cr–Cr bond in **4** with respect to 2.76 Å in **3** one could expect decreasing of $-2J$ value but its unexpected increasing up to 324 cm^{-1} (μ_{eff} reduced from 1.51μ_B down to 0.53μ_B in the 292–79 K temperature range) was observed. The reason is still not clear. We could only suppose that it is a result of some electronic features of μ_4-Se atom which has no lone pair (particularly, in **4** the significant shortening of the Mn–Se bond lengths (av. 2.418(3) Å) takes place in comparison with Mn–Se distance (2.5506(6) Å in **3**). But in the case of two known clusters with μ_4-S-bridge atom took place the significant decreasing of $-2J$ values in comparison with μ_3-S-containing clusters, particularly containing $Mn_2(CO)_9$ group (Table 1). Probably some role could play the presence of Mn–Mn bond in **4** whereas known μ_4-S-containing clusters had two ML groups linked by two iodine bridges only without M–M bond between them (Table 1).

The conservation of the structure of **1** during the photochemical inter-reaction with $Fe_3(\mu_3\text{-}Se)_2(CO)_9$ or $Mn_2(CO)_{10}$ and formation of the adducts **2**–**4** is in contrast to the known photochemical transformations of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ into pentanuclear metal–spirane cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Fe(\mu_3\text{-}S)_2Fe_2(CO)_9$ [15] and triangular cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Mn(CO)_3$ [16], respectively. Probably this difference results from the longer distance between ML group and chromium atoms in the presence of bulky selenide bridge in comparison with sulfide bridge, on one hand, and on the other hand — the stronger S–Ph bond in respect to S–CMe_3 bond, does not favour the elimination of CMe_3 accompanying the transformation of SPh into μ_3-S bridging ligand.

The photochemical reaction of **1** and $Mn_2(CO)_{10}$ at higher temperature (in refluxing benzene) unexpectedly leads to $Cp'Cr(\mu\text{-}SPh)_3Mn(CO)_3$ (**5**) instead of triangular $Cp'_2Cr_2(\mu\text{-}SPh)(\mu_3\text{-}Se)(\mu_3\text{-}S)Mn(CO)_3$ supposed by analogy with known $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Mn(CO)_3$ [16,17].



According to the X-ray data (Fig. 4, Tables 4 and 5) the Cr(1)–Mn(1) bond (3.0239(7) Å) has probably an order 0.5 in accordance with the observed paramagnetic properties of **5** — three unpaired electrons ($\mu_{\varepsilon\phi}$ (3.67μ_B) does not depend on the temperature).

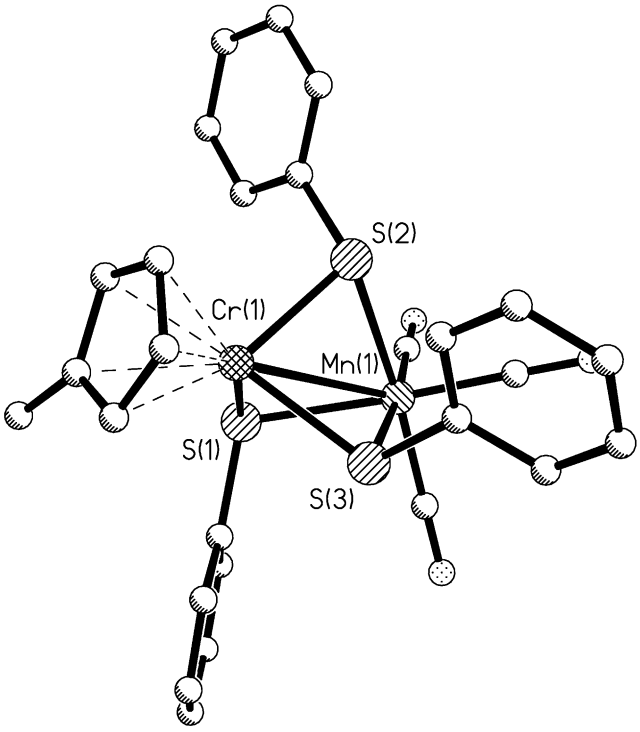
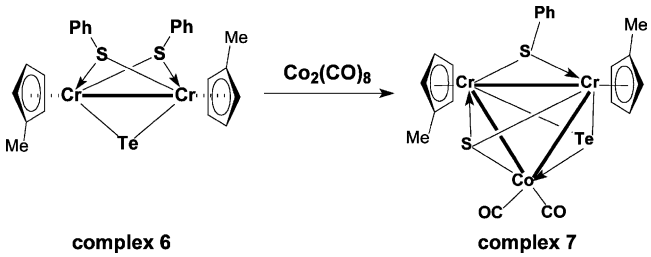


Fig. 4. Molecular structure of complex **5**.

