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ANTIFERROMAGNETIC COMPLEXES WITH A METAL—METAL BOND

VIII *. SYNTHESIS AND STRUCTURE OF THE ANTIFERROMAGNETIC HETERONUCLEAR CLUSTER, "BUTTERFLY" (OR "METAL-CHAIN"), $(Cp_4Cr_2Ni_2)(\mu^3\text{-}S)_2(\mu^4\text{-}S)$

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Summary

By heating the mixture of solutions of $(CpCrSCMe_3)_2S$ (I) in benzene and $[CpNi(CO)]_2$ in pentane followed by chromatography on alumina, dark cherry-red needles of the heteronuclear cluster $(Cp_4Cr_2Ni_2)(\mu^3\text{-}S)_2(\mu^4\text{-}S)$ (II) were obtained, whose structure was established on the basis of a complete X-ray analysis. The crystals are rhombic, spatial group *Pbca*; a =12.07(1), b = 18.50(2), c = 17.36(1) Å, Z = 8. The metallic skeleton of II has the "butterfly" or "metal-chain" structure with a direct Cr—Cr bond (2.62(1) Å) and inequivalent Cr—Ni bonds, 2.86(1) and 2.64(1) Å, while the Ni···Ni distance is nonbonding (4.34(1) Å). The $NiCr_2$ triangle planes produce a dihedral angle of 127°. The two μ^3-bridged sulfur atoms locate under these triangles whereas the third sulfur atom is μ^4-bridging coordinating all four metal atoms in the cluster with mean Ni—S and Cr—S distances of 2.29(1) and 2.25(1) Å, respectively. The Ni_2S_3 group is planar and almost perpendicular to the Cr—Cr axis. Complex II is antiferromagnetic and its exchange parameter $-2J$ (418 cm^{-1}) is close to that found for the initial binuclear complex I ($-2J$ = 430 cm^{-1} with a Cr—Cr bond length of 2.689(8) Å). The role of the Ni coordination number in the generation of II is discussed.

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* For part VII see ref. 4.

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Introduction

In our earlier works of these series we have shown [1—4] that the binuclear complex $(CpCrSCMe_3)_2S$ (I) [5] may be used as an unusual ligand in reactions with metal carbonyl Lewis acids LM(CO), the transformations of I depending on the metal M coordination number (CN). For CN = 6 the structure of I in $(CpCrSCMe_3)S \cdot ML$ complexes is practically the same (ML(CO) = $M(CO)_6$ (M = Mo, W, Cr) [1]; $Mn_2(CO)_{10}$ [3]) while for CN = 5 (ML(CO) = $Fe(CO)_5$ [2], $Co_2(CO)_8$ [3]) one observes a loss of one t-butyl group and formation of a $(Cp_2Cr_2SCMe_3)(S)_2Fe(CO)_3$ metallochain [2] and a $(Cp_2Cr_2SCMe_3)(S)_2Co(CO)_2$ metallocycle [3], respectively. In this view it was of interest to study the reactions of I with cyclopentadienylmetal carbonyls, CpML(CO), in which metal coordination number may vary from 5 to 7. We have shown [4] that when CN = 6 (CpML(CO) = $CpMn(CO)_3$) the structure of I in the complex $[(CpCrSCMe_3)_2S \cdot M(CO)_2Cp]$ is unchanged, while for CN = 7 (CpML(CO) = $CpV(CO)_4$ and $CpNb(CO)_4$) it undergoes a transformation, yielding the paramagnetic metallotetrahedra $Cp_4Cr_3M(\mu^3\text{-}S)_4$.

In this paper we describe the reaction of I with $[CpNi(CO)]_2$, having for Ni CN = 5 in an unbridged structure and the structure and magnetic properties of generated complex: $(Cp_4Cr_2Ni_2)(\mu^3\text{-}S)_2(\mu^4\text{-}S)$ (II).

Results

1. Synthesis and structure of complex II

On refluxing a mixture of a violet benzene solution of I and a red pentane solution of $[CpNi(CO)]_2$ (prepared from Cp_2Ni and $Ni(CO)_4$ and used without isolation), the complex disappears completely and the solution becomes brown, from which complex II was obtained after chromatography on alumina, elution with benzene and crystallization from benzene/heptane:

$$\underset{(I)}{(CpCrSCMe_3)_2S} \xrightarrow[C_6H_6/\text{pentane},]{[CpNi(CO)]_2} \underset{(II)}{(Cp_4Cr_2Ni_2)(\mu^3\text{-}S)_2(\mu^4\text{-}S)}$$

Note that under analogous conditions the reaction of I with Cp_2Ni does not proceed. Complex II is in the form of dark cherry-red needles, stable in air but decomposing without melting at 200° C, moderately soluble in THF and benzene, and insoluble in saturated hydrocarbons. The structure of II was established by means of a complete X-ray analysis (Fig. 1). The atomic coordinates are listed in Table 1, the bond lengths in Table 2, and the bond angles in Table 3.

