

Antiferromagnetic Complexes Involving Metal–Metal Bonds. II. The Conditions for Observation and Means of Intended Variation of Antiferromagnetic Properties of Binuclear Complexes Involving Cr–Cr and V–V Bonds

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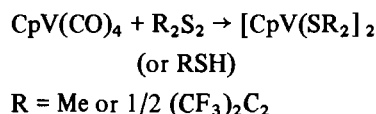
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The complex, $(\text{CpCrSCMe}_3)_2\text{S}$ (I), contains a Cr–Cr bond (2.689 Å) and at the same time shows anti-ferromagnetic properties ($-2J = 430 \text{ cm}^{-1}$). It reacts with PhEH (E is S, Se) or MeI to give binuclear complexes $(\text{CpCrEPH})_2\text{S}$ or $[(\text{CpCrSCMe}_3)_2\text{SMe}]^+\text{I}^-$ characterized by exchange parameter, $-2J$, values of 496, 378, and 350 cm^{-1} , respectively. Reaction between Cp_2Cr and PhEH yields the antiferromagnetic trimer $[\text{CpCr(SPh)}_2]_3$ ($-2J = 194 \text{ cm}^{-1}$) and dimer $[\text{CpCr(SePh)}_2]_2$ ($-2J = 208 \text{ cm}^{-1}$). CpV(CO)_4 reacts with PhEH to give dimeric complexes $[\text{CpV(EPH)}_2]_2$ one of which shows antiferromagnetic behaviour (E = Se, $-2J = 700 \text{ cm}^{-1}$) and the other one is a diamagnetic substance (E = S, $-2J \gg 1000 \text{ cm}^{-1}$). The magnetic properties of the complexes are treated in terms of the exchange channel model. It is shown that antiferromagnetic behaviour (magnetic moment decreases with temperature) of binuclear complexes involving direct metal–metal bonds may be expected when the paramagnetic ions are in high-spin states ($S \geq 1$). In such complexes, variations in metal–metal bond strength caused by ligand substitution may be studied by the methods of magnetochemistry.

Introduction

Recently, we have described the first antiferromagnetic organometallic complex containing a metal–metal bond, $(\text{CpCrSCMe}_3)_2\text{S}$ (I) in which the Cr(III) ions (d^3 configuration) interact via a direct Cr–Cr bond 2.689 Å long and also via two tert.butylthiolate and one sulphide bridges (μ_{eff} (μ_{B}) 0.97 (295 K); 0.02 (150 K); the exchange parameter, $-2J$, of 430 cm^{-1}) [1]. One more example of antiferromagnetic complexes studied by X-ray diffraction and shown to contain direct metal–metal bonds though with an

inorganic environment of the central ions is provided by three-valent iron binuclear complexes $[(\text{RS})_2\text{FeS}]_2^{2-}$ (R = $n\text{-CH}_3\text{C}_6\text{H}_4$ or $1/2 (\text{CH}_2)_2\text{C}_6\text{H}_4$) (Fe–Fe 2.69 Å, $-2J$ of 300 cm^{-1}) [2, 3]. A partially double metal–metal bond is also believed to occur in V(III) complexes obtained by the reaction [4, 5]:

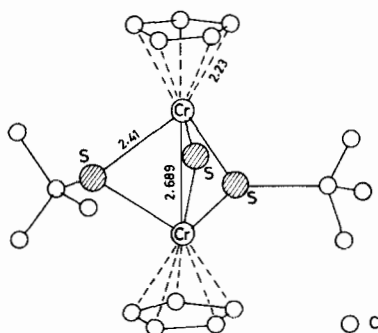


The dithiethene complex $[\text{CpVS}_2\text{C}_2(\text{CF}_3)_2]_2$ has unit cell dimensions and space group [6] that show it to be isostructural with a similar diamagnetic molybdenum complex containing four thiolate bridges and a short (2.62 Å) Mo–Mo bond [7, 8]. Both vanadium complexes exhibit low effective magnetic moment values (μ_{eff} of 0.9 and $0.6 \mu_{\text{B}}$ at 295 K, respectively). The authors [4] point to a reversible increase of magnetic susceptibility of vanadium methylthiolate in the range 195 to 345 K, though they give no quantitative data. On the other hand, all the other numerous complexes known to contain M–M bonds show diamagnetic behaviour [9]. The data available are insufficient to determine the conditions for observation of antiferromagnetic properties in binuclear complexes containing metal–metal bonds. That prompted us to undertake a detailed investigation of binuclear Cr(III) and V(III) cyclopentadienylchalcogenates and to compare the results obtained with the data on Ti(III) [10], Mo(III) [8], and Mo(V) [11] derivatives.

