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ANTIFERROMAGNETIC COMPLEXES WITH METAL–METAL BONDS

X *. SYNTHESIS AND MOLECULAR STRUCTURE OF AN ANTIFERROMAGNETIC BIS[CYCLOPENTADIENYL(t-BUTOXY)-CHROMIUM]IRON TETRACARBONYL CLUSTER CONTAINING A Cr_2Fe METALLACYCLE

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Summary

Photochemical reaction of $Fe(CO)_5$ with the $Cp_2Cr_2(OR)_2$ (I) complex ($Cp = \pi$-C_5H_5, $R = CMe_3$) in toluene gives brown-black prisms of the $CpCr(\mu\text{-}OR)_2CrCp \cdot Fe(CO)_4$ (II) cluster. An X-ray analysis of II shows that the metal atoms form an almost equilateral Cr_2Fe triangle with normal Cr–Fe bonds (2.707(1) and 2.691(1) Å) and the short Cr–Cr bond (2.635(1) Å) supplemented by two bridged OR groups. Each Cr atom is coordinated by a planar π-C_5H_5 ligand while the Fe atom coordinates four terminal CO groups. A qualitative MO diagram gives an explanation of the Cr–Cr bond length in II which is the same as in the starting complex I, although the antiferromagnetic exchange parameter $-2J$ is simultaneously increased from 246 cm^{-1} in I to 304 cm^{-1} in II.

Introduction

In recent years heteronuclear clusters with different metals in the same molecule, which possess unusual catalytic properties and are of interest as starting materials for polymetallic coatings, have been studied quite intensively [1]. Special attention has been paid to the directed synthesis of such clusters by sequential growing of the

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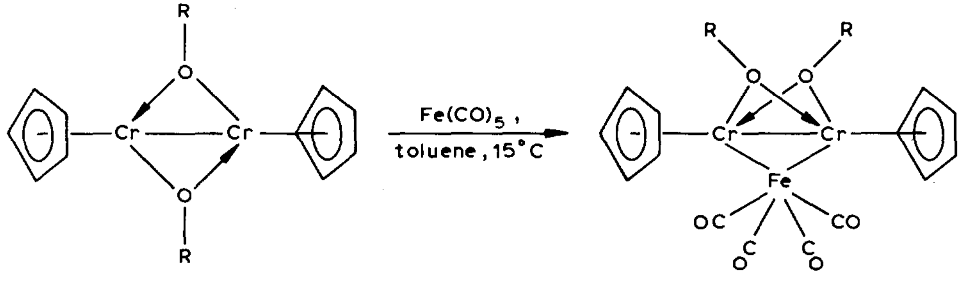
* For part IX see ref. 23.

metal chain using metal complexes as donor ligands to metal-containing Lewis acids. The electron donor of this type can be a phosphorus- or arsenic-containing complex [2], a complex with thiolate [3] or sulfide groups [4], a carbonylmetallate fragment [5], a complex with multiple metal–carbon bonds [6,7] or finally one with multiple metal–metal bonds [6,8]. Formally the latter complexes may include $(CpCrOR)_2$ ($R = CMe_3$ (I), $SiMe_3$, $SiPh_3$) described by Chisholm and Cotton et al. and having a Cr–Cr bond length of 2.635 Å [9] which is significantly shorter than the ordinary Cr–Cr bond in $[CpCr(NO)]_2(\mu\text{-}SR)(\mu\text{-}SSR)$ ($R = CMe_3$, Cr–Cr 2.906 Å) [10] and $[CpCr(CO)_3]_2$ (Cr–Cr 3.28 Å) [11]. Complex I is important as a model of the ethylene polymerization catalyst obtained by coating silica gel with chromocene [12]. I may combine with the electron-attracting NO, CO and $F_3CC{\equiv}CCF_3$ molecules giving $(CpCrOR)_2(NO)_2$, $(CpCrOR)_2(CO)_4$ and $(CpCrOR)_2(C_4F_6)$ [9], respectively. Thus it seemed of interest to investigate the reaction of I with an electron-attracting $Fe(CO)_4$ group.

Results

Photochemical reaction of $(CpCrOR)_2$ ($R = CMe_3$) (I) with iron pentacarbonyl in toluene leads to the trinuclear cluster $Cp_2Cr_2(\mu\text{-}OR)_2\text{-}Fe(CO)_4$ (II):



(I) (II)

Complex II was isolated by recrystallization from heptane as brown-black prisms sensitive to oxygen and atmospheric moisture, especially in solutions. The IR spectrum of the complex shows the bands of $\eta^5\text{-}C_5H_5$ ring vibrations (812, 1020, 1455 and 3130 cm^{-1}), CMe_3 groups (1178, 2900–3000 cm^{-1}) and the terminal CO groups (1920 and 1990 cm^{-1}). Complex II is paramagnetic, its effective magnetic moment decreases with lowering temperature (μ_{eff}(B.M.) 1.51 (283 K); 1.33 (225 K); 0.75 (78 K)). Magnetic properties of complexes II were interpreted in terms of the HDVV model [13]. Theoretical data converged to the experimental values employing the reported procedure [14] giving an exchange parameter $-2J = 304$ cm^{-1} (mean-square error is 1.8% taking into account a 2% admixture of a paramagnetic monomer).

