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Synthesis and Molecular Structures of Cyclopentadienyl Sulfide Complexes of Chromium with Cymantrenyl-Thiolate Bridging Ligands[1]

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Abstract—Interaction of $[Cp_2Cr_2(CO)_4[\mu\text{-}SC_5H_4Mn(CO)_3]_2$ with sulphur gave binuclear complex $Cp_2Cr_2[\mu\text{-}SC_5H_4Mn(CO)_3]_2(\mu\text{-}S)$ (**I**) ($Cp = \pi\text{-}C_5H_5$) and triangular cluster $Cp_3Cr_3[\mu\text{-}SC_5H_4Mn(CO)_3](\mu\text{-}S)_2(\mu_3\text{-}S)$ (**II**). **I** was also synthesized from $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ and $(CO)_3Mn(C_5H_4SH)$. Interaction between **I** and $Co_2(CO)_8$ resulted in triangular mixed-metal cluster $Cp_2Cr_2[\mu\text{-}SC_5H_4Mn(CO)_3](\mu_3\text{-}S)_2Co(CO)_2$ (**III**). The molecular structures of **I**–**III** were determined by means of single-crystal X-ray diffraction analysis.

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INTRODUCTION

Cyclopentadienyl-thiolate-chalcogenides of Cr(III), $Cp_2Cr_2(\mu\text{-}SR)_2(\mu\text{-}X)$ (X = S, Se, Te; R = CMe_3 or Ph) and their mixed-metal cluster derivatives [1–4] are interesting as possible precursors for preparing of mixed-metal chalcogenide materials of the definite composition. For example the thermodestruction of $(C_5H_4CH_3)_2Cr_2Fe_3(SPh)_2Se_3(CO)_8$ gives the same composition $Cr_2Fe_3S_2Se_3$ as metal-chalcogenide core of cluster [3, 5]. We tried here to include the manganese atoms in organic R groups by their substitution of organometallic cymantrenyl group $C_5H_4Mn(CO)_3$ (Cym).

EXPERIMENTAL

All syntheses were performed under the atmosphere of pure argon. Solvents were dried, purified and distilled under the atmosphere of pure argon as well. $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$, $Cp_2Cr_2(CO)_4[\mu\text{-}SC_5H_4Mn(CO)_3]_2$, and $[SC_5H_4Mn(CO)_3]_2$ were prepared as in [1, 6, 7], respectively.

IR spectra were recorded as KBr pellets on a Specord 75 IR spectrophotometer. Elemental analyses were performed on Carlo Erba CHNS-analyser. Cyclic voltammetry of **I**–**III** was carried on a PAR (Princeton Applied Research) 273 potentiostat with standard software. The measurements were carried out in a three-electrode electrochemical cell maintained at a constant temperature in dichloromethane (with 0.1 M $Bu_4N^+PF_6^-$ as the supporting electrolyte) under argon. An SU-2000 glassy carbon disc (0.0058 cm^2) pressed into Teflon served as the working electrode, and a platinum plate (1 cm^2) was an auxiliary electrode. The potentials were measured versus an Ag/AgCl reference electrode in the same solution.

The crystallographic data for complexes **I**–**III** are represented in Table 1. The structures were solved by the direct method and refined by full-matrix least squares against F^2 in the anisotropic (H-atoms isotropic) approximation using SHELXTL-97 package [8]. Positions of the hydrogen atoms in **I**–**III** were calculated from the geometrical point of view. Selected bonds and angle values are presented in Table 2.

Crystallographic data (excluding structure factors) for the structures **I**–**III** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (nos. 266531 (**I**), 266530 (**II**), 266532 (**III**); http://www.ccdc.cam.ac.uk/data_request/cif).

