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ANTIFERROMAGNETIC COMPLEXES INVOLVING METAL—METAL BONDS

III *. SYNTHESIS, STRUCTURE AND MAGNETIC PROPERTIES OF HETEROTRINUCLEAR COMPLEXES OF THE TYPE $M(CO)_5L$ (M = Cr, Mo AND W) CONTAINING $[(C_5H_5CrSCMe_3)_2S]$AS UNUSUAL ANTIFERROMAGNETIC LIGAND L

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Summary

Isostructural heterotrinuclear complexes $(C_5H_5CrSCMe_3)_2S \cdot M(CO)_5$ (II—IV) were isolated from photochemical reactions between the antiferromagnetic complex $(C_5H_5CrSCMe_3)_2S$ (I) (with the Cr—Cr bond 2.689 Å long and with the exchange parameter $-2J = 430$ cm^{-1}) and metal hexacarbonyls, $M(CO)_6$, where M is Cr, Mo, or W. According to the X-ray structural data on III and IV, complex I plays the role of an unusual antiferromagnetic ligand L bound to M through the sulphide bridge (M—S 2.58(2) Å). Its geometry remains practically unaffected by the complex formation (the Cr—Cr bond length in III and IV is 2.73(1) Å). The exchange parameter, $-2J$ (410, 440 and 440 cm^{-1} in II to IV, respectively), also shifts only insignificantly from that of I, which probably means that indirect exchange via the sulphide bridge in I is of minor importance compared with the direct Cr—Cr exchange. The Cr—Cr bond length may thus be correlated with the observed overall exchange coupling.

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* For part II see ref. 9.

Introduction

The chemistry of polynuclear transition metal complexes, whose foundations have already been laid by Werner [1], has developed during the past few decades into a new interesting branch, the chemistry of so-called "exchange clusters", viz. "polynuclear groupings screened by ligands from coordinative interactions over the whole lattice and containing not less than two exchange-coupled paramagnetic transition metal ions".

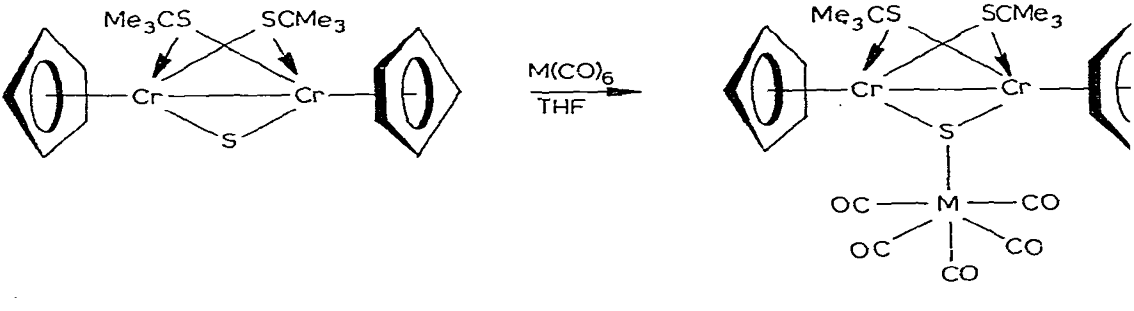
The study of exchange interactions in those systems, which was stimulated by Bleany and Bowers' classic work on the properties of copper(II) acetate hydrate [2], requires the synthesis of such systems. Hence the study of the effects of electronic and steric properties on the structures and magnetic properties of exchange clusters is of utmost importance [3,4]. The synthesis of heteronuclear exchange clusters is a particularly complex task, and the use of paramagnetic metal complexes as ligands grouped around a diamagnetic or paramagnetic metal centre is one of the most promising ways to its achievement [5—7]. There are, however, no examples thus far of the use of antiferromagnetic complexes as ligands attached to metal-containing Lewis acids.