Complex II is a cluster, in which the Cr_2Ni_2 metallic skeleton forms an open, "butterfly", tetrahedron, including two $NiCr_2$ triangles with a common Cr(1)—Cr(2) bond (2.62(1) Å), and with Ni···Ni distance (4.34(1) Å) excluding direct bonding between these atoms. One of the two Ni—Cr sides of each triangle is 0.2 Å longer than the other, having mean lengths of 2.86(1) and 2.64(1) Å, respectively. The $NiCr_2$ triangle planes produce a dihedral angle of 127°. The bisectorial plane of this angle contains the μ^4-bridged S(1) atom, bonded to all four metal atoms with mean Ni—S(1) and Cr—S(1) distances of 2.29(1) and 2.25 Å, respectively.

TABLE 1

ATOMIC COORDINATES ($\times 10^3$) (for Ni, Cr and S $\times 10^4$) AND ANISOTROPIC TEMPERATURE FACTORS 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}
Ni(1)	1284(7)	4859(4)	1785(5)	2.6(3)	2.1(3)	1.9(4)	0.2(3)	0.7(4)	0.3(3)
Ni(2)	1050(7)	7040(4)	880(4)	2.4(4)	1.9(4)	1.9(4)	0.3(3)	0.0(4)	0.6(3)
Cr(1)	2283(8)	5712(5)	795(5)	2.1(5)	2.0(4)	1.6(4)	0.0(4)	0.5(5)	0.0(4)
Cr(2)	1783(8)	6337(5)	2105(5)	1.5(4)	2.8(5)	1.3(4)	0.0(4)	0.0(4)	−0.2(4)
S(1)	564(13)	5861(8)	1237(10)	1.7(7)	1.9(7)	2.2(8)	−0.4(7)	−0.7(7)	0.2(6)
S(2)	2774(13)	6853(8)	1171(9)	2.1(8)	1.5(7)	2.8(8)	−0.4(7)	0.5(7)	−0.4(6)
S(3)	2882(13)	5351(8)	1947(9)	3.9(8)	2.8(8)	2.2(8)	−0.4(7)	0.4(7)	1.1(7)
C(1)	37(5)	396(4)	138(4)	4(2)	11(5)	3(4)	−3(3)	−4(3)	1(3)
C(2)	−28(5)	434(3)	198(3)	7(4)	4(3)	0(3)	−3(3)	2(3)	−1(3)
C(3)	36(6)	429(3)	264(4)	7(4)	−1(3)	3(4)	−4(3)	5(3)	0(3)
C(4)	148(7)	392(2)	253(4)	8(5)	−1(2)	4(3)	0(3)	2(4)	1(3)
C(5)	138(4)	368(3)	177(4)	5(3)	5(3)	2(4)	2(3)	4(3)	0(3)
C(6)	66(5)	821(3)	97(2)	0(4)	4(4)	0(2)	4(3)	3(2)	1(2)
C(7)	−41(5)	738(3)	40(4)	−1(2)	2(4)	2(4)	3(4)	0(3)	1(3)
C(8)	46(6)	754(4)	−11(4)	7(4)	4(3)	3(5)	2(3)	2(4)	1(3)
C(9)	122(1)	806(1)	23(1)	−7.8(6)	−5.2(6)	10(2)	4.9(4)	−5.8(7)	−2.0(7)
C(10)	−30(5)	776(3)	110(4)	5(4)	4(3)	2(3)	−2(3)	1(3)	1(3)
C(11)	352(6)	498(4)	20(4)	13(5)	5(4)	1(3)	0(4)	3(3)	−1(3)
C(12)	353(5)	572(3)	−15(3)	4(4)	8(3)	1(3)	3(3)	1(3)	−1(3)
C(13)	240(5)	593(3)	−47(3)	10(3)	1(3)	0(3)	−5(3)	2(3)	−1(3)
C(14)	176(6)	523(4)	−32(4)	8(4)	8(4)	2(3)	7(3)	−1(3)	−2(3)
C(15)	236(6)	474(4)	6(3)	3(4)	5(4)	2(3)	−2(4)	3(3)	−1(3)
C(16)	56(5)	646(4)	309(3)	0(4)	9(4)	1(3)	3(4)	−2(3)	−3(3)
C(17)	153(7)	611(3)	335(3)	4(6)	6(4)	0(2)	−6(4)	2(3)	−2(3)
C(18)	243(5)	653(4)	324(3)	1(3)	6(5)	2(3)	−2(3)	−4(3)	−4(3)
C(19)	209(7)	718(4)	295(4)	5(5)	2(4)	2(3)	−2(3)	−4(3)	0(3)
C(20)	99(6)	723(4)	281(4)	6(4)	4(5)	2(3)	−1(4)	0(3)	0(3)