The mass spectrum of II contains no molecular ion peak P^+ (m/e 548). The ion with the greatest mass (m/e 520) corresponds to a CO group elimination product ($P^+ - 28$) followed by complete decarbonylation to $(CpCrOR)_2Fe^+$ (m/e 436) and formation of the $(CpCrOR)_2{}^+$ ion (m/e 380). Then fragmentation of $(CpCrOR)_2{}^+$ proceeds as described [9] via sequential elimination of CMe_3 and isobutylene (intense $Cp_2Cr_2O(OR)^+$ (m/e 323) and $Cp_2Cr_2O(OH)^+$ (m/e 267) peaks). Intense peaks of Cp_2Fe^+ and Cp_2Cr^+ are observed as well.

(Continued on p. 296)

TABLE 1

ATOMIC COORDINATES (for Fe and Cr × 10^5, others × 10^4) AND TEMPERATURE FACTORS IN THE FORM $T = \exp[(-1/4)(B_{11}a^{*2}h^2 + \ldots + 2B_{12}a^{*}b^{*}hk + \ldots)]$

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	37433(3)	24273(10)	43847(5)	1.66(3)	1.73(4)	0.69(3)	0.20(3)	0.40(3)	−0.08(3)
Cr(1)	33909(3)	10598(10)	27810(6)	1.04(3)	1.17(3)	0.67(3)	−0.11(3)	0.16(3)	0.09(3)
Cr(2)	41116(3)	25932(10)	32618(5)	0.96(3)	1.03(3)	0.55(3)	−0.06(3)	0.01(3)	0.01(3)
O(1)	3987(1)	514(4)	2967(2)	1.4(1)	1.2(2)	1.0(1)	0.1(1)	0.3(1)	0(1)
O(2)	3531(1)	2730(4)	2204(2)	1.2(1)	1.5(2)	0.6(1)	0(1)	−0.1(1)	0.4(1)
O(3)	3046(2)	2078(6)	4934(3)	2.9(2)	5.6(3)	2.1(2)	0(2)	1.4(2)	−0.2(2)
O(4)	4430(1)	3734(5)	6008(3)	2.5(2)	4.1(2)	1.5(2)	−0.6(2)	0.3(2)	−1.0(2)
O(5)	3402(1)	5144(5)	3389(3)	3.8(2)	2.1(2)	2.2(2)	1.1(2)	0.8(2)	0.2(2)
O(6)	4124(2)	−510(5)	4799(3)	6.0(3)	2.8(2)	1.6(2)	1.9(2)	1.7(2)	1.0(2)
C(1)	3059(2)	−1153(7)	2698(4)	2.0(2)	2.1(3)	2.8(3)	−0.8(2)	1.0(3)	0(2)
C(2)	2862(2)	−496(7)	1824(4)	1.9(2)	2.9(2)	2.2(3)	−1.2(2)	0.4(2)	−0.5(2)
C(3)	2652(2)	822(8)	1891(4)	1.4(2)	3.4(3)	2.1(3)	−0.7(2)	0.2(2)	0.1(2)
C(4)	2729(2)	1003(7)	2802(4)	1.5(2)	2.7(3)	2.2(3)	−0.3(2)	0.6(2)	0.4(2)
C(5)	2975(2)	−237(7)	3289(4)	1.6(2)	2.3(3)	2.3(3)	−0.3(2)	0.8(2)	0.3(2)
C(6)	4849(2)	2661(7)	3676(4)	1.1(2)	2.5(3)	2.3(2)	−0.3(2)	0.2(2)	0(2)
C(7)	4628(2)	3640(7)	2943(4)	1.3(2)	2.8(3)	2.0(2)	0.7(2)	0.4(2)	0.1(2)
C(8)	4430(2)	4752(7)	3233(4)	1.8(2)	1.8(3)	2.1(3)	−0.7(2)	0.2(2)	0.2(2)
C(9)	4517(2)	4468(7)	4131(4)	1.6(2)	1.9(3)	1.9(3)	−0.8(2)	−0.1(2)	−0.5(2)
C(10)	4770(2)	3158(7)	4403(4)	1.1(2)	2.3(3)	1.6(2)	−0.6(2)	−0.1(2)	−0.1(2)
C(11)	4197(2)	−571(6)	2656(4)	1.7(2)	1.4(2)	1.1(2)	0.4(2)	0.5(2)	0.1(2)
C(12)	4346(2)	123(6)	1996(4)	3.1(3)	2.3(3)	1.6(2)	0.4(2)	1.6(2)	0.2(2)
C(13)	3864(2)	−1778(7)	2159(4)	2.3(3)	1.5(3)	1.9(2)	0(2)	0.4(2)	−0.7(2)
C(14)	4584(2)	−1217(7)	3475(4)	1.7(3)	2.3(3)	1.4(2)	0.9(2)	0(2)	0.4(2)
C(15)	3330(2)	3319(6)	1297(3)	1.9(2)	1.5(2)	0.7(2)	0.2(2)	0(2)	0.5(2)
C(16)	3149(2)	2056(7)	621(4)	3.0(3)	2.2(3)	0.8(2)	−0.3(2)	0(2)	−0.1(2)
C(17)	2966(2)	4364(7)	1217(4)	2.5(3)	3.2(3)	1.8(3)	1.8(2)	0.2(2)	0.6(2)
C(18)	3675(2)	4115(8)	1109(4)	2.5(3)	3.5(3)	1.4(2)	−1.1(2)	0.3(2)	0.9(2)
C(19)	3322(2)	2196(7)	4719(4)	2.3(3)	3.0(3)	1.0(2)	0(2)	0.5(2)	0(2)
C(20)	4155(2)	3244(7)	5363(4)	2.6(3)	2.5(3)	1.7(2)	0.5(2)	1.1(2)	0(2)
C(21)	3533(2)	4039(7)	3738(4)	2.1(2)	2.2(3)	1.2(2)	0.2(2)	0.4(2)	−0.7(2)
C(22)	3974(2)	645(7)	4595(4)	2.7(3)	3.0(3)	0.8(3)	0.3(2)	0.7(2)	0(2)