Synthesis of $Cp_2Cr_2[\mu\text{-}SC_5H_4Mn(CO)_3]_2(\mu\text{-}S)$ (I) and $Cp_3Cr_3[\mu\text{-}SC_5H_4Mn(CO)_3](\mu\text{-}S)_2(\mu_3\text{-}S)$ (II). The crimson solution of 1.1 g (1.3 mmol) of $Cp_2Cr_2(CO)_4[\mu\text{-}SC_5H_4Mn(CO)_3]_2$ in 30 mL of benzene was refluxed for 0.5 h under argon until disappearing of the spot of the initial compound on the TLC (Silufol–benzene). Resulting dark-yellow solution was cooled down till 5°C and the solution of 0.04 g (1.3 mmol) of sulfur in 15 mL of benzene was added

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[1] The article is published in the original.

Table 1. Crystallographic data and details of the experiment and refinement of structures **I–III**

Parameter	Value		
	I	**II**	**III**
Formula weight	736.46	682.56	648.36
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Temperature, K	120(2)	120(2)	120(2)
Radiation (λ, Å)	MoK_α (0.71073)		
a, Å	22.855(2)	9.324(2)	10.565(1)
b, Å	9.704(2)	11.064(3)	10.600(1)
c, Å	12.582(2)	12.198(3	12.057(2)
α, deg	90	78.102(5)	65.533(6)
β, deg	105.022(5)	85.439(6)	67.327(6)
γ, deg	90	76.728(5)	89.545(6)
V, Å^3	2695.3(8)	1197.7(5)	1115.4(3)
Z	4	2	2
$F(000)$	1472	684	644
ρ_{calcd}, g/cm^3	1.815	1.893	1.931
Scan type	ω		
θ Range, deg	0.92–27.00	1.71–29.00	2.04–28.00
μ, cm^{-1}	19.74	22.15	25.44
Reflections collected	10591	9985	7636
Independent reflections (R_{int})	5542 (0.0743)	6024 (0.0321)	5067 (0.0343)
Reflections with $I > 2\sigma(I)$	2670	3836	3298
GOOF(F^2)	0.971	1.078	1.082
R_1, wR_2 ($F^2 > 2\sigma(F^2)$)	0.0662, 0.1321	0.0473, 0.0894	0.0559, 0.1162
R_1, wR_2 (all data)	0.1429, 0.1491	0.0805, 0.0955	0.0856, 0.1237
$\Delta\rho(max)/\Delta\rho(min)$, e Å^{-3}	0.652/–0.600	0.791/–0.609	0.866/–0.601

dropwise during 10 min under stirring. Brown-violet reaction mixture was concentrated to the half of initial volume and after adding of 15 mL of hexane was separated on column (10 cm Al_2O_3; CH_2Cl_2–hexane = 1 : 1). Brown-green fraction was concentrated to half of initial volume and kept for 24 h at room temperature. Black needle-like crystals of **I** were separated, washed by 5 mL of hexane and dried in vacuum. The yield was 0.03 g (3%).

IR spectrum (KBr; ν, cm^{-1}): 2000 s, 1935 s, 1905 s, 1410 w, 1000 m, 880 w, 800 s, 665 w, 620 s.

For $C_{23}H_{19}O_3S_4Cr_3Mn$

anal. calcd., %:	C, 40.47;	H, 2.81;	S, 18.79.
Found, %:	C, 40.14;	H, 2.38;	S, 18.69.

Violet fraction was concentrated to 5 mL and violet crystals **II** were separated, washed by 5 mL of hexane and dried in vacuum. The yield was 0.09 g (10%).

IR spectrum (KBr; ν, cm^{-1}): 2010 s, 1930 s, 1415 w, 1055 w, 1035 w, 1010 w, 880 w, 805 s, 660 s, 625 s, 530 m.

For $C_{26}H_{18}O_6S_3Cr_2Mn_2$

anal. calcd., %:	C, 42.4;	H, 2.46;	S, 13.06.
Found, %:	C, 43.9;	H, 2.47;	S, 13.6.

The crystals suitable for X-ray investigation were obtained after crystallization from CH_2Cl_2–hexane.