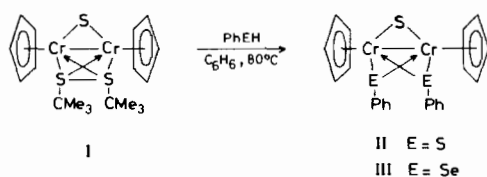
Results and Discussion

The study of the chemical behaviour of $(\text{CpCrSCMe}_3)_2\text{S}$ (I) (Fig. 1) has provided means for diverse modifications of the compound without rupture of the Cr–Cr bond. Compound I comprises a

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Fig. 1. The structure of $(\text{CpCrSCMe}_3)_2\text{S}$ (I).

stable sulphide bridge together with rather labile tert-butylthiolate groups that are easy to replace by thio- and selenophenolate residues:



Compounds II and III are crystalline brown solids stable in the air which, unlike I, do not melt up to 300°C , are only poorly soluble in benzene and insoluble in heptane. The magnetic properties of II and III resemble those of I, their effective magnetic moments decreasing from 0.94 to $0.39 \mu_{\text{B}}$ for II and from 1.23 to $0.43 \mu_{\text{B}}$ for III in the range 297 to 79 K. The Heisenberg-Dirac-Van Vleck [12] calculations for a binuclear system containing spins $S_1 = S_2 = 3/2$ fit the experimental data with the $-2J$ values set equal to 496 cm^{-1} for II and 378 cm^{-1} for III (Fig. 2), which is rather close to the $-2J$ value of 430 cm^{-1} observed in I (the g value of 1.98 was assumed for all the compounds). A relatively weak dependence of $-2J$ on R and E seems to be due to the retention

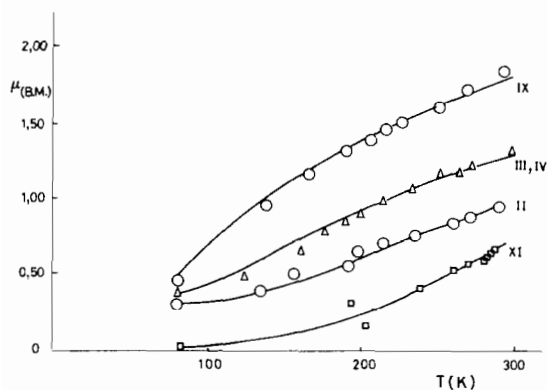


Fig. 2. The plots of temperature dependence of magnetic moments for II-IV, IX and XI.

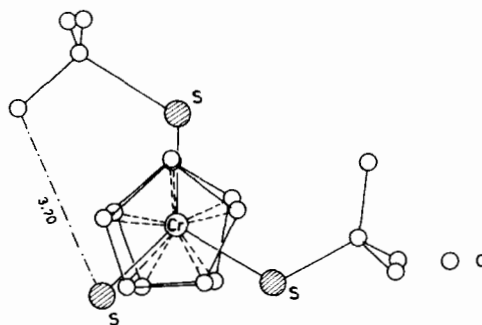
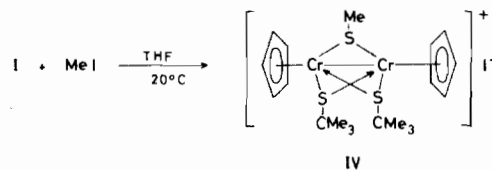


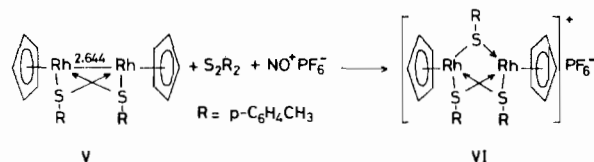
Fig. 3. The projection of I along the Cr-Cr axis.

of the Cr-Cr bond and of basic structure of the binuclear unit. A similar structure occurs in the diamagnetic Mo(V) complex, $[(\text{Et}_2\text{NCS}_2)\text{MoO}]_2(\text{SPh})_2\text{O}$ [13], containing two thiophenolate and one oxygen bridges and a direct Mo-Mo bond 2.678 \AA long.