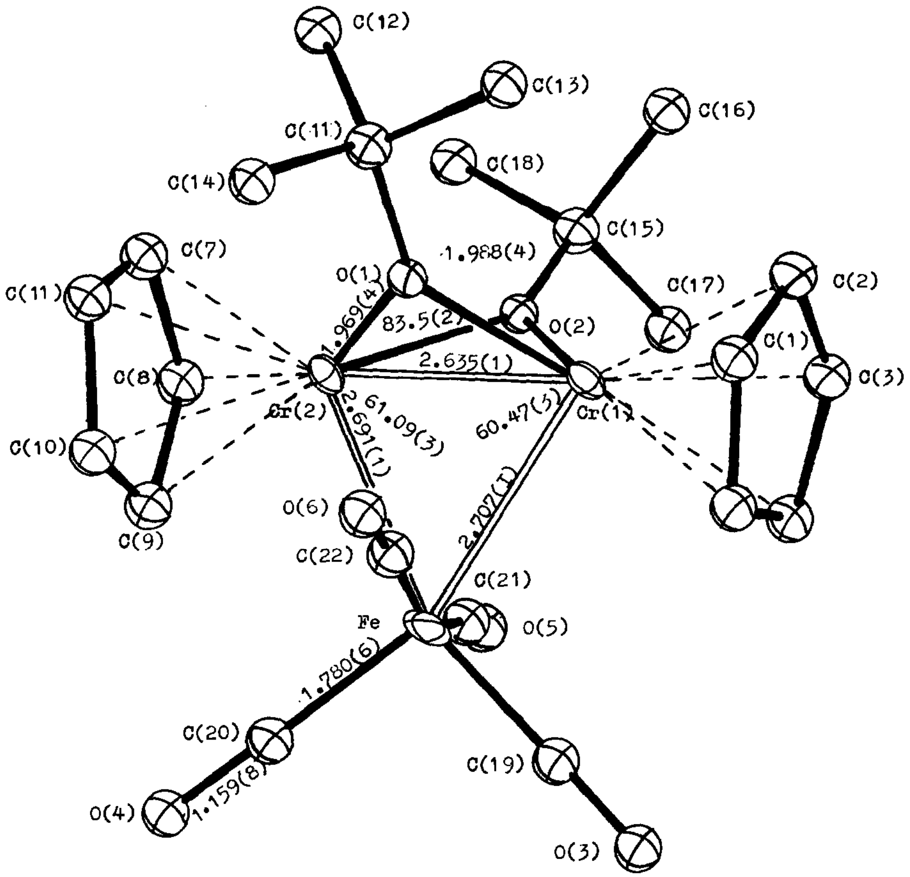


Fig. 1. The molecular structure of II with main bond lengths and bond angles.