Recently, we reported on the synthesis of the first binuclear organometallic complex, $(CpCrSCMe_3)_2S$ (I) (Cp = π-C_5H_5) where the presence of the direct Cr—Cr bond (2.689 Å long) does not result in diamagnetism: the complex is antiferromagnetic, the μ_{eff} value decreases from 0.97 to 0.02 B.M. in the range 295 to 79 K, and the exchange parameter, —2J, value is 430 cm^{-1} [8]. The compound readily undergoes methylation at the bridge sulphur atom under the action of CH_3I to give the antiferromagnetic complex $(CpCrSCMe_3)_2SCH_3^+I^-$ ($-2J = 350$ cm^{-1}) [9]. The ability of I to add electrophiles and to change its exchange parameter value in these reactions prompted us to study the reactions of I with other electrophiles, in particular, with metal-containing Lewis acids of the type $M(CO)_5$, generated photochemically from $M(CO)_6$ (M = Cr, Mo, or W) (see the premininary communication ref. 10).

Results and discussion

a) Synthesis of adducts $M(CO)_5L$ where L = $(CpCrSCMe_3)_2S$

Complex I reacts with $M(CO)_6$ quantitatively and at a high rate under UV irradiation in THF, with the elimination of one CO molecule and formation of black crystals of the composition $M(CO)_5L$ (M = Cr, Mo, W) (II to IV, respectively) (Table 1):



(II —IV)

TABLE 1

MAGNETIC PROPERTIES OF II—IV

No.	Compound	μ_{eff} (B.M.)			Monomer admixture (%)	$-2J$(Cr—Cr) (cm^{-1})
		295 K	150 K	77 K		
II	$(CpCrSCMe_3)_2SCr(CO)_5$	1.30	0.81	0.65	3.0	410
III	$(CpCrSCMe_3)_2SMo(CO)_5$	1.08	0.43	0.02	0.3	440
IV	$(CpCrSCMe_3)_2SW(CO)_5$	1.09	0.48	0.04	0.2	440

The IR spectra of II—IV each contain three bands of terminal CO stretches which is characteristic of $M(CO)_5L'$ complexes having C_{4v} local symmetry [11]. The complex compositions were determined by elemental analyses. In addition, treatment of the molybdenum derivative III with α-α′-dipyridyl (Dipy) results in the recovery of I and formation of red crystals of a known complex, (Dipy)-$Mo(CO)_4$ [12], the probable product of replacement of one of the CO groups in the $M(CO)_5$ fragment generated from III.

b) Structure of the adducts $M(CO)_5L$ with M = Mo and W (III and IV, respectively)

To prove the structures of the adducts II—IV, unambiguously, and to determine structural effects of the complex formation on the geometry of I, we undertook an X-ray study of III and IV.

Both structures were solved by the direct method. The crystals are rhombic, space group *Pcmm*, $Z = 8$. The unit cells of both compounds contain four independent molecules each. Two of the molecules include disordered $SCMe_3$ groups in which the methyl carbon atoms could not be located. For two other molecules, the positions of all the carbon atoms have been determined.

The molecules III and IV are isostructural (Fig. 1, Table 2) and comprise the $(CpCrSCMe_3)_2S$ and $M(CO)_5$ fragments linked by the M—S(sulphide) bond, 2.58(2) Å long, which is hardly shortened from the sum of covalent radii (1.58 + 1.04 = 2.62 Å [13]). The structure of the molecule I undergoes only insignificant change upon coordination to $M(CO)_5$: the Cr—Cr bond only lengthens from 2.689 to 2.73(1) Å, whereas changes in the Cr—S(sulphide), 2.27(2) Å, Cr—S(thiolate), 2.37(2) Å and Cr—$C(C_5H_5)$, 2.27(5) Å bond lengths from the corresponding parameters of the free molecule I (2.24(1), 2.38(1) and 2.23(4) Å, respectively) are within the uncertainties.