On the other hand, alkylation of I at the sulphide bridge lone pair should lead to a structure containing three thiolate bridges. The thiolate group is sterically accessible, as may be seen from Fig. 3 where I is depicted in projection down the Cr-Cr axis. Methyl iodide reacts with I quite readily even at ambient temperature to give binuclear complex IV as crystalline precipitate:



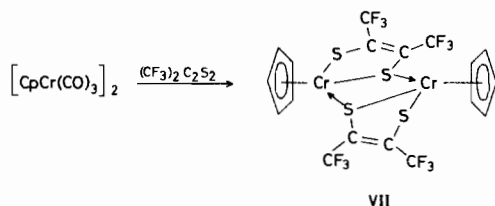
Compound IV represents brown prisms only poorly soluble in THF and moderately soluble in CHCl_3 and CH_2Cl_2 to give cherry-coloured solutions. The product is insoluble in benzene and heptane and is stable in the air. It shows antiferromagnetic properties and effective magnetic moment temperature dependence (μ_{eff} decreases from 1.32 to $0.48 \mu_{\text{B}}$ in the range 295 to 79 K) and $-2J$ value (350 cm^{-1}) similar to those found in III) (Fig. 2). An analogous complex cation VI occurs in the oxidation of binuclear complex V containing a short (2.644 \AA) Rh(II)-Rh(II) bond [14]:



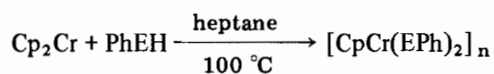
The oxidation of Rh(II) to Rh(III) should result in the removal of electrons from the M-M bond so that the 18-electron outer shell configuration in VI is attained without the formation of a Rh-Rh bond. As the methylation of the sulphide bridge in IV does not

change the number of binuclear system electrons, it seems likely that the Cr–Cr bond is retained in IV. This conclusion is consistent with a relatively insignificant variation of the $-2J$ parameter in the isoelectronic series I–IV. It thus appears that the structures of I through IV comprise the direct Cr–Cr bond and three bridge groupings.

On the other hand, the Cr(III) dithiethene complex described in [5] is supposed, on the basis of the preliminary X-ray diffraction data [6], to be a dimer with only two bridges and no direct metal–metal bond (VII):



Unfortunately, no data on bond lengths and valence angles and magnetic properties is available for that compound. This prompted us to synthesize and study Cr(III) cyclopentadienylchalcogenates of the composition $[\text{CpCr}(\text{EPh})_2]_n$ where E is S or Se (see preliminary communication [15]):



E = S, $n = 3$ (VIII)

E = Se, $n = 2$ (IX)

Compounds VIII and IX are black infusible crystalline solids which undergo hydrolysis in the air to a marked extent. They are involatile under vacuum and insoluble in the usual organic solvents which bars the determination of their molecular weights. The IR spectra of VIII and IX are closely similar (Fig. 4) so we assigned [15] the same dimeric structure analogous to VII to both. A detailed analysis of their

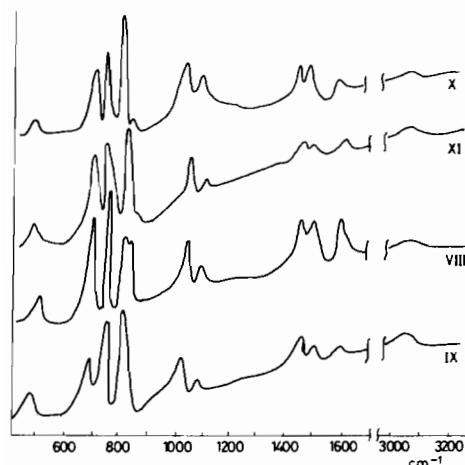


Fig. 4. IR spectra of VIII–XI.