TABLE 2

BOND LENGTHS *d* (Å)

Bond	*d*	Bond	*d*	Bond	*d*
Fe–Cr(1)	2.707(1)	Cr(2)–O(1)	1.969(4)	C(1)–C(5)	1.419(9)
Fe–Cr(2)	2.691(1)	Cr(2)–O(2)	1.989(4)	C(2)–C(3)	1.436(9)
Fe–C(19)	1.775(7)	Cr(2)–C(6)	2.301(7)	C(3)–C(4)	1.435(9)
Fe–C(20)	1.780(6)	Cr(2)–C(7)	2.273(7)	C(4)–C(5)	1.434(9)
Fe–C(21)	1.783(6)	Cr(2)–C(8)	2.272(6)	C(6)–C(7)	1.433(9)
Fe–C(22)	1.781(7)	Cr(2)–C(9)	2.280(6)	C(6)–C(10)	1.430(9)
Cr(1)–Cr(2)	2.635(1)	Cr(2)–C(10)	2.271(6)	C(7)–C(8)	1.423(9)
Cr(1)–O(1)	1.988(4)	O(1)–C(11)	1.451(7)	C(8)–C(9)	1.419(9)
Cr(1)–O(2)	1.980(4)	O(2)–C(15)	1.461(6)	C(9)–C(10)	1.432(9)
Cr(1)–C(1)	2.301(7)	O(3)–C(19)	1.156(9)	C(11)–C(12)	1.544(9)
Cr(1)–C(2)	2.301(7)	O(4)–C(20)	1.159(8)	C(11)–C(13)	1.541(9)
Cr(1)–C(3)	2.302(7)	O(5)–C(21)	1.157(8)	C(11)–C(14)	1.538(8)
Cr(1)–C(4)	2.283(7)	O(6)–C(22)	1.161(8)	C(15)–C(16)	1.543(8)
Cr(1)–C(5)	2.288(7)	C(1)–C(2)	1.440(9)	C(15)–C(17)	1.531(9)
				C(15)–C(18)	1.537(9)

TABLE 3

BOND ANGLES ω (°)

Angle	ω	Angle	ω	Angle	ω	Angle	ω
Cr(1)FeCr(2)	58.44(3)	FeCr(1)Cr(2)	60.47(3)	Cr(1)O(2)Cr(2)	83.2(1)	O(1)C(11)C(14)	108.1(5)
Cr(1)FeC(19)	100.9(2)	FeCr(1)O(1)	89.4(1)	Cr(1)O(2)C(15)	133.4(3)	C(13)C(11)C(13)	108.2(5)
Cr(1)FeC(20)	157.8(2)	FeCr(1)O(2)	91.5(1)	Cr(2)O(2)C(15)	140.1(3)	C(12)C(11)C(14)	111.5(5)
Cr(1)FeC(21)	84.4(2)	O(1)Cr(1)O(2)	79.4(2)	C(2)C(1)C(5)	108.0(6)	C(13)C(11)C(14)	109.9(5)
Cr(1)FeC(22)	74.5(2)	Cr(2)Cr(1)O(1)	47.9(1)	C(1)C(2)C(3)	107.3(6)	O(2)C(15)C(16)	109.3(5)
Cr(2)FeC(19)	157.6(2)	Cr(2)Cr(1)O(2)	48.6(1)	C(2)C(3)C(4)	108.6(6)	O(2)C(15)C(17)	108.1(5)
Cr(2)FeC(20)	101.0(2)	FeCr(2)Cr(1)	61.09(3)	C(3)C(4)C(5)	107.1(6)	O(2)C(15)C(18)	109.8(5)
Cr(2)FeC(21)	73.7(2)	FeCr(2)O(1)	90.2(1)	C(1)C(5)C(4)	109.0(6)	C(16)C(15)C(17)	111.2(5)
Cr(2)FeC(22)	83.4(2)	FeCr(2)O(2)	91.7(1)	C(7)C(6)C(10)	107.4(5)	C(16)C(15)C(18)	107.5(5)
C(19)FeC(20)	100.5(3)	Cr(1)Cr(2)O(1)	48.6(1)	C(6)C(7)C(8)	108.0(6)	C(17)C(15)C(18)	110.8(5)
C(19)FeC(21)	98.5(3)	Cr(1)Cr(2)O(2)	48.2(1)	C(7)C(8)C(9)	108.7(6)	FeC(19)O(3)	178.5(6)
C(19)FeC(22)	100.3(3)	O(1)Cr(2)O(2)	79.6(2)	C(8)C(9)C(10)	107.6(5)	FeC(20)O(4)	177.9(6)
C(20)FeC(21)	98.5(3)	Cr(1)O(1)Cr(2)	83.5(2)	C(6)C(10)C(9)	108.3(5)	FeC(21)O(5)	173.9(6)
C(20)FeC(22)	96.1(3)	Cr(1)O(1)C(11)	138.9(3)	O(1)C(11)C(12)	110.3(5)	FeC(22)O(6)	174.4(6)
C(21)FeC(22)	154.8(3)	Cr(2)O(1)C(11)	131.9(3)	O(1)C(11)C(13)	108.7(5)		