In the $M(CO)_5$ unit, the metal atom environment, including the M—S bond, is an almost regular octahedron (the S—M—C and C—M—C angles are equal to 90°). As shown in Fig. 1, complex I may in principle reacts as a bidentate agent as it bears lone pairs at both the sulphide and thiolate bridge sulphur atoms. One might, therefore, expect the formation of $(CpCrSCMe_3)_2S \cdot M(CO)_4$ complexes by analogy to the $(MeSCH_2CH_2SMe)Mo(CO)_4$ [14], and $Cp_2Ti(SR)_2 \cdot Mo(CO)_4$ [15] ones.

That this is not case may be due to the following reasons. First, to the large M—S(sulphide) distance (2.58 Å), responsible for the large M...S(thiolate) separation (of more than 3.6 Å). Secondly, approach of the thiolate sulphur

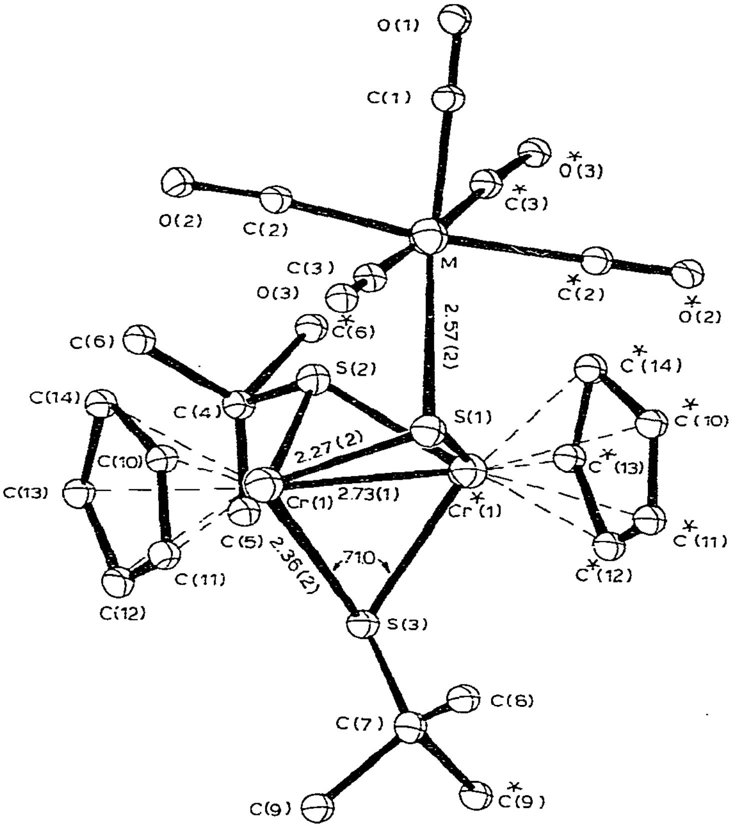


Fig. 1. The structure of complexes II—IV.

TABLE 2

THE BOND LENGTHS AND BOND ANGLES IN THE STRUCTURES III AND IV

Bond	d(Å)		Angle	ω(°)	
	M = Mo	M = W		M = Mo	M = W
M—S(sulph.)	2.58(2)	2.57(2)	MS(sulph.)Cr	129.5(7)	128.7(6)
M—C(CO)	1.96(7)	1.98(6)	S$_1$MC(CO)$_{cis}$	90(1)	88(1)
Cr—Cr	2.73(1)	2.73(1)	S$_1$MC(CO)$_{trans}$	174(2)	173(2)
Cr—S(sulph.)	2.27(2)	2.28(2)	C(CO)$_{cis}$MC(CO)$_{trans}$	90(2)	91(2)
Cr—S(thiol)	2.37(2)	2.35(3)	MCO	175(4)	173(4)
Cr—C(C$_5$H$_5$)	2.27(5)	2.24(5)	CrS(sulph.)Cr	73.9(5)	73.7(5)
S—C(CMe$_3$)	1.88(7)	1.89(8)	CrS(thiol)Cr	70.3(7)	71.7(6)
C—C(C$_5$H$_5$)	1.43(6)	1.42(5)	S(sulph.)CrCr	53.1(5)	53.1(5)
C—C(CMe$_3$)	1.55(8)	1.55(8)	S(thiol)CrCr	54.9(7)	54.3(6)
C—O	1.15(6)	1.16(6)	S(sulph.)CrS(thiol)	87.2(7)	85.6(7)
			S(thiol)CrS(thiol)	91.6(7)	90.6(8)
			CrS(thiolC(CMe$_3$)	118(2)	117(2)
			S(thiol)C(CMe$_3$)C(Me)	109(3)	109(4)
			CCC(CMe$_3$)	110(4)	113(4)
			CCC(C$_5$H$_5$)	107(3)	109(4)