The Te-bridged binuclear chromium complex $[CpCr(\mu\text{-}SPh)]_2(\mu\text{-}Te)$ (**6**) was prepared by the reaction of elemental tellurium with $[Cp'Cr(CO)(\mu\text{-}SPh)]_2$ which was obtained while the decarbonylation of $[Cp'Cr(CO)_2(\mu\text{-}SPh)]_2$:

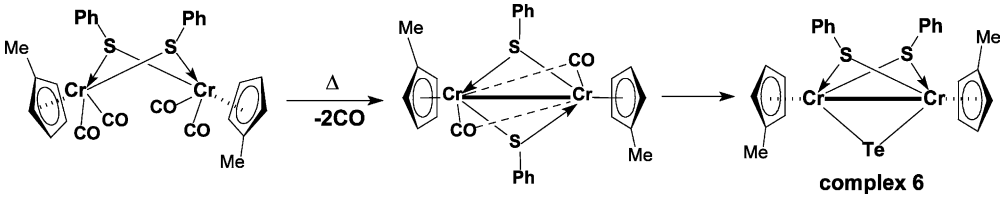


complex 6 complex 7

Single-crystal X-ray diffraction analysis of **7** (Fig. 6, Tables 4 and 5) demonstrated the similarity of its core to those found earlier for $Cp'_2Cr_2(SR)(\mu_3\text{-}S)(\mu_3\text{-}X)Co(CO)_2$ (X = S; R = CMe_3 (**8**) [8] or X = Se; R = Ph (**9**) [1]). In **7** μ_3-telluride and μ_3-sulfide bridging atoms are situated over and under Cr_2Co triangle (Cr–S 2.299(1) Å, Co–S 2.199(1) Å, Cr–Te 2.6303(9) Å, Co–Te 2.466(1) Å). Diamagnetic properties of **7** are unexpected because the metal–metal bonds (Cr–Cr 2.646(1) Å, Cr–Co 2.628(1) Å) in **7** are elongated in respect to **8** (Cr–Cr 2. 590 Å, Cr–Co 2.530 and 2.569 Å) and **9** (Cr–Cr 2. 624 Å, Cr–Co av. 2. 612 Å) which appeared antiferromagnetic properties. Apparently in **7** the super-exchange interactions via tellurium atom are more important than direct spin–spin interactions via M–M bonds.

3. Experimental

All manipulations were carried out in pure argon atmosphere with using of absolute solvents. Commercial $Mn_2(CO)_{10}$ was recrystallized from hexane.



complex 6

The structure of the black crystals of **6** was studied by single-crystal X-ray diffraction analyses (Fig. 5, Tables 4 and 5). It contains two Cp′Cr groups linked by direct Cr–Cr bond (2.772(3) Å), two thiolate bridge groups (Cr–S av. 2.359 Å) and one telluride bridge atom (Cr–Te 2.601(2)–2.607(2) Å, Cr–Te–Cr 64.30(7)°). Complex **6** is unstable and it was impossible to get the clear data on its magnetic properties.

The reaction of **6** with $Co_2(CO)_8$ gives mixed-metal heterochalcogenic cluster $[Cp'_2Cr_2(\mu\text{-}SPh)](\mu_3\text{-}S)(\mu_3\text{-}Te)Co(CO)_2$ (7) as diamagnetic brown crystals which are stable under argon.

$[Cp'Cr(CO)_3]_2$ was prepared in accord with [18]. $Fe_3(CO)_9(Se)_2$ was prepared as in Ref. [19]. IR-spectra were recorded at 'Specord-75 IR' in KBr pellets. Differential scanning calorimetry (DSC) was studied with thermoanalyser 'Mettler' TA-3000 in dry argon.