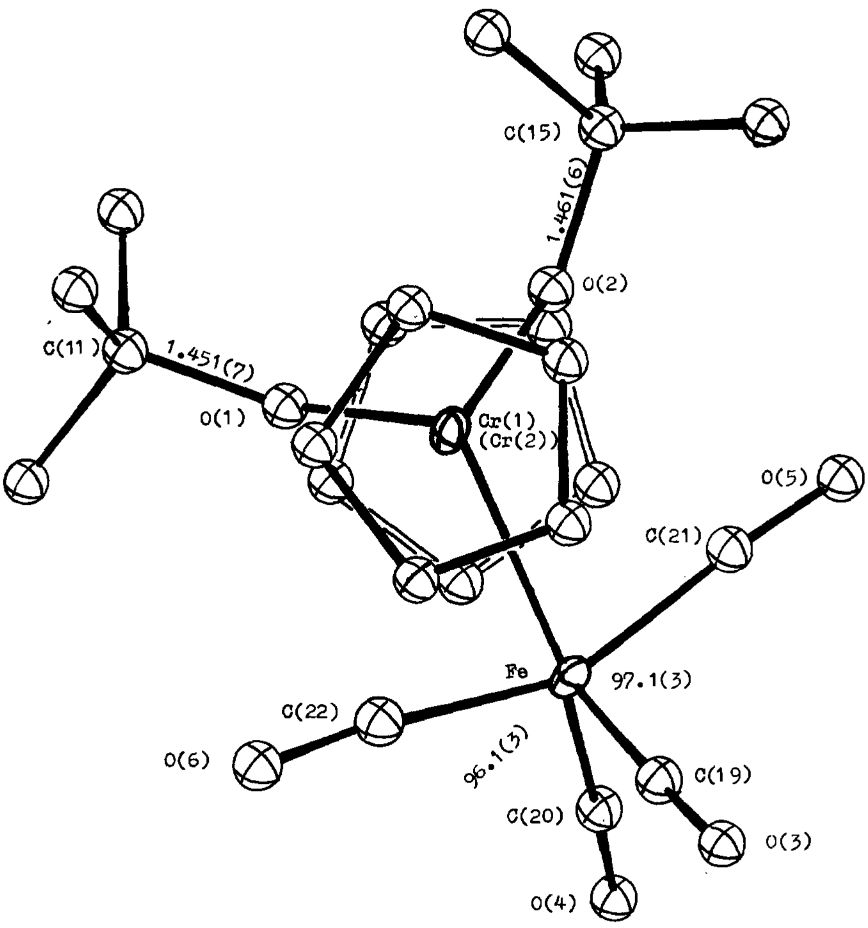


Fig. 2. Projection of the molecule of complex II along the Cr–Cr axis.

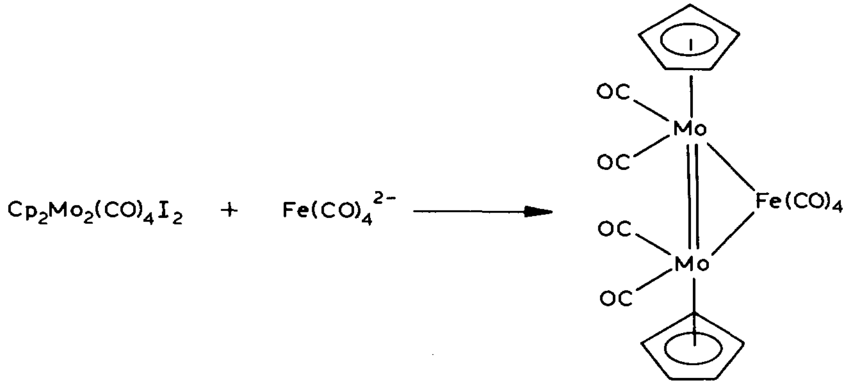
Molecular structure of $(CpCrOR)_2Fe(CO)_4$ (II)

In order to establish the structure of II unequivocally its X-ray study was carried out. Crystals of II are monoclinic, space group $P2_1/c$ with $a = 34.230(30)$, $b = 9.175(8)$, $c = 16.710(10)$ Å, $\beta = 116.46(5)°$, $V = 4698.2$ Å^3, $Z = 8$. The molecule of complex II (Figs. 1 and 2) contains a Cr_2Fe triangle with a short Cr–Cr bond (2.635(1) Å) and normal Fe–Cr bonds (2.707(1) and 2.691(1) Å). Each chromium atom is coordinated by the planar π-C_5H_5 ligand (Cr–C_{mean} 2.287(7) Å) and the Cr–Cr bond is bridged by two $OCMe_3$ groups with practically equivalent Cr–O distances (mean 1.981(7) Å) and a CrOCr angle of 83.3(2)°(mean) (Tables 2 and 3). The Fe atom in II has a distorted trigonal antiprismatic coordination involving two Fe–Cr bonds and four carbonyl groups (mean Fe–C 1.780(7) Å, mean C–C 1.158(8) Å, FeCO 178.5(4)–173.4(6)°). The molecule of II has strong steric strains reflected in short O(OR) ⋯ C(CO) (2.7–2.8 Å) and O(OR) ⋯ O(OR) (2.53 Å) contacts and in essentially nonvalent $C(C_5H_5)$ ⋯ C(CO) interactions (3.0–3.1 Å).