The alternative synthesis of I. The dark-violet solution of 0.28 g (0.64 mmol) of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ and 0.35 g (1.3 mmol) of $HSC_5H_4Mn(CO)_3$ in 7 mL of benzene was refluxed for 4.5 h. The fine black-violet crystalline precipitate was formed at the concentration. The yield was 0.26 g (55%). Crystals suitable for X-ray investigation were obtained after crystallisation from solution in CH_2Cl_2–hexane. According to IR-spectra and TLC this substance was identical to the **I**.

Synthesis of $Cp_2Cr_2[\mu\text{-}SC_5H_4Mn(CO)_3](\mu_3\text{-}S)_2Co(CO)_2$ (III). A violet solution of 0.27 g (0.36 mmol) of **I** in 20 mL CH_2Cl_2 was added to the yellow-brown solution of 0.06 g (0.18 mmol) $Co_2(CO)_8$ in 4 mL of CH_2Cl_2. The mixture was stirred 20 min at room temperature and then evaporated in vacuum, the residue was washed by 10 mL of hexane and extracted by Et_2O (2 × 20 mL) of. This extract was concentrated to the half of initial volume, 5 mL of hexane was added and the mixture was kept for 24 h at −10°C. Dark-brown needle-like crystals of **III** · $1/2Et_2O$ were separated, washed by 5 mL of hexane and dried in vacuum. The yield was 0.05 g (20%).

Table 2. Selected intramolecular bond lengths (Å) and bond angles (deg) for complexes **I**–**III**

Bond	*d*, Å	Bond	*d*, Å
	I		
Cr(1)–Cr(2)	2.679(2)	Cr(2)–S(1)	2.364(2)
Cr(1)–S(3)	2.240(2)	Cr(2)–S(2)	2.383(2)
Cr(1)–S(2)	2.371(2)	S(1)–C(11)	1.788(7)
Cr(1)–S(1)	2.376(2)	S(2)–C(19)	1.760(8)
Cr(2)–S(3)	2.251(2)		
	II		
Cr(1)–Cr(2)	2.806(1)	Cr(2)–S(2)	2.202(1)
Cr(1)–Cr(3)	2.875(1)	Cr(2)–S(4)	2.249(1)
Cr(2)–Cr(3)	2.850(1)	Cr(3)–S(3)	2.205(1)
Cr(1)–S(2)	2.198(1)	Cr(3)–S(4)	2.242(1)
Cr(1)–S(1)	2.332(1)	Cr(3)–S(1)	2.327(1)
Cr(2)–S(3)	2.198(1)		
	III		
Co(1)–Cr(1)	2.578(1)	Cr(2)–S(2)	2.308(2)
Cr(1)–Cr(2)	2.600(1)	Cr(2)–S(1)	2.342(2)
Co(1)–S(2)	2.190(1)	Co(1)–C(11)	1.796(7)
Co(1)–S(3)	2.206(1)	Co(1)–C(12)	1.779(6)
Cr(1)–S(2)	2.291(2)	S(1)–C(13)	1.783(5)
Cr(1)–S(1)	2.332(2)	O(1)–C(11)	1.140(7)
Cr(2)–S(3)	2.267(2)	O(2)–C(12)	1.142(6)
Angle	ω, deg	Angle	ω, deg
	I		
C(11)S(1)Cr(1)	111.5(2)	Cr(1)(2)Cr(2)	68.62(6)
Cr(2)S(1)Cr(1)	68.84(6)	Cr(1)S(3)Cr(2)	73.25(7)
	II		
Cr(2)Cr(3)Cr(1)	58.69(2)	Cr(2)S(3)Cr(3)	80.68(5)
Cr(3)S(1)Cr(1)	76.20(4)	Cr(3)S(4)Cr(1)	79.62(4)
Cr(1)S(2)Cr(2)	79.23(4)	Cr(3)S(4)Cr(2)	78.79(5)
	III		
Co(1)Cr(1)Cr(2)	59.72(3)	Cr(1)S(2)Cr(2)	68.87(5)
Co(1)Cr(2)Cr(1)	59.70(3)	Co(1)S(3)Cr(2)	70.38(5)
Cr(1)S(1)Cr(2)	67.60(4)	Co(1)S(3)Cr(1)	70.25(5)
Co(1)S(2)Cr(1)	70.20(4)	Cr(2)S(3)Cr(1)	69.88(5)
Co(1)S(2)Cr(2)	69.90(5)		