The temperature dependence of the magnetic susceptibilities (χ_m) of the investigated compounds was determined by the Faraday technique between 77 and 296 K using original device [20]. The effective magnetic moments of compounds were calculated by formula (1)

$$\mu_{eff} = 797.7(B_m T)^{1/2} \quad (1)$$

Table 4
Crystal data and structure refinement for **5**–**7**

	5	**6**	**7**
Empirical formula	$C_{27}H_{22}CrMnO_3S_3$	$C_{24}H_{24}Cr_2S_2Te$	$C_{20}H_{19}CoCr_2O_2S_2Te$
Formula weight	597.57	608.15	646.00
Diffractometer	Smart 1000 CCD	Siemens P3	Smart 1000 CD
Temperature (K)	190(2)	298(2)	110(2)
Radiation, λ(Mo–K_α) (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbca*	$P2_1/n$	$P2_1/c$
Unit cell dimensions			
a (Å)	14.5207(9)	12.447(6)	10.220(3)
b (Å)	18.623(1)	13.827(7)	16.187(5)
c (Å)	19.380(1)	13.719(7)	13.373(4)
β (°)	90	92.24(4)	101.07(3)
V (Å^3)	5240.5(5)	2359.4(19)	1636.3(9)
Z	8	4	4
ρ_{calc} (g cm^{-3})	1.515	1.712	1.681
Linear absorption, μ (cm^{-1})	11.63	23.18	32.61
Absorption correction	Semiempirical from equivalents	ψ-curve	Empirical from equivalents
F(000)	2440	1200	1256
T_{max}/T_{min}	0.967/0.77	0.756/0.643	0.801/0.543
Scan type	ω-scan 0.3°/10 s exposure per frame	$\theta/2\theta$	ω-scan with 0.3°/10 s exposure per frame
θ Range (°)	2.07–29.06	2.62–20.04	2.61–27.52
Measured	38037	2099	20742
Unique	6973 ($R_{int} = 0.0543$)	1974 ($R_{int} = 0.0434$)	4966 ($R_{int} = 0.0477$)
With [$I > 2\sigma(I)$]	3757	1577	3353
Parameters	404	262	329
Final $R(F_{hkl})$: R_1	0.0472	0.0447	0.0367
wR_2	0.1000	0.1136	0.0833
GOF	0.977	1.027	0.980
ρ_{max}/ρ_{min} (e Å^{-3})	1.008/−0.315	0.579/−0.464	1.110/−1.076

The best-fit of the values was obtained with the Heisenberg–Dirak–Van Vlek (HDVV) theoretical model for two exchange-coupled paramagnetic ions in the absence of orbital degeneracy of the complex ground

Table 5
Selected bond lengths (Å) and bond angles (°) for **5**–**7**

5		**6**		**7**	
Bond lengths					
Cr(1)–S(2)	2.3429(8)	Cr(2)–Te(1)	2.609(2)	Cr(2)–Te(1)	2.618(1)
Cr(1)–S(1)	2.3591(9)	Cr(1)–Te(1)	2.602(2)	Cr(1)–Te(1)	2.630(1)
Cr(1)–S(3)	2.3711(9)	Cr(1)–S(1)	2.359(3)	Cr(1)–S(1)	2.282(2)
Cr(1)–Mn(1)	3.0239(7)	Cr(1)–S(2)	2.357(3)	Cr(1)–S(2)	2.335(1)
Mn(1)–S(2)	2.3985(8)	Cr(2)–S(1)	2.358(3)	Cr(2)–S(1)	2.290(1)
Mn(1)–S(1)	2.3997(9)	Cr(2)–S(2)	2.364(3)	Cr(2)–S(2)	2.333(1)
Mn(1)–S(3)	2.4210(8)			Cr(1)–Co(1)	2.628(1)
				Cr(2)–Co(1)	2.623(1)
				Co(1)–S(1)	2.199(1)
				Te(1)–Co(1)	2.466(1)
Bond angles					
Cr(1)–S(1)–Mn(1)	78.90(3)	Cr(2)–Te(1)–Cr(1)	64.28(6)	Cr(2)–Te(1)–Cr(1)	60.56(3)
Cr(1)–S(2)–Mn(1)	79.24(3)	Cr(1)–S(1)–Cr(2)	71.97(10)	Cr(1)–S(1)–Cr(2)	70.55(5)
Cr(1)–S(3)–Mn(1)	78.24(3)	Cr(2)–S(2)–Cr(1)	71.90(10)	Cr(2)–S(2)–Cr(1)	69.05(4)
				Co(1)–Te(1)–Cr(2)	62.03(3)
				Co(1)–Te(1)–Cr(1)	61.97(3)
				Co(1)–S(1)–Cr(1)	71.77(4)
				Co(1)–S(1)–Cr(2)	71.28(4)