Discussion

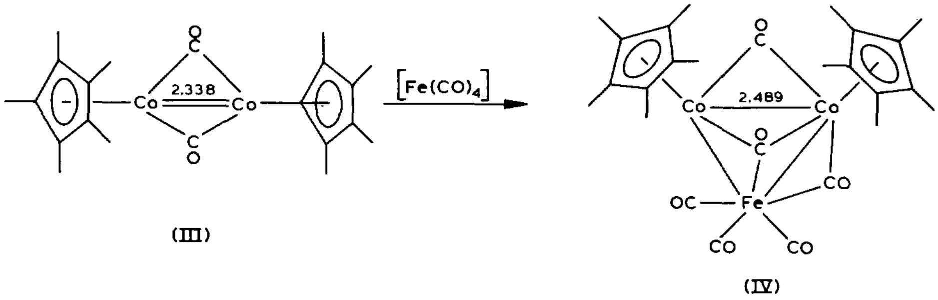
To expand the methods of synthesis of antiferromagnetic heteronuclear clusters we used an addition of metal-containing Lewis acids at multiple metal–metal bonds.

Examples of such reactions are the addition of L_2Pt ($L = 0.5$ COD, CO or PPh_3) at the multiple Rh=Rh bond in $(R_5C_5)_2Rh_2(\mu\text{-}CO)_2$ (R = H, Me) complexes giving $(R_5C_5)_2Rh_2(\mu^3\text{-}CO)_2PtL_2$ clusters with a metallocyclic Rh_2Pt skeleton [15]. The triple $Mo{\equiv}Mo$ bond in $Cp_2Mo_2(CO)_4$ has been shown to add the L_2Pt ($L = PPh_3$) moiety giving rise to the triangular $Cp_2Mo_2(CO)_4PtL_2$ cluster in which the presence of bridging carbonyl groups has been suggested on the basis of CO stretching modes at 1980 and 1800 cm^{-1} in the IR spectrum [16]. The product of the formal addition of a $Fe(CO)_4$ group to $Cp_2Mo_2(CO)_4$ has been obtained indirectly:



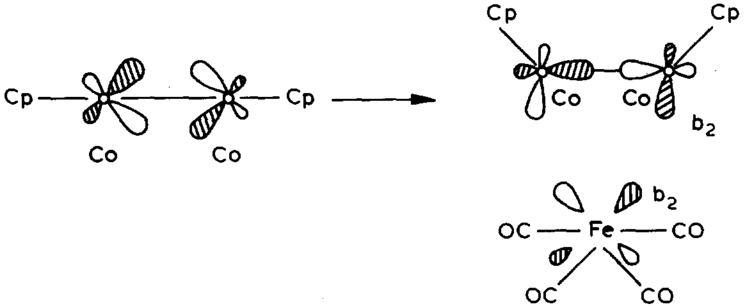
The authors [16] assigned the bands at 2050, 2020 and 2000 cm^{-1} to the stretching vibrations of terminal CO groups in $Fe(CO)_4$ while the bands at 1900, 1875 cm^{-1} were assigned to those of the terminal CO groups of a dimolybdenum fragment. Such an assignment cannot be regarded as unequivocal since in the spectrum of II the stretching modes of terminal carbonyl groups on the Fe atom (see below) appear only at 1920 and 1990 cm^{-1} (with a ca. 2 : 1 intensity ratio).

Addition of the photochemically regenerated carbenoid fragment $Fe(CO)_4$ to the binuclear $(CpCrOR)_2$ complex (I) ($R = CMe_3$) producing $(CpCrOR)_2Fe(CO)_4$ (II) may by compared to the addition of $Fe(CO)_4$ to the double Co=Co bond in $(Me_5C_5)_2Co_2(CO)_2$ (III) [17], giving $[(Me_5C_5)Co(CO)]_2Fe(CO)_4$ [18].



Here the transformation of III into IV leads to elongation of the Co=Co bond by 0.15 Å and conversion of one carbonyl group to a μ^3-bridging ligand (moreover, one of carbonyl groups on the Fe atom also becomes bridging across one of the Fe–Co bonds). This is different from that found in the complex II where the Cr–Cr bond retains its length (2.635(1) Å) and t-butoxy groups are displaced from the iron atom but bridge only the chromium atoms. The second difference between II and IV is expected since in IV the electronically saturated iron atom interacts with the π^*-acceptor orbital of bridging CO while in II the t-butoxyl bridges possess only lower energy occupied orbitals while the vacant Fe orbitals are too high in energy.