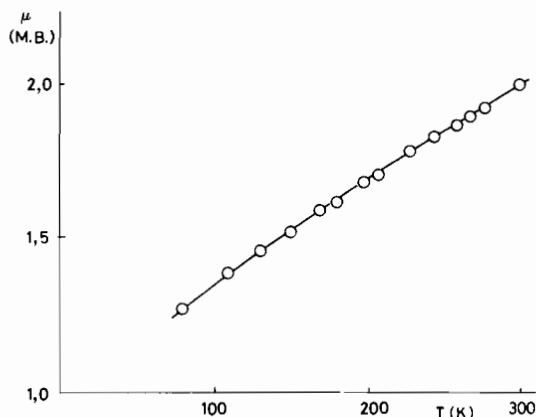
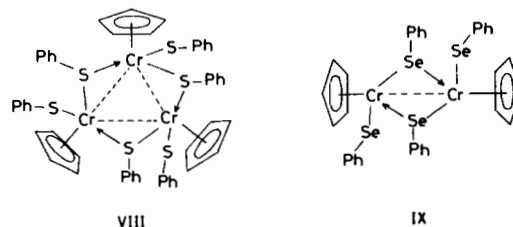


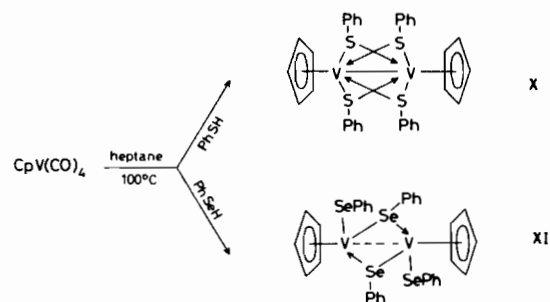
Fig. 5. The plot of temperature dependence of magnetic moment for $[\text{CpCr}(\text{SPh})_2]_3$ (VIII).

magnetic properties however has shown that VIII is a trimer while IX is a dimer. Thus, the μ_{eff} value decreases in VIII from 2.00 to 1.26 μ_{B} in the range 295 to 79 K, and its temperature dependence fits the HDVV trimeric model [12] characterized by the parameter $-2J_{12} = -2J_{23} = 2J_{13} = 194 \text{ cm}^{-1}$ (Fig. 5). With IX, the μ_{eff} value decreases from 1.90 to 0.46 μ_{B} in the same temperature range which fits the dimeric model with $S_1 = S_2 = 3/2$ and $-2J$ value of 208 cm^{-1} (Fig. 2). By analogy with chromium environment in VII where the central ion is surrounded with only three sulphur atoms, VIII and IX may be suggested to have the structures



The reason why these compounds have different structures remains unclear at present.

The works [4, 5] on the synthesis of $[\text{CpV}(\text{SR})_2]_2$ ($\text{R} = \text{Me}$ or $1/2 (\text{CF}_3)_2\text{C}_2$) lack data on temperature dependence of μ_{eff} in those compounds, and the corresponding exchange parameters cannot be estimated. We have studied their thio- and selenophenolate analogues prepared as follows [16]:



Compound X is a light-brown and XI a dark-brown crystalline solid. Both are rather stable in the air and decompose at about 300 °C without melting. The complexes are insoluble in organic solvents. The thiophenolate is however volatile under high vacuum. The heaviest ion in its mass spectrum is the binuclear fragment $\text{Cp}_2\text{V}_2(\text{S})(\text{SPh})_2^+$ (m/e 482), seemingly, having the structure analogous to I and II. The presence of an intense Ph_2S^+ ion (m/e 186) may be interpreted as indicative of the formation of the binuclear ion from a four-bridge molecule similar to $\text{Cp}_2\text{V}_2[(\text{CF}_3)_2\text{C}_2\text{S}_2]_2$. The IR spectra of the thiolate and selenate complexes practically coincide (Fig. 4), while the magnetic properties of the compounds differ, the former showing diamagnetic* and the latter antiferromagnetic behaviour. Selenate effective magnetic moment decreases from 0.67 to 0 μ_B on cooling the compound from 295 to 150 K which well fits the HDVV theoretical curve for two exchange coupled equivalent ions having spins $S_1 = S_2 = 1$ with the exchange parameter value $-2J = 700 \text{ cm}^{-1}$ and $g_1 = g_2 = 1.98$ (Fig. 2). The ESR spectrum of XI shows a fine structure at 1000–5000 Oe typical for the triplet state of a dimeric molecule and may be described by rhombic Hamiltonian with $g = 1.99$, $D = 0.19 \text{ cm}^{-1}$, $E = -0.005 \text{ cm}^{-1}$ (the lines having parallel orientation are resolved only poorly) (Fig. 6).