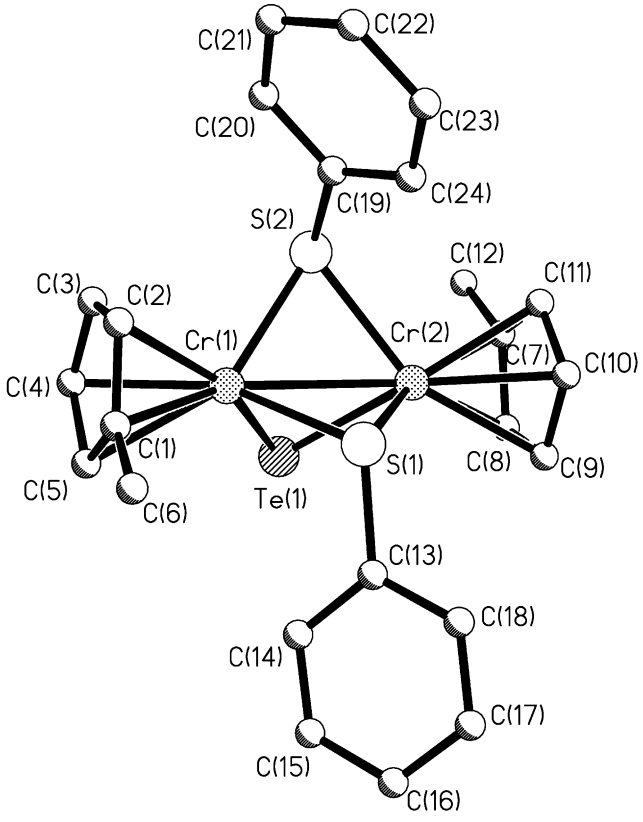


Fig. 5. Molecular structure of complex **6**.

states. The spin Hamiltonian has the form (2)

$$H = -2JS_1S_2 + g\beta H(S_{1z} + S_{2z}) \quad (2)$$

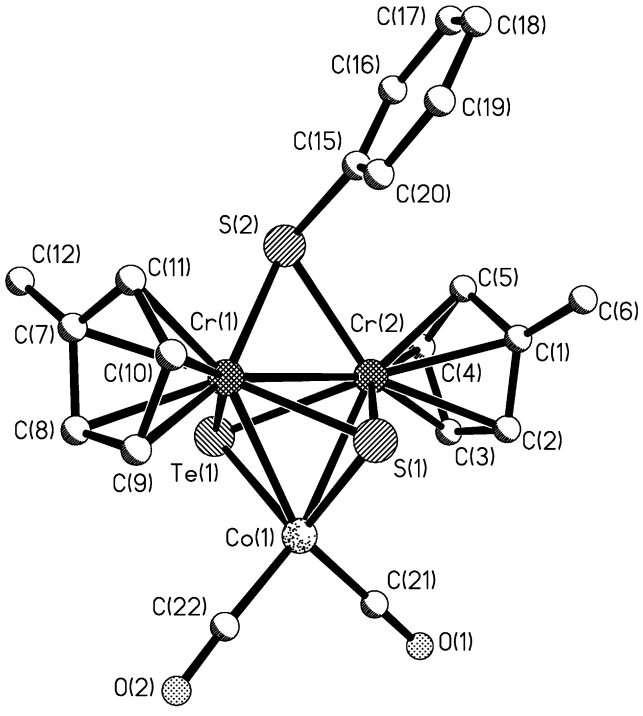


Fig. 6. Molecular structure of complex **7**.

where J is the isotropic exchange parameter, g is the isotropic g factor and S are the spins of the exchange coupled ions. The calculation of the theoretical μ_{eff} values and the least-squares treatment were carried as reported [21].