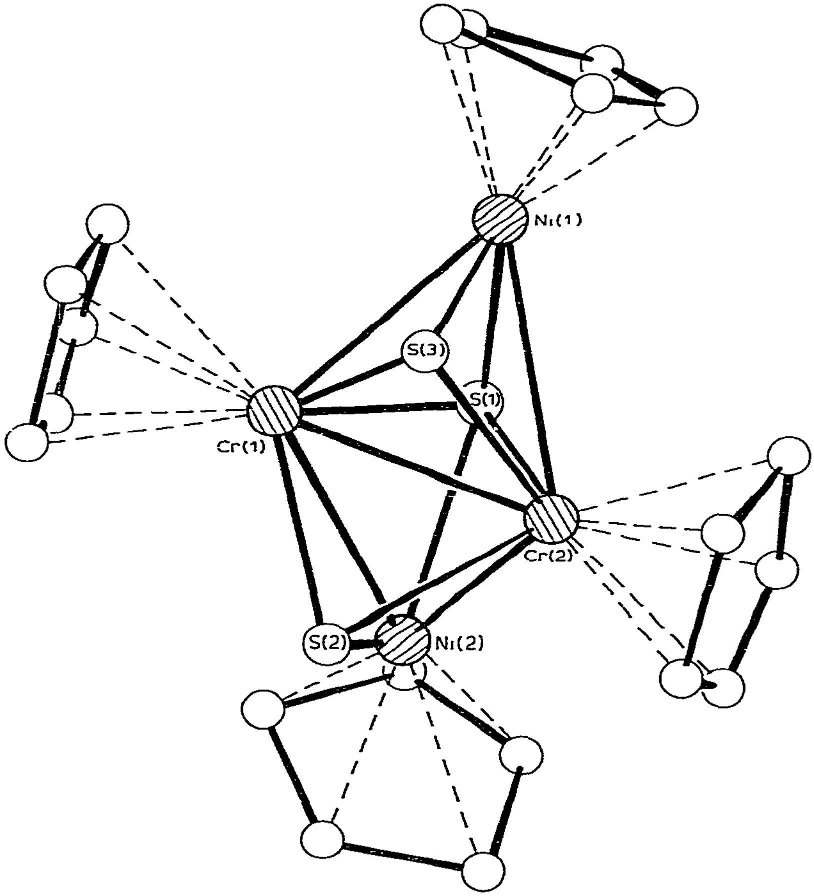


Fig. 1. The structure of $(Cp_4Cr_2Ni_2)(\mu^3\text{-}S)_2(\mu^4\text{-}S)$.

TABLE 2

BOND LENGTHS

Bond	d (Å)	Bond	d (Å)	Bond	d(Å)
Ni(1)—Cr(1)	2.63(1)	Cr(2)—S(1)	2.26(2)	Ni(2)—C(10)	2.14(6)
Ni(1)—Cr(2)	2.85(1)	Cr(2)—S(2)	2.27(2)	Cr(1)—C(11)	2.27(7)
Ni(2)—Cr(1)	2.88(1)	Cr(2)—S(3)	2.23(2)	Cr(1)—C(12)	2.23(6)
Ni(2)—Cr(2)	2.65(1)	Ni(1)—C(1)	2.11(7)	Cr(1)—C(13)	2.23(5)
Cr(1)—Cr(2)	2.62(1)	Ni(1)—C(2)	2.14(6)	Cr(1)—C(14)	2.23(6)
Ni(1)—S(1)	2.30(1)	Ni(1)—C(3)	2.14(7)	Cr(1)—C(15)	2.21(7)
Ni(1)—S(2)	2.15(1)	Ni(1)—C(4)	2.17(5)	Cr(2)—C(16)	2.27(6)
Ni(2)—S(1)	2.29(1)	Ni(1)—C(5)	2.19(6)	Cr(2)—C(17)	2.22(5)
Ni(2)—S(3)	2.17(1)	Ni(2)—C(6)	2.22(6)	Cr(2)—C(18)	2.15(6)
Cr(1)—S(1)	2.24(1)	Ni(2)—C(7)	2.05(6)	Cr(2)—C(19)	2.17(6)
Cr(1)—S(2)	2.23(1)	Ni(2)—C(8)	2.08(7)	Cr(2)—C(20)	2.26(7)
Cr(1)—S(3)	2.29(1)	Ni(2)—C(9)	2.21(5)		