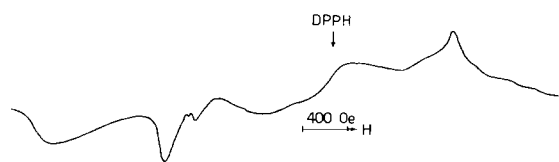
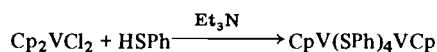


Fig. 6. ESR spectrum of $[\text{CpV}(\text{SePh})_2]_2$ (XI).

The ESR results thus confirm the magnetic data. It thus appears that the replacement of sulphur atoms in four chalcogeno bridges with selenium results in a drastic weakening of exchange interactions on going from X to XI. The significantly large value of E in the ESR spectrum of XI points to a considerable symmetry lowering, probably caused by the formation of the two-bridge structure shown in the Scheme above. The geometry of XI should then be similar to IX. The

*It should be noted that just recently [17], the thiophenolate has been claimed to occur in the reaction



The complex is described as a paramagnetic compound with μ_{eff} of 1.14 μ_B at 297 K. The analytical data (a discrepancy of ca. 3% between the calculated and found values for C percentage) and the isolation procedure applied (in the air, with washing by water) make it likely that impurity paramagnetism was observed.

larger $-2J$ value is, however, indicative of marked interactions across the direct V–V bond due to the larger vanadium covalent radius (*cf.* 1.49 for V and 1.46 Å for Cr [18]).

Magnetic Properties and Metal–Metal Bond

The existence of the derivatives $(\text{CpCrSCMe}_3)_2\text{S}$ (1) having similar properties and likely to contain the Cr–Cr bond shows that antiferromagnetic behaviour in metal–metal bond containing compounds is not a merely accidental feature. The variations of the magnetic characteristics in the series of the binuclear complexes under consideration depending on the ligands and on the central atom make it possible to discuss the nature of that phenomenon and the conditions favouring the observation of antiferromagnetism. It is, in particular, essential to find out why all the organometallic complexes known earlier and containing M–M bonds show diamagnetic behaviour [9].

To explain antiferromagnetic properties of the complexes containing direct M–M bonds, the exchange channel model developed recently by Eremin and two of us will be applied [19, 20]. According to this theory,

$$-2J_{\Sigma} = -2 \sum_{ij} J_{ij} = -2J \cdot 4S_a S_b \quad (1)$$

where $-2J_{\Sigma}$ is the algebraic sum of the exchange parameter $-2J_{ij}$ pair interaction energies between the i -th unpaired electron on the a ion and j -th unpaired electron on the b ion, S_a and S_b are the ion spins, and the product $4S_a S_b$ is the number of exchange channels. In particular, with Cr(III) having spin of 3/2 we obtain for complex I:

$$-2J_{\Sigma} = 430 \cdot 4 \cdot 3/2 \cdot 3/2 = 430 \cdot 9 = 3870 \text{ cm}^{-1}$$

The total exchange coupling is thus nine times as large as the experimental singlet–triplet splitting, $-2J$. The $-2J$ value obtained may be shown to correspond to the expected antiferromagnetic contribution, $-2J_{\alpha\beta} = -2J^d$, from only *direct* overlap of two unpaired electron orbitals (α and β) involved in bonding at a distance of 2.69 Å ($\alpha = d_{Z^2}^a$, $\beta = d_{Z^2}^b$).

In fact, the antiferromagnetic Weiss temperature point, θ , was determined for mixed Cr(III) oxides as depending on the metal–metal distance, R [21]. The analysis of the observed dependence showed that at small distances, of 2.88 to 2.98 Å, antiferromagnetic properties were determined by direct overlap of unpaired chromium electrons. We have extrapolated the observed θ vs. R dependence to R of 2.69 Å on the assumption that direct coupling varies with R following the exponential, $Ae^{-x/R}$, or power, $B \cdot R^{-n}$, law. Both functions predict similar θ values of about 2000 K, whence $-2J^d$ is equal to 3000 cm^{-1} .