Crystal structures were solved by direct method and refined in full-matrix anisotropic–isotropic (H-atoms) approximation. All calculations were carried out with the complex of programs SHELXTL PLUS 5 [22]. The important crystallographic data and refinement parameters for **2**–**7** are given in Tables 2 and 4. The most important bond lengths and angles of the complexes **2**–**7** are presented in the Tables 3 and 5.

3.1. Preparation of $Cp'_2Cr_2(SPh)_2SeFe_3Se_2(CO)_8$ (**2**)

The solution of 0.15 g (0.26 mmol) of **1** and 0.15 g (0.26 mmol) $Fe_3Se_2(CO)_9$ in benzene (20 ml) was irradiated by UV-light for 9 h while stirring and cooling by running water. Resulting dark brown reaction mixture was evaporated to dryness and the residue was extracted with 25 ml of hexane and then with 30 ml of ether. To the ether solution 15 ml of hexane was added and both extracts were concentrated in vacuo to 1/4 of initial volume and kept at −18 °C for 48 h. Black–brown crystals were separated, washed by hexane and recrystallized from Et_2O+hexane (1:2) mixture. Yield 0.17g (57%).

IR-spectra (cm^{-1}): 584 w, 608 w, 688 w, 744 w, 816 w, 800 m, 1952 m, 1976 s, 1990 s, 2016 s, 2048 s. Anal. Found: C, 34.58; H, 2.16; S, 6.27; (DSC) CO, 20.2. C_6H_5 13.9; Cp′ 14.3. Residue after pyrolyses: $Cr_2Fe_3S_2Se_3$. $C_{32}H_{24}S_2Se_3Cr_2Fe_3O_8$. Calc.: C, 34.66; H, 2.18; S, 5.78; CO, 20.0; C_6H_5, 13.6; Cp′, 14.4%.

The single crystals of **2** were used for X-ray analysis.

3.2. Preparation of $Cp'_2Cr_2(\mu\text{-}SPh)_2(\mu_3\text{-}Se)Mn_2(CO)_9$ (**3**)

The solution of 0.5 g (0.89 mmol) of **1** and 0.4 g (0.96 mmol) of $Mn_2(CO)_{10}$ in benzene (30 ml) was irradiated by UV-light for 1.5 h while stirring and cooling by running water. Reaction mixture was evaporated to dryness and the residue was extracted with 30 ml of Et_2O. Hexane (10 ml) was added to extract, the mixture was concentrated until the beginning of crystallization and kept at −10 °C for 12 h. Black needle-like crystals were dried in vacuo. Yield 0.45 g (54%).

IR (cm^{-1}): 2960 w, 2920 w, 2360 w, 2072 s, 2000 s, 1975 s, 1936 s, 1905 s, 1665 w, 1576 m, 1470 w, 1065 w, 1025 w, 1000 w, 825 s, 745 s, 688 m, 650 s, 615 m, 480 m, 410 m. Anal. Found: C, 43.12; H, 3.87; S, 7.09. Calc. for $C_{33}H_{24}S_2SeCr_2Mn_2O_9$: C, 43.01; H, 2.63; S, 6.96.%.

The single crystals of **3** were used for X-ray analysis.

3.3. Preparation of $Cp'_2Cr_2(\mu\text{-}SPh)_2(\mu\text{-}Se)Mn_2(CO)_8$ (4)

A mother solution left after precipitation of **3** was evaporated to dryness, extracted with 20 ml of Et_2O, concentrated to 20 ml after addition of 10 ml of hexane and then kept at −10 °C for 48 h. Black–green crystals were separated, washed with hexane and dried in vacuo. Yield 0.08 g (10%). IR (cm^{-1}): 2045 m, 1970 s, 1925 s, 1900 s, 825 m, 740 s, 700 w, 655 m, 620 s.

The single crystals of **4** recrystallized from CH_2Cl_2+ hexane were used for X-ray analysis.