atom to M is hindered by repulsion between this atom and two nearest equatorial carbonyl groups around the octahedrally coordinated M atom. This and saturation of the metal valence shell with electrons prevents the formation of chelate complexes and replacement of CO with S(thiolate) by the S_N2-type mechanism.

c) Magnetic properties of the adducts $M(CO)_5L$ (II—IV)

The structural data on the complexes III and IV proved very useful for the understanding of their magnetic properties. The effective magnetic moments,

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

where χ_M is the molar magnetic susceptibility were calculated from the temperature dependences of the magnetic susceptibilities.

The data obtained (Table 1) show the complexes to be antiferromagnetic and to have temperature dependences of the effective magnetic moments similar to that observed in I. The experimental data fit the Heisenberg-Dirac-Van Vlek (HDVV) model well for two exchange-coupled ions (the M atom is diamagnetic) in the absence of orbital degeneracy of the ground states of the complexes. The spin Hamiltonian has the form [16]:

$$\hat{H} = -2JS_1S_2 - g\beta H(\hat{S} + \hat{S}_{2Z})$$

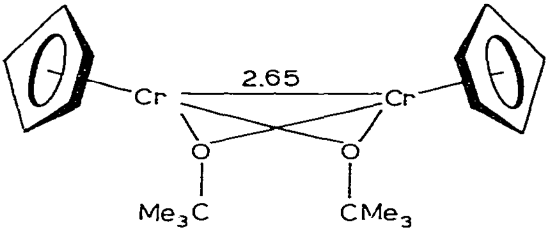
where J is the isotropic exchange interaction parameter, g the isotropic g-factor, $\hat{S}$ are the spins of exchange coupled ions (in our case, $S_1 = S_2 = 3/2$).

The calculations of the theoretical χ_M values and minimization of mean square deviations were performed using the programme described in ref. 17. The $-2J$ values for II to IV were found to be 410, 440 and 440 cm^{-1}, respectively (Table 1).

The fact that the $-2J$ values characterizing the adducts hardly differ from the free ligand value, 430 cm^{-1}, seems rather unexpected as considerable withdrawal of electrons from the sulphide bridge between two paramagnetic Cr^{III} ions to the $M(CO)_5$ group should occur in the complex formation. This should lead to weakening of indirect exchange interactions through the sulphur atom. One has, therefore, to suggest that indirect exchange contributions are negligible compared with direct exchange via the Cr—Cr bond which remains unaffected by the complex formation.

This is an important point, as the complexes prepared earlier containing both metal—metal bonds and bridging ligands are diamagnetic [18], which bars the possibility of even a qualitative estimation of the relative contributions from direct and indirect exchange. To a rough approximation, indirect exchange contributions may be neglected and the summarized exchange interactions ($-2J_\Sigma$) may be directly related to metal—metal bond strengths. The $-2J_\Sigma$ values in complexes containing bridging ligands should, in particular, be approximately the same and depend only insignificantly on the nature of the bridging ligand provided the M—M bond lengths are similar.

From this point of view, it seems interesting to compare the magnetic properties of Cr^{III} complexes I, III, and IV with those of the product of the reaction between chromocene and t-butyl alcohol, the binuclear Cr^{II} complex recently described in ref. 19:



In the $(CpCrOCMe_3)_2$ (V) complex, two CpCr fragments are linked by two tert.-butoxy bridges and a direct Cr—Cr bond, whose length (2.65(2) Å) is close to that observed in I (2.689 Å) [8]. Complex V was reported to be antiferromagnetic and to have the following $\mu_{eff.}$ vs. temperature dependence (determined from proton NMR spectra in toluene solutions [20]; the results were independent of the solution concentration):

$\mu_{eff.}$ B.M.(T°K): 1.88(333.5), 1.84(316), 1.77(293), 1.73(278), 1.67(256), 1.57(228.5), 1.49(214).