It is worthwhile mentioning that the χ value in the exponential function $-2J^d(R) = Ae^{-x/R}$ is equal to

6.3. The $-2J^d$ value thus changes by a factor of about 2 when R varies by 0.1 Å (similar dependences were obtained in [22, 23]). The $-2J^d$ value of 3000 cm^{-1} may be shown to indicate the presence of a Cr–Cr bond of *ca.* 30 kcal/mol energy in I. In fact, according to [24], antiferromagnetic interactions involving overlap of unpaired electrons may be approximated by

$$2J^d = \frac{(\epsilon_1 - \epsilon_2)^2}{J_{aa} - J_{ab}} \quad (2)$$

where ϵ_1 and ϵ_2 are the energies of the bonding and antibonding orbitals and J_{aa} and J_{ab} are the one and two-centre Coulomb integrals, respectively. Substitution of $(\epsilon_1 - \epsilon_2) = 30$ kcal/mol and $(J_{aa} - J_{ab}) = 5$ eV (the values cited in [24]) into (2) yields $-2J^d$ of 3000 cm^{-1} . This is, of course, a very rough estimate. Nevertheless, it clearly shows that even large overlap ($-2J$ of the order of thousands cm^{-1}) may be insufficient to make the compound a pure diamagnetic. As the complexes usually become diamagnetic at $-2J$ exceeding 1000 cm^{-1} , expression (1) may be written as the condition for the observation of antiferromagnetism:

$$-2J = \frac{-2J_{\Sigma}}{4S_a S_b} < 1000 \text{ cm}^{-1} \quad (3)$$

Expression (3) shows that systems with high spins, that is, characterized by large values of the denominator, $4S_a S_b$, may prove antiferromagnetic irrespective even of strong exchange coupling, *e.g.* in the presence of M–M bonds. That explains the antiferromagnetic properties of the aforementioned complexes, $[(RS)_2FeS]_2^{2-}$ [2, 3], where the Fe(III) ions removed by as little as 2.69 Å from each other have spins of 5/2. According to (1) the total exchange coupling in that case, $-2J_{\Sigma}$, proves 25 times larger than the exchange parameter value, $-2J = 300 \text{ cm}^{-1}$, *i.e.* $-2J_{\Sigma} = 7500 \text{ cm}^{-1}$ which corresponds to strong exchange across the Fe–Fe bond.

With lower spin values, antiferromagnetic coupling should be expected when the total exchange coupling over all the channels, $-2J_{\Sigma}$ (and accordingly, the M–M bond energy) is not very large. Thus, the V(III) ions in $[\text{CpV}(\text{SePh})_2]_2$ (XI) have the d^2 configuration ($S = 1$). Therefore

$$-2J_{\Sigma} = -2J \cdot 4S_a S_b = 700 \cdot 4 \cdot 1 \cdot 1 = 2800 \text{ cm}^{-1}$$

That value is noticeably lower than 3870 cm^{-1} observed in I, though it greatly exceeds 1000 cm^{-1} , the value characteristic of indirect coupling through bridge ligands only [25]. It is likely that a weak V–V bond is present in XI.

Lastly, with spins as low as 1/2, the product $4S_a S_b$ is equal to unity and $-2J_{\Sigma} = -2J$. In this case, even very weak M–M bonding or strong indirect exchange

(of *ca.* 1000 cm^{-1}) should lead to diamagnetism. The latter situation is characteristic for Mo(V) complexes (*e.g.* $[\text{CpMoO}]_2(\text{X})_2$ ($\text{X} = \text{O}, \text{S}$) [26], $[(\text{Et}_2\text{NCS}_2)\text{MoO}]_2(\text{SPh})_2\text{O}$ [13]) and Ti(III) complexes ($[\text{Cp}_2\text{TiY}]_2$ ($\text{Y} = \text{NR}_2, \text{SR}$) [10]). Also, all the organometallic compounds involving M–M bonds known earlier are diamagnetic probably because of exchange interactions between the ions having spins of 1/2. In fact, organic ligands are mostly strong field ligands prohibiting the formation of high-spin systems. The conclusion may be drawn that the spin state of a system is of the greatest importance for determining the possibility of the observation of antiferromagnetic properties in the presence of M–M bonds.