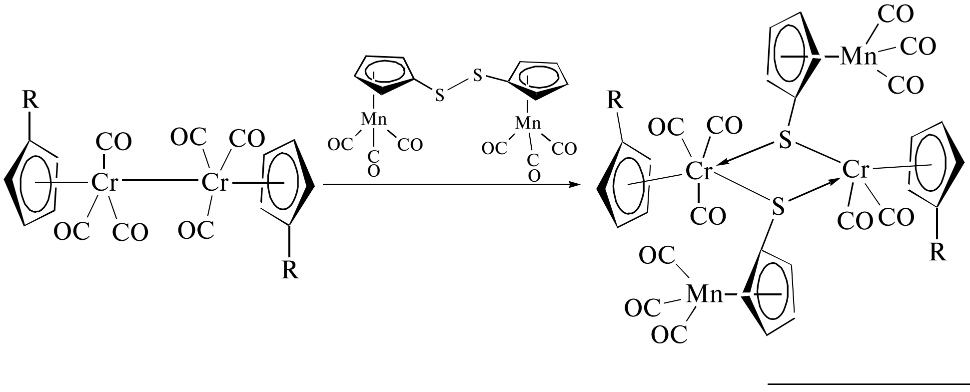
IR spectra (KBr; ν, cm^{-1}): 2020, 1980 s, 1950 s, 1930 s, 830 m., 735 w, 535 w.

For $C_{22}H_{19}O_{5.5}S_3Cr_2MnCo$

anal. calcd., %:	C, 38.55;	H, 2.79.
Found, %:	C, 38.68;	H, 1.99.