The μ^3-bridged atoms S(2) and S(3) are located under each of the $NiCr_2$ triangles, displaced from their planes by 0.197 and 0.195 Å, respectively, and they are furthest separated from the Cr atom with shorter Ni—Cr bonding (Table 2). The mean Cr—S distances are close to those of Cr—S(1) bonds (2.25 Å), while

TABLE 3

BOND ANGLES ω

Angle	ω (°)	Angle	ω (°)
Cr(1)Ni(1)S(1)	53.5(5)	S(2)Cr(2)Ni(2)	52.0(5)
Cr(1)Ni(1)S(3)	54.5(5)	Ni(2)Cr(2)S(1)	54.9(5)
Cr(2)Ni(1)S(1)	50.7(5)	S(1)Cr(2)Ni(2)	52.0(5)
Cr(2)Ni(1)S(3)	51.7(5)	Ni(1)Cr(2)Cr(1)	57.2(3)
Cr(1)Ni(2)S(1)	49.8(5)	S(3)Cr(2)Cr(1)	55.5(5)
Cr(1)Ni(2)S(2)	51.6(5)	S(2)Cr(2)Cr(1)	53.6(5)
Cr(2)Ni(2)S(1)	54.0(5)	Ni(2)Cr(2)Cr(1)	57.2(3)
Cr(2)Ni(2)S(2)	54.1(5)	S(1)Cr(2)Cr(1)	53.9(5)
Ni(1)Cr(1)S(3)	51.8(5)	Ni(1)S(1)Cr(1)	70.7(6)
S(3)Cr(1)S(2)	86.3(6)	Cr(1)S(1)Ni(2)	78.9(8)
S(2)Cr(1)Ni(2)	48.1(5)	Ni(2)S(1)Cr(2)	71.6(6)
Ni(2)Cr(1)S(1)	51.4(5)	Cr(2)S(1)Ni(1)	77.4(6)
S(1)Cr(1)Ni(1)	55.8(5)	Cr(1)S(1)Cr(2)	71.3(6)
Cr(2)Cr(1)Ni(1)	65.9(3)	Ni(1)S(1)Ni(2)	141.7(8)
Cr(2)Cr(1)S(3)	53.5(5)	Ni(2)S(2)Cr(1)	80.3(6)
Cr(2)Cr(1)S(2)	55.1(5)	Cr(1)S(2)Cr(2)	71.0(6)
Cr(2)Cr(1)Ni(2)	57.3(3)	Cr(2)S(2)Ni(2)	73.9(6)
Cr(2)Cr(1)S(1)	54.8(5)	Ni(1)S(3)Cr(1)	73.7(6)
Ni(1)Cr(2)S(3)	48.0(5)	Cr(1)S(3)Cr(2)	71.3(6)
S(3)Cr(2)S(2)	86.7(6)	Cr(2)S(3)Ni(1)	80.3(6)

the Ni—S(2) and Ni—S(3) mean bond lengths (2.16(1) Å) are significantly shorter than the mean Ni—S(1) distance (2.29(1) Å). The NiSCr angles facing the shorter Ni—Cr bonds (2.63 Å) are smaller (70.7(6)—73.9(6)°) than those facing the longer Ni—Cr bonds (2.85 and 2.87 Å) (77.4(6)—80.3°) (Table 3).

The Ni(1)Cr(1)Cr(2) and Ni(2)Cr(1)Cr(2) planes are almost perpendicular to the Ni_2S_3 plane (dihedral angles of 88.2 and 87.6°), the latter plane being also almost perpendicular to the Cr—Cr bond (angle 85.3°) cutting it into equal parts (1.31 Å). In general, analysis of the planar fragments shows an approximate *mm* symmetry of the inorganic nucleus of the molecule.