The third important difference concerns the relative positions of the cyclopentadienyl centroids and the chromium atoms: on formation of II from I they retain their colinearity, whereas in IV the Cp–Co–Co angles (angle θ) change from 180 to 154° [18]. On the basis of reported data [19] this can be explained by different distortion effects of the initial binuclear skeletons upon their vacant orbital energies. For $Cp_2Co_2(CO)_2$ with a d^8-d^8 electron configuration the b_2 orbital is vacant and displacement of carbonyl groups out of the Co_2C_2 plane (necessary for addition of the $Fe(CO)_4$ moiety) is unfavourable due to the increase of the energy of the highest occupies a_1 and a_2 orbitals (their interaction with CO becomes weaker). This can be balanced, however, by tilting of the Cp ligand from its axial position [19]. Moreover such a displacement can slightly distort the vacant b_2 orbital orientation [20] facilitating its interaction with the occupied b_2 orbital of $Fe(CO)_4$. In its turn filling of the b_2 vacant orbital in $Cp_2Co_2(CO)_2$ is another factor favouring the deviation of CO from the Co_2C_2 plane:



Furthermore, displacement of Cp and CO in $Cp_2Co_2(CO)_2$ weakens interaction of the a_1 and a_2 occupied orbitals with bridging CO but facilitates formation of the tridentate μ^3-CO bridge due to additional interaction of the μ^2-CO bridge vacant orbital with an occupied $Fe(CO)_4$ orbital. Finally, the shape of the b_2 orbital in the $Cp_2Co_2(CO)_2$ moiety and calculations [19] demonstrate that this orbital is definitely π-antibonding with respect to the cobalt–cobalt bond. Thus a considerable weakening of the Co–Co bond in $Cp_2Co_2(CO)_2$ on addition of $Fe(CO)_4$ is quite understandable.

On the other hand, the $(CpCrOR)_2$ dimer (I) with a planar Cr_2O_2 fragment has donor OR groups and so the energy of both its high energy a_1 and b_2 orbitals is increased by deviation from planarity [19]. In this case the Cr^{II}–Cr^{II} bond corresponds to the d^4–d^4 interaction. Thus on addition of $Fe(CO)_4$ the lowest b_2 orbital will be occupied, whose energy is independent of the OR deviation out of the Cr_2O_2 plane. The OR groups have no vacant orbitals to interact with the donor $Fe(CO)_4$ group and attack of the latter causes OR displacement in the opposite direction. On the other hand, tilting of cyclopentadienyl ligands is hindered first by the OR groups and secondly by the added $Fe(CO)_4$ group.

In the absence of deviation of the cyclopentadienyl ligands from axial positions the following qualitative MO diagram can be proposed for interactions in complex II explaining its main features, viz. 1) the constant length of the Cr–Cr bond, 2) the

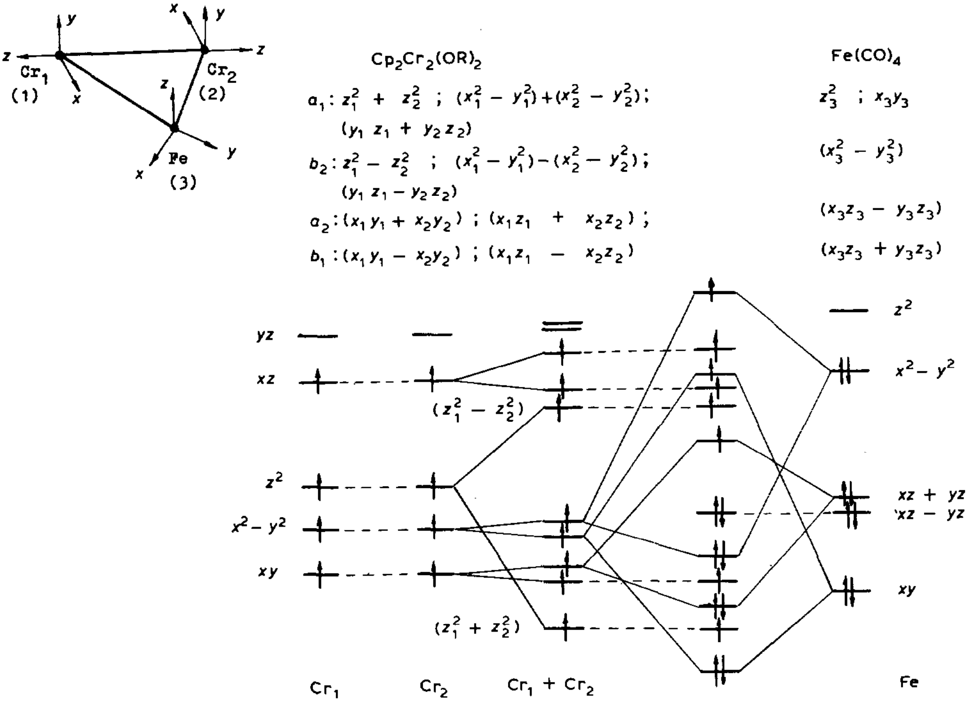


Fig. 3. In order to make the orbitals which contribute to exchange interaction through the metal-metal bond clear, the figure corresponds to the state with maximum spin S when these orbitals are half-occupied.