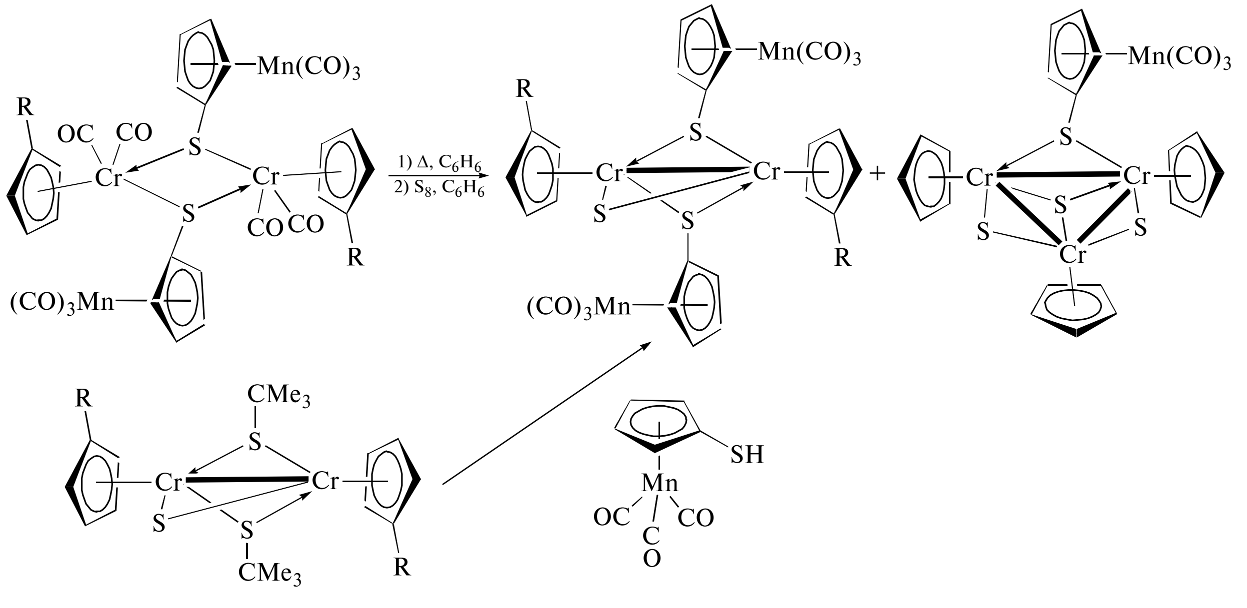
RESULTS AND DISCUSSION

Recently we have reported the preparation of binuclear complex $Cp_2Cr_2(CO)_4[\mu\text{-}SC_5H_4Mn(CO)_3]_2$ (Cr–S 2.450 Å) from $Cp_2Cr_2(CO)_6$ and $[(CO)_3MnC_5H_4S]_2$ [6].



Its decarbonylation in refluxing benzene and further treatment with elemental sulfur gives the violet crystals of **I** which according to X-ray analyses data has direct Cr–Cr bond (2.679(2) Å), two thiolate bridges with ordinary Cr–SR bonds (2.364(2)–2.383(2) Å) and strongly shortened Cr–S(sulfide) bonds (2.240(2) and 2.251(2) Å) (Fig. 1, Table 2). Each chromium atom is coordinated with planar Cp ligand too. The geometry of **I** is similar to known complex $(CpCrSCMe_3)_2S$ [1] which being treated with cymantrenyl-thiol $HSC_5H_4Mn(CO)_3$ gives **I** in a high yield.

The substitution of highly electron-releasing *t*-Bu groups by cymantrenyl groups in **I** increases the potentials of single-electron reversible oxidation from +0.2 up to +0.6 V and of multielectron irreversible oxidation from +1.25 up to +1.40 V.



Along with binuclear **I** the triangular cluster **II** was isolated from the reaction mixture in the form of air-stable black needles soluble in CH_2Cl_2 and insoluble in hexane. Its IR-spectra contains two peaks of cymantrenyl CO stretching vibration (2010, 1935 cm^{-1}). According to X-ray analyses data (Fig. 2, Table 2) triangular core in **II** contained three chromium atoms, probably Cr(III)Cr(III)Cr(IV), linked by ordinary Cr–Cr bonds (2.806(1)–2.875(1) Å). There is one CymS bridge (Cr–S av. 2.329(1) Å) at one Cr–Cr bond and two μ-sulfide bridges (Cr–S 2.198(1)–2.205(1) Å) at two other Cr–Cr bonds laying over the