On the other hand, variations of exchange interactions within series of systems characterized by the same spin value may be rationalized from consideration of spatial effects on the M–M bond strength. The presence of the M–M bond in I results in repulsion between the bridge sulphur atoms and cyclopentadienyl carbon atoms (Fig. 1) on the one hand and the sulphur atoms and *tert.*-butylthiolate bridge methyl groups $\text{S} \dots \text{C}_{\text{CH}_3}$ (3.7 Å) (Fig. 3) on the other. This steric strain in turn hinders the further shortening of the Cr–Cr bond. Clearly, increase (decrease) of steric strain would weaken (strengthen) the Cr–Cr bond. Thus, the replacement of bulky *tert.*-butyl substituents with phenyl ones should have a loosening effect on the structure strain and thus strengthen the Cr–Cr bond. In fact, the $-2J$ value increases from 430 to 496 cm^{-1} on going from I to II.

Conversely, the addition to the sulphide bridge of one more methyl group with the formation of the C–S bond *ca.* 1.8 Å long (by analogy to the S–CMe₃ bond in I) should lead to an increase of steric strain in IV compared with I and thus weaken the Cr–Cr bond which is in agreement with the observed decrease of $-2J$ from 430 to 350 cm^{-1} .

The replacement of bridge chalcogeno atoms has a particularly strong effect on the M–M bond strength and, accordingly, exchange coupling. Thus, the substitution of larger Se atoms for smaller S ones in chalcogeno bridges should be expected to result in shortening and a significant strengthening of the M–M bond, analogous to that observed for the Mo–Mo bond (2.9 and 2.5 Å, respectively) on the replacement of sulphide bridges with oxide ones in $(\text{CpMoO})_2(\text{S})_2$ [26]. In fact, exchange coupling increases on going from selenophenolate derivative III ($-2J$ of 378 cm^{-1}) to the thiophenolate complex II ($-2J$ of 496 cm^{-1}). Likewise, shortening of the V–V bond in the thiophenolate X from selenophenolate XI causes increase of exchange interactions to the extent that the former compound shows diamagnetic behaviour at room temperature ($-2J > 1000 \text{ cm}^{-1}$).

Lastly, increase of the number of chalcogeno groupings attached to the binuclear system to four

hinders the formation of a strong Cr–Cr bond. This is why dimeric selenophenolate IX shows a *ca.* 1000 cm^{-1} smaller $-2J_{\Sigma}$ value ($-2J_{\Sigma} = -2J \cdot 4S_a S_b = 206 \cdot 4 \cdot 3/2 \cdot 3/2 = +1854 \text{ cm}^{-1}$) than its vanadium analogue XI supposed to contain a V–V bond.

The phenomenon of antiferromagnetic behaviour of complexes involving metal–metal bonds studied in this work thus not only provides insight into the nature of exchange interactions but also opens the possibility to (i) study M–M bonds in exchange clusters of high-spin ions by magnetochemistry methods and (ii) intentionally modify antiferromagnetic properties by utilizing the effects of steric factors on M–M bond strength.

Experimental

All synthetic experiments were carried out in absolute solvents under pure argon. Cp_2Cr and $\text{CpV}(\text{CO})_4$ were obtained as described in [27]. Thiophenol and tert.-butyl mercaptane were commercial products purified by fractional distillation. Selenophenol was obtained as recommended in [28]. Melting points were determined in capillaries sealed under argon, not corrected. The IR spectra were recorded on an UR-20 instrument (KBr pellets). Magnetic susceptibility was measured by the Faraday method using samples sealed in ampoules under vacuum in the range 295 to 79 K.

$\text{Cp}_2\text{Cr}_2(\text{S})(\text{SCMe}_3)_2$ (I)

Me_3CSH (1 ml) was added to a filtered red solution of Cp_2Cr (0.50 g, 2.7 mM) in 30 ml heptane. The mixture was refluxed for 4 hr. Violet needle-like crystals precipitated on cooling the inky-violet reaction mixture. These were separated, washed with pentane, and dried under vacuum at 20 °C. The yield was 73%. Found (calcd.), %: C, 48.73 (48.64); H, 6.35 (6.30); Cr, 23.80 (23.42). IR spectrum (cm^{-1}): 570 w, 600 w, 810 w, 848 w, 1025 m, 1070 w, 1135 m, 1165 s, 1360 m, 1395 w, 1440 m, 1460 m, 2870 w, 2910 w, 2980 m, 2990 m, 3115 w.