The peripheral π-cyclopentadienyl ligands are planar (the C—C distances and CCC angles are normal). The rings C(11)···C(15) and C(16)···C(20), bonded to Cr(1) and Cr(2), respectively, are almost perpendicular to the Cr···Cr axis and almost parallel to the Ni_2S_3 plane. The Ni—C and Cr—C bond lengths are 2.05(6)—2.21(2) Å and 2.15(6)—2.27(6) Å, respectively.

2. *The magnetic properties of complex II*

The effective magnetic moments,

$$\mu_{\text{eff}} = \sqrt{8\chi_M T}$$

where χ_M is the molar magnetic susceptibility, were estimated from the temperature dependence of the magnetic susceptibility of complex II (Table 4). Complex II is antiferromagnetic, the temperature dependence of its effective magnetic moment being similar to that observed for the initial complex I [5]. The experimental data agree best with the Heisenberg-Dirac-Van Vleck (HDVV) theoretical model for two coupled ions (the nickel atoms are diamagnetic) in the absence of orbital degeneracy of the complex ground states. The spin Hamiltonian has the form [6]

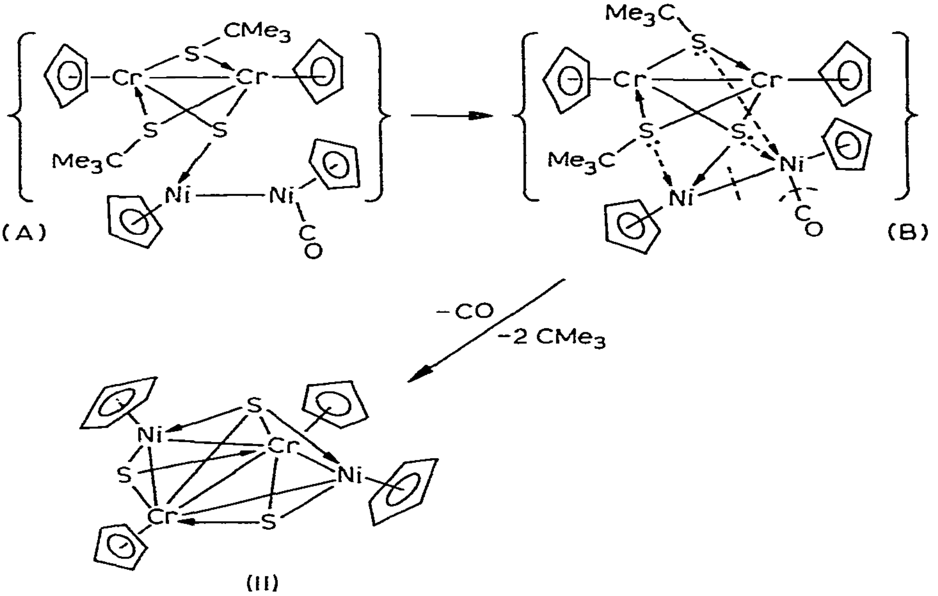
$$\hat{H} = -2J\hat{S}_1\hat{S}_2 - g\beta H(S_{1z} + S_{2z})$$

where J is the isotropic exchange coupling parameter, g is isotropic g-factor, and S are the spins of the exchange-coupled ions (here $S_1 = S_2 = 3/2$).

The computation of theoretical values of χ_M and minimization of the mean-square deviations were performed using the program described in ref. 7. For II the value of $-2J = 418\ \text{cm}^{-1}$, μ_{eff}, B.M. (T, °K): 1.16 (295), 0.62 (150), 0.42 (78); monomer admixture = 1%.

Results and discussion

The unexpected formation of the $(\text{Cp}_4\text{Cr}_2\text{Ni}_2)(\mu^3\text{-S})_2(\mu^4\text{-S})$ (II) cluster in the reaction of $(\text{CpCrSCMe}_3)_2\text{S}$ (I) with the dimer $[\text{CpNi(CO)}]_2$ is a result of the tendency of I towards loss of the t-butyl groups upon interaction with metal carbonyl Lewis acids having a metal CN of 5 [2,3], as mentioned in the Introduction. The first step of this reaction may be the replacement of a carbonyl group in $[\text{CpNi(CO)}]_2$ by a lone electron pair of the sulfide bridge of I, giving an intermediate complex A:



This step is similar to the generation of the complex $(\text{CpCrSCMe}_3)_2\text{S} \cdot \text{Mn}_2(\text{CO})_9$ (III) in the photochemical reaction of I with $\text{Mn}_2(\text{CO})_{10}$ [3]. However, in III, with Mn CN = 6, the metal cannot interact further with the lone electron pairs of thiolate sulfur atoms, as it does in the assumed $(\text{CpCrSCMe}_3)_2\text{S} \cdot \text{Fe}(\text{CO})_4$ [2] or $(\text{CpCrSCMe}_3)_2\text{S} \cdot \text{Co}_2(\text{CO})_7$ [3] intermediates with CN = 5. In the latter case the CMe_3 fragment is eliminated, with cleavage of the Co—Co bond and loss of the Co(CO)_4 fragment. Thus, after decarbonylation of the $(\text{Cp}_2\text{Cr}_2 \cdot \text{SCMe}_3)(\mu^3\text{-S})_2\text{Co(CO)}_3$ intermediate the heteronuclear metallocycle is generated, $(\text{Cp}_2\text{Cr}_2\text{SCMe}_3)(\mu^3\text{-S})_2\text{Co(CO)}_2$ (IV) [3]. In fact, intermediate A undergoes similar transformation with the cleavage of the Ni—Ni bond to form B. In this case, however, the second CpNi(CO) fragment combines with another lone electron pair of the sulfide bridge, losing its CO, and with another thiolate sulfur atom with elimination of the second t-butyl group.

Thus, the geometry and ligand environment of each $NiCr_2$ triangle are similar to the structure of the inorganic skeleton in the metallocyclic cluster IV. In particular, the Cr—Cr bonds have practically equal lengths (2.62(1) and 2.617(1) Å, respectively), the Co—Cr bond lengths (2.586(1) Å) are close to the shorter Ni—Cr bond (2.63(1) Å). On the other hand, a considerable elongation of the second Ni···Cr distance to 2.86(1) Å, which is greater than the sum of Ni and Cr covalent radii (1.30 + 1.46 = 2.76 [8]) may be regarded as evidence for absence of such bonding. The Ni CN is equal to 6 rather than 7. Finally, the number of electrons in cluster II is equal to 66:

$$4\,C_5H_5 + 2\,Cr + 2\,Ni + 2(\eta^3\text{-}S) + (\eta^4\text{-}S) = 20 + 12 + 20 + 8 + 6 = 66$$

This is 4 electrons greater than the value needed for generation of a "metal-butterfly" skeleton, and corresponds to the formation of a zigzag Ni—Cr—Cr—Ni "metal-chain".

Experimental

All operations were performed under pure argon atmosphere. The dimers $(CpCrSCMe_3)_2S$ and $[CpNi(CO)]_2$ were prepared by reported methods [5,9]. The solvents were purified by distillation over a sodium suspension under argon counterflow. The IR spectra were taken on Specord IR-75 instrument in KBr pellets. The magnetic susceptibility was measured by the Faraday method at 298—77 K [10]. The X-ray data were obtained on a Syntex $P2_1$ diffractometer (λ Mo-K_α, graphite monochromator, scanning at —100° C, $\theta/2\theta$ scan). The structure was decoded by the direct method using the MULTAN program and refined by LSM using the anisotropic approximation for Ni, Cr and S atoms and the isotropic approach for C atoms to R = 0.072 and R_w = 0.065 for 1413 reflections.

The atomic coordinates are shown in Table 1, and the bond lengths and angles are in Tables 2 and 3. The molecular structure is shown in Fig. 1.

$(Cp_4Cr_2Ni_2)(\mu^3\text{-}S)_3(\mu^4\text{-}S)$ (II)

A dark-red solution of $[CpNi(CO)]_2$ in 30 ml of pentane was added to a violet solution of $(CpCrSCMe_3)_2S$ (0.8 g, 1.8 mmol) in 30 ml of benzene. The obtained cherry-red solution was refluxed for 1 h and had a stable red-brown colour. The brown solution was kept at room temperature for 12 h and separated on an alumina column (35 X 5 cm); the brown zone was eluted with benzene. 5 ml of heptane was added to the brown solution (50 ml), which was concentrated at 60° C/10 torr and then cooled to —5° C. The dark cherry-red needles precipitated were separated from the solution, washed with heptane and dried under vacuum. Yield 0.5 g. IR spectrum (ν, cm^{-1}): 405w, 622w, 678w, 782s, 802s, 829w, 900w, 1000m, 1012m, 1028w, 1048m, 1068m, 1120w, 1140w, 1330w, 1420m, 3090—3110(br)w.

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