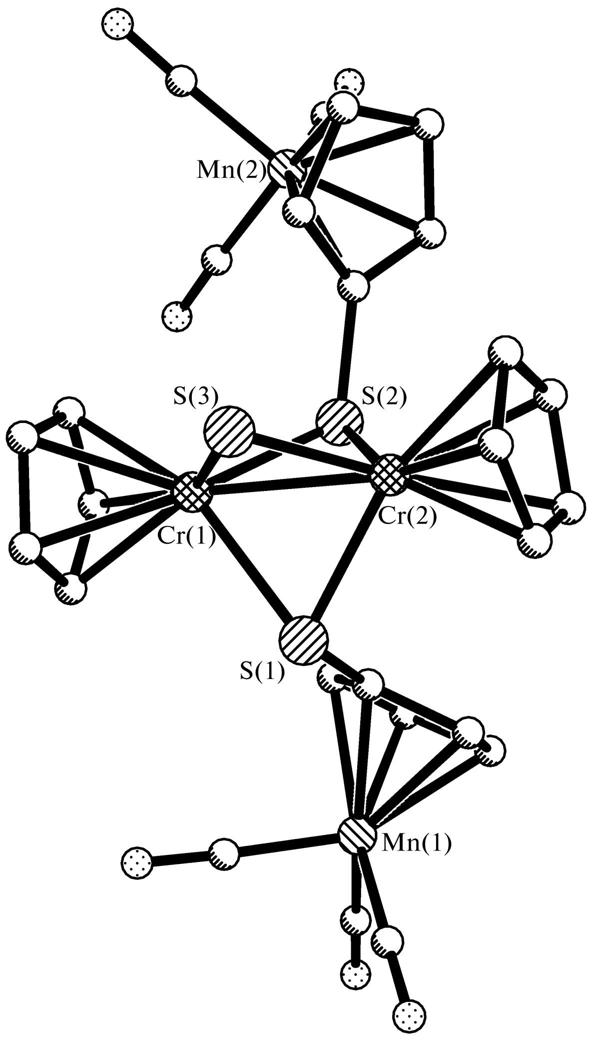
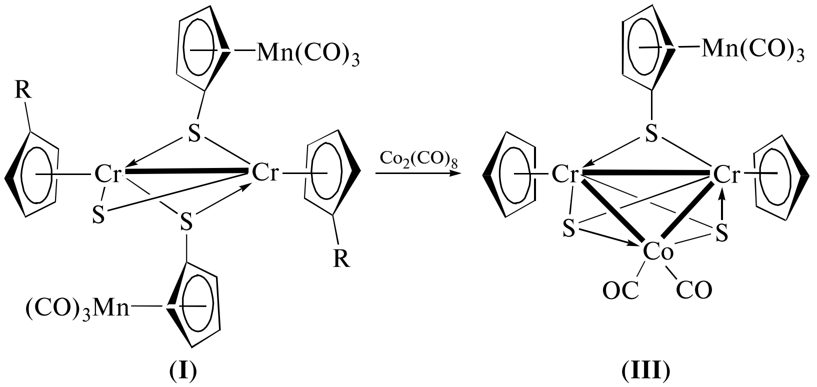


Fig. 1. Molecular structure of complex **I**.

Cr_3 plane. Under it one μ_3-sulfide ligand (Cr–S 2.242(1)–2.249(1) Å) lays. Such kind of structure is new because fragment $M_3(\mu_3\text{-}S)$ is typically linked by three μ-sulfide bridges (as in $Cp_3Mo_3S_4^+Me_3SnCl_2^-$ [9]), or by three thiolate bridges (as in $[(SMe)_3Ni_3(SMe)_3(\mu_3\text{-}S)]^{2-}[NMe_4^+]_2$ [10] and $[(CN)_3Ni_3(S\text{–}{}^tBu)_3S]^{2-}[PPh_4^+]_2$ [11]).

Trinuclear mixed-metal cluster **III** was prepared from **I** and cobalt carbonyl by analogy with reaction of $(CpCrSCMe_3)_2S$ [12]:



(I) **(III)**

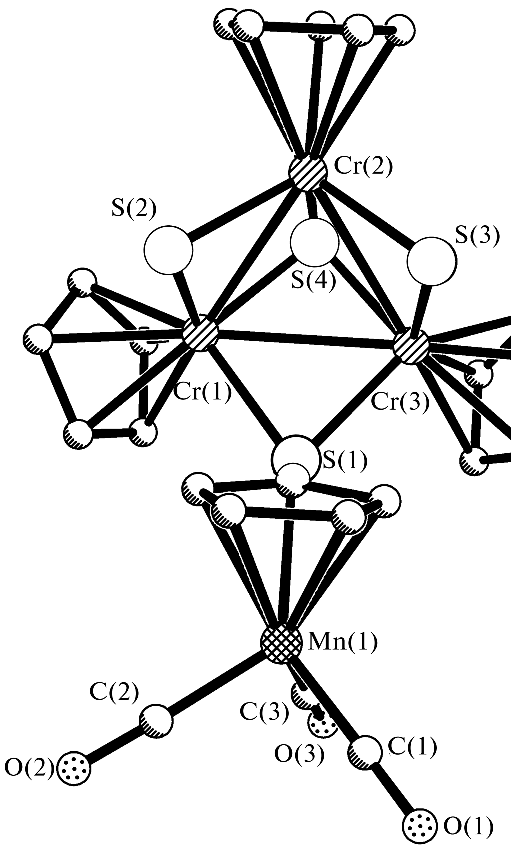


Fig. 2. Molecular structure of complex **II**.