$(\text{CpCrSPh})_2\text{S} \cdot (0.5\text{C}_6\text{H}_6)$ (II)

A solution of $(\text{CpCrSCMe}_3)_2\text{S}$ (0.50 g) and thiophenol (0.3 g) in 5 ml benzene was heated in a sealed ampoule at 80 °C for 8 hr. Dark-violet crystalline precipitate was formed. The amount of precipitate increased on cooling the mixture and allowing it to stay for a day. The crystals were then separated from a dark-violet solution, washed with pentane, and dried under vacuum at 20 °C. The yield was 0.35 g. Found (calcd.), %: C, 57.73 (57.36); H, 4.54 (4.39); S, 17.91 (18.35); Cr, 19.91 (19.88). IR spectrum (cm^{-1}): 445 w, 485 m, 695 s, 750 s, 795 vs, 825 w, 1025 m, 1070 w, 1440 m, 1480 w, 1580 w, 3070 w.

$(\text{CpCrSePh})_2\text{S}$ (III)

A violet solution of $(\text{CpCrSCMe}_3)_2\text{S}$ (0.45 g) and 0.30 ml selenophenol in 5 ml benzene was heated in a sealed ampoule at 80 °C for 3.5 hr. The solution turned brown and dark-brown crystalline precipitate was formed. This was separated, washed with a small quantity of benzene and dried under vacuum. Some more crystals were obtained by concentrating and cooling the mother liquor after the addition to it of 5 ml heptane. The total yield was 0.30 g. Found (calcd.), %: C, 44.80 (45.67); H, 3.41 (3.46); Cr, 18.70 (17.99). IR spectrum (cm^{-1}): 415 m, 670 w, 690 m, 735 m, 820 s, 1005 sh w, 1025 m, 1070 w, 1180 vs, 1440 m, 1475 w, 1580 w, 3070 w b.

$(\text{CpCrSCMe}_3)_2\text{SCH}_2\text{I}^-$ (IV)

Methyl iodide (1.0 ml) was added to a violet-blue solution of $(\text{CpCrSCMe}_3)_2\text{S}$ (0.10 g) in 5 ml THF. The solution turned to reddish-violet, then after 2 min shaking, to inky-violet and in 5 min to dark-green, with the formation of black crystalline precipitate (small-sized prisms). The crystals were separated, washed with pentane and dried under vacuum at 20 °C. The yield was 0.09 g. Found (calcd.), %: C, 39.68 (38.90); H, 6.25 (5.29); S, 16.26 (16.38); I, 21.46 (21.67); Cr, 16.90 (17.74). IR spectrum (cm^{-1}): 560 w, 862 v s, 930 w, 962 w, 1030 m, 1075 w, 1160 vs, 1176 s, 1320 w, 1380 m, 1460 m, 1480 m sh, 2945 m, 2980 m, 3100 w b.

$[\text{CpCr}(\text{SPh})_2]_3$ (VIII)

Thiophenol (1 ml) was added to a red solution of Cp_2Cr (0.50 g) in 30 ml heptane. The reaction mixture was refluxed for 2 hr. Dark-green precipitate was then separated, washed with benzene and pentane, and dried under vacuum. The yield was 0.55 g. Found (calcd.), %: C, 60.74 (60.89); H, 4.60 (4.47); Cr, 15.00 (15.52); S, 19.22 (19.10). IR spectrum: see Fig. 4.

$[\text{CpCr}(\text{SePh})_2]_2$ (IX)

This was synthesized like the thio derivative from Cp_2Cr and selenophenol. The yield of black crystals was 0.62 g. Found (calcd.), %: C, 47.91 (47.55); H, 3.69 (3.49). IR spectrum: see Fig. 4.

$[\text{CpV}(\text{SPh})_2]_2$ (X)

Thiophenol (0.5 ml) was added to an orange solution of $\text{CpV}(\text{CO})_4$ (0.3 g) in 15 ml heptane. The mixture was refluxed for 3 hr. The brown crystalline precipitate formed was separated, washed with pentane, and dried at 20 °C/0.1 mm Hg. The yield was 0.25 g. Found (calcd.), %: C, 60.94 (61.07); H, 4.63 (4.49); V, 15.26 (15.23). IR spectrum: see Fig. 4.

$[\text{CpV}(\text{SePh})_2]_2$ (XI)

This was synthesized as the previous compound with selenophenol instead of thiophenol. The yield of

brown crystals was 0.36 g. Found (calcd.), %: C, 47.60 (48.34); H, 3.98 (3.55). IR spectrum: see Fig. 4.

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