3.4. Preparation of $Cp'Cr(\mu\text{-}SPh)_3Mn(CO)_3$ (5)

The solution of 0.3 g (0.53 mmol) of **1** and 0.2 g (0.51 mmol) of $Mn_2(CO)_{10}$ in boiling benzene (20 ml) was irradiated by UV-light for 2 h. Reaction mixture was evaporated to dryness, washed with 10 ml of hexane and the residue was extracted with 40 ml of ether. To this extract 10 ml of hexane was added and the solution was concentrated in vacuo to 20 ml and kept at −10 °C for 12 h to give black prisms washed with hexane and dried in vacuo. Yield 0.05 g (23%). IR (KBr, cm^{-1}): 2010 s, 1930 s, 1905 s, 1020 w, 820 m, 740 s, 690 m, 620 m.

The single crystal of **5** was used for X-ray analysis.

3.5. Preparation of $[Cp'Cr(\mu\text{-}SPh)]_2(\mu\text{-}Te)$ (6)

3.5.1. Preparation of $[Cp'Cr(CO)(\mu\text{-}SPh)]_2$

Ph_2S_2 (1.06 g, 4.8 mmol) was added to the green solution of 2.1 g (4.8 mmol) $[Cp'Cr(CO)_3]_2$ in 50 ml of hexane at 0 °C and was stirred for 0.5 h. Resulting dark-orange solution was refluxed for 1 h until the disappearing of intermediate $[Cp'Cr(CO)_2]_2(\mu\text{-}SPh)_2$ (TLC, Silufol: orange spot, R_f −0.6 in benzene). Black crystalline precipitate was filtered from green solution, extracted with CH_2Cl_2 and after evaporation of cherry-brown solution the resulting tar was crystallized at the treating by benzene. The solid substance was separated, washed by hexane and dried in vacuo. Yield $[Cp'Cr(CO)(\mu\text{-}SPh)]_2$ 0.35 g (37%). IR spectra (cm^{-1}): 1870 s, 810 m, 730 s, 680 m.

3.5.2. The reaction of $[Cp'Cr(CO)(\mu\text{-}SPh)]_2$ with Te

To the solution of 0.35g (0.65 mmol) $Cp'Cr(CO)(\mu\text{-}SPh)]_2$ in 50 ml of THF 0.14 g (1.1mmol) of Te powder was added and the mixture was stirred for 18 h at the room temperature (r.t.). The green–brown mixture was evaporated to dryness, washed with 20 ml of hexane, extracted with 20 ml of CH_2Cl_2 and filtered. The addition of hexane gave black crystals which were washed by hexane and dried in vacuum. Yield 0.1 g (23%). IR spectra (cm^{-1}): 1080 m, 1020 m, 810 s, 730 s, 680 m.

The single crystals of **6** were used for X-ray analysis.

3.6. Preparation of $Cp'_2Cr_2(\mu\text{-}PhS)(\mu\text{-}S)(\mu\text{-}Te)Co(CO)_2$ (7)

A violet solution of 0.1 g (0. 16 mmol) of **6** in 10 ml CH_2Cl_2 was added to the yellow–brown solution of 0.1 g (0.32 mmol) $Co_2(CO)_8$ in 20 ml of CH_2Cl_2. The mixture was evaporated in vacuum, the residue was washed by 10 ml of hexane and extracted by 20 ml of Et_2O. This extract after addition of 10 ml of hexane was concentrated until the small quantity of brown precipitate forms. The solution was filtered and after addition of 5 ml of hexane was again concentrated to 3 ml and then kept at −10 °C for 12 h. Needle-like crystals of **6** were washed by cold hexane and dried in vacuo. Yield 0.02g (19%).

IR spectrum (cm^{-1}): 1975 s, 1935 s, 830 m, 735 w, 535 w. Anal. Found: C, 36.82; H, 3.41; S, 9.66. Calc. for $C_{20}H_{19}S_2SeCr_2CoO_2$: C, 37.21; H, 2.94; S, 9.92%.

The single crystal of **7** was used for X-ray analysis.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 183565 (**2**), 183564 (**3**), 183566 (**4**), 183567 (**5**), 172670 (**6**) and 172671 (**7**). 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).

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