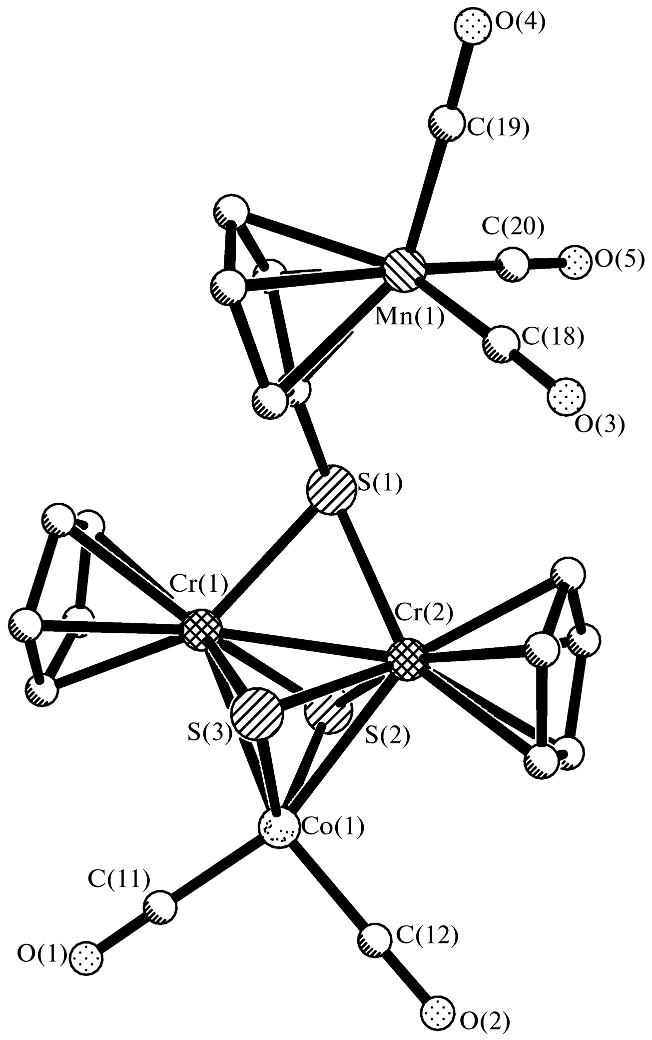


Fig. 3. Molecular structure of complex **III**.

Dark-brown needles of **III** are air-stable, soluble in polar organic solvents (solutions are not air-stable) and insoluble in hexane. IR-spectrum (in KBr) contains peaks of stretching vibration of CO groups at cobalt (1980, 1950 cm^{-1}) and manganese (2020, 1930 cm^{-1}) atoms. Molecular structure of **III** (Fig. 3, Table 2) determined by single crystal X-ray analysis contains triangular Cr_2Co core with ordinary Cr–Cr (2.600(1) Å) and Cr–Co (2.578(1) Å) bonds supported by two μ_3-sulfide bridges (av. Cr–S 2.287(2), Co–S 2.198(1) Å) and one thiolate bridge [μ-$SC_5H_4Mn(CO)_3$] (av. Cr–S 2.337(2) Å). Each chromium atom is coordinated with planar Cp ring. It is noteworthy that geometry of **III** is quite similar to those for $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ [12]. According to cyclic voltammogramme data for **III** only irreversible multielectron oxidation is observed (nonseparated waves at +1.25 and 1.4 V).

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