Unfortunately, the authors [19] did not calculate the exchange parameter value. Neither did they give any interpretation of the results obtained.

The calculations made by us using the approximative HDVV model [16,17] for a system of two interacting Cr^{II} ions (spin S of 2) gave the best fit to the experimental data [19] (Fig. 2) at $-2J = 246$ cm^{-1} ($g = 1.92$, monomer admixture 2.9%, mean square deviation 1.4%). According to the "exchange channel model" [21], the summarized exchange coupling, $-2J_\Sigma$, is related to the $-2J$ parameter by the equation:

$$-2J_\Sigma = -2J \times 4S_1S_2$$

where S_1 and S_2 are the electronic spins of the interacting metal ions, and $4S_1S_2$

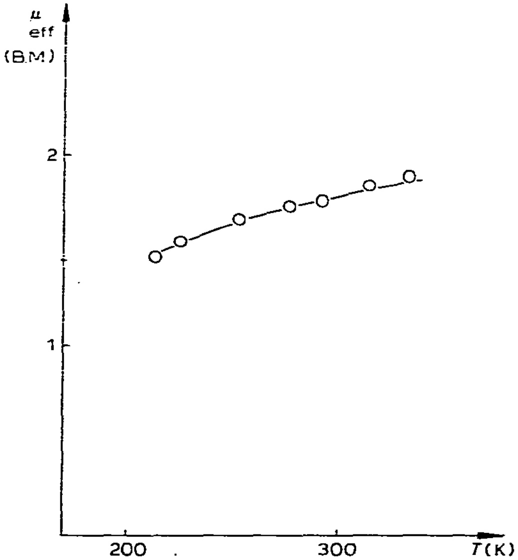


Fig. 2. The plot of temperature dependence of magnetic moment for $(CpCrOCMe_3)_2$.

is the sum of exchange channels. For the pair of Cr^{II} ions in V, $S_1 = S_2 = 2$, whereas for Cr^{III} pairs in I to IV, $S_1 = S_2 = 3/2$. The $-2J_\Sigma$ value for V is therefore equal to $246 \times 4 \times 2 \times 2 = 3936$ cm^{-1} which practically coincides with the corresponding values for I ($430 \times 4 \times 3/2 \times 3/2 = 3870$ cm^{-1}) and III and IV ($440 \times 4 \times 3/2 \times 3/2 = 3960$ cm^{-1}).

This result lends support to our suggestion of negligibly small contributions from indirect exchange through bridging ligands compared with direct exchange through metal—metal bonds.

As for the lowering of the summarized exchange coupling on going to II ($-2J_\Sigma = 410 \times 4 \times 3/2 \times 3/2 = 3690$ cm^{-1}), and especially the methylated complex $(CpCrSCMe_3)_2SMe^+I^-$ [9] ($-2J_\Sigma = 350 \times 4 \times 3/2 \times 3/2 = 3150$ cm^{-1}), this may be due to Cr—Cr bond elongation caused by decrease of the covalent radii of the electrophile atoms (r Cr = 1.46 Å [13], r C = 0.77 Å), and, hence, deeper penetration of the electrophile into the structure of the initial complex I (this problem is discussed in more detail in ref. 9).

Experimental

Complexes II—IV were synthesized using absolute solvents under pure argon. $(CpCrSCMe_3)_2S$ was prepared as recommended in ref. 8. Commercial $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ purified by sublimation under vacuum were employed. The IR spectra were obtained on an UR-20 instruments (KBr pellets). Magnetic measurements were taken by the Faraday technique on a apparatus for magnetic measurements constructed in this Institute [22]. X-ray diffraction patterns were obtained on a Syntex $P2_I$ autodiffractometer (λ Mo-K_α, $\theta/2\theta$ scan). A total of 2723 reflections for complex III and 2993 reflections for complex IV were collected. Space group *Pcmm*, $Z = 8$ (4 independent molecules). The cell parameters were: Complex III: a 23.785(4), b 14.190(2), c 16.842(2) Å; $V = 5677.7$ Å^3, $D_{\text{exptl.}}$ 1.59, $D_{\text{calcd.}}$ 1.60 g/cm^3, $R = 0.089$. Complex IV: a 23.720(7), b 14.171(3), c 16.809(3) Å; $V = 5650.2$ Å^3, $D_{\text{exptl.}}$ 1.83, $D_{\text{calcd.}}$ 1.82 g/cm^3, $R = 0.070$.

$(CpCrSCMe_3)_2S \cdot Cr(CO)_5$ (II)

A violet solution of I (0.32 g, 0.7 mmol) and $Cr(CO)_6$ (0.015 g, 0.7 mmol) in 25 ml THF was irradiated in a quartz Schlenk vessel, the jacket cooled by running water, with stirring with a magnetic stirrer for 3 h until 15.7 ml (0.7 mmol) CO was evolved. During the reaction, the solution colouration changed to brown, and the IR band of $Cr(CO)_6$, ν(CO) 1990 cm^{-1} disappeared. The product gave a dark brown spot on thin-layer chromatography (Al_2O_3, eluent benzene/heptane 1/1), $R_f = 0.83$ (only trace amounts of I with R_f of 0.1 were detected). The solution was concentrated under vacuum at 50°C/15 Torr to a volume of 7 ml. The addition of the same volume or heptane resulted in precipitation of black needles. These were separated, washed with pentane and dried under vacuum. The yield was 0.31 g (70%). Found: C, 43.33; H, 5.06; Cr, 25.30; S, 15.49. $C_{23}H_{28}Cr_3O_5S_3$ calcd.: C, 43.39; H, 4.40, Cr, 24.52; S, 15.09%. The product decomposes above 145°C to $Cr(CO)_6$. The IR spectrum (ν, cm^{-1}): 450m, 652m, 667s, 815s, 1030w, 1160m, 1370w, 1440w, 1460w, 1475w, 1904s, 1925s, 2050s, 2058s, 2930w, 3110w.

$(CpCrSCMe_3)_2S \cdot Mo(CO)_5$ (III)

Black prisms of III (0.14 g, 50%) were obtained from I (0.20 g, 0.45 mmol) and $Mo(CO)_6$ (0.10 g, 0.38 mmol) in 35 ml THF using a similar procedure. M.p. 160° C (decomposes). Found: C, 40.52; H, 4.21; Cr, 15.04; Mo, 13.87; S, 13.92. $C_{23}H_{28}Cr_2MoO_5S_3$ calcd.: C, 40.60; H, 4.12; Cr, 15.02; Mo, 14.11; S, 14.11%. IR spectrum (ν, cm^{-1}): 595s, 615m, 818s, 1025w, 1160s, 1370w, 1440w, 1460w, 1475w, 1910s, 1940s, 2070s, 2940w, 3115w.

$(CpCrSCMe_3)_2S \cdot W(CO)_5$ (IV)

The same technique was applied to obtain IV from I (0.34 g, 0.7 mmol) and $W(CO)_6$ (0.24 g, 0.7 mmol) in 30 ml THF (Yield 0.25 g, 46%, black prisms). M.p. 168° C (decomposes). Found: C, 36.10; H, 3.75; S, 12.22. $C_{22}H_{28}Cr_2O_5S_3W$ calcd.: C, 35.93; H, 3.64; S, 12.50%. IR spectrum (ν, cm^{-1}): 585s, 063w, 817m, 1027w, 1070w, 1160m, 1370w, 1440w, 1475w, 1898s, 1920s, 2059s, 2065s, 2930w, 3120w.

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