formation of normal Fe–Cr bonds, 3) the increase of the antiferromagnetic exchange parameter with the constant Cr–Cr bond length. Figure 3 shows axes orientations, atomic numbering and orbital assignment over irreducible representations. Symmetry considerations reveal that the Cr–Cr bond which is formed mainly by the d_{z^2} orbitals should not change on coordination of Fe(CO)$_4$, perturbing only a low-occupied z_1^2-z_2^2 antibonding orbital of the dichromium fragment. Secondly, Fe(CO)$_4$ addition gives rise to three occupied bonding and three half-occupied antibonding orbitals so that there are three electrons per two Fe–Cr bonds and the order of each bond (0.75) is close to unity which is observed experimentally (Fe–Cr distances are 2.707(2) and 2.691(1) Å).

Finally, the splitting of two degenerate pairs (xy and x^2-y^2) of the dichromium fragment leads to increase of the antiferromagnetic exchange according to

$$J_\Sigma = \sum \frac{\Delta i^2}{2K_{ab}} \quad (\text{with } 2K_{ab} = \text{const} \approx 10 \text{ eV})$$

As it is mentioned above the structural parameters of the dichromium fragment Cp$_2$Cr$_2$(OR)$_2$ in II (the Cr–Cr and Cr–O bond length and the CrOCr and CpCrCr bond angles) are similar to those in the starting I. Thus the considerable increase of the antiferromagnetic exchange parameter $-2J$ (from 246 to 304 cm^{-1}) is due only the formation of a metal-containing Fe(CO)$_4$ bridge. Earlier we have shown that a considerable increase of $-2J$ parameter (from 430 to 530 cm^{-1}) was observed on going from the binuclear $(CpCrSCMe_3)S$ complex (V) to the metallocyclic cluster $[CpCr(SCMe_3)CrCp](\mu^3\text{-}S)_2 \cdot Co(CO)_2$ wherein the dichromium fragment (Cr–Cr 2.617 Å) is bridged by a metal-containing $Co(CO)_2$ group (Cr–Co 2.592 Å) [21]. At the same time no significant change in the value of exchange parameter ($-2J = 418$ cm^{-1}) in VI, which is close to 430 cm^{-1} in V, occurs in the absence of strong metal-containing bridges as in the cluster $Cp_4Cr_2Ni_2(\mu^3\text{-}S)_2(\mu^4\text{-}S)$ (VI) [4] (Cr–Cr 2.596, Cr–Ni 2.620 and 2.655 Å, Cr ··· Ni 2.844 and 2.851 Å).

Thus along with direct exchange through the Cr–Cr bond an indirect exchange via the metal-containing bridge makes a much greater contribution to antiferromagnetic exchange than via nonmetallic bridging atoms and groups.

Experimental

All operations were carried out under pure argon. Hydrocarbons were distilled over Na powder under argon. Commercial $Fe(CO)_5$ was purified by distillation in vacuo. IR spectra were measured with an UR-20 instrument in KBr pellets. Mass-spectra were recorded with an automatic DS-50 system. Magnetic susceptibility was measured by Faraday's method with an apparatus designed at the Institute of General and Inorganic Chemistry of Academy of Sciences of the USSR [22]. Experimental data for the X-ray study were obtained with a Syntex P 2_1 autodiffractometer ($\lambda(Mo\text{-}K_\alpha)$, $T = -100°C$, θ–2θ scan, $2° \leqslant 2\theta \leqslant 54°$). The structure was solved by the direct method and refined in block-diagonal anisotropic approximation for all nonhydrogen atoms to $R = 0.055$, $R_w = 0.062$ for 4767 reflections.

$Cp_2Cr_2(\mu\text{-}OCMe_3)_2Fe(CO)_4$ (II)

$HOCMe_3$ (1.7 g) was added to a solution of 2.3 g of Cp_2Cr in 40 ml of toluene and the mixture was refluxed for 3.5 hours. The dark red solution obtained was filtered into a quartz Schlenk vessel and 1.40 ml of $Fe(CO)_5$ in 10 ml of THF was added. The reaction mixture was UV-irradiated (PRK-4 lamp) for 1.5 hours at 10°C. The obtained brown solution was evaporated to dryness (60°/0.1 Torr) and extracted with heptane (80 ml). The heptane extract was concentrated to 10–15 ml and cooled to −5°C. The brown-black prisms precipitated were separated from the solution, washed with pentane and dried in vacuo.

Yield 46%. Found: C, 48.15; H, 4.73. $C_{22}H_{28}Cr_2FeO_6$, calcd.: C, 48.46; H, 5.38%. IR spectrum (ν, cm^{-1}): 445w, 610vs, 658w, 772m, 812s, 850w, 1020m, 1078w, 1178s, 1242w, 1368m, 1389m, 1455m, 1920vs, 1990vs, 2915m, 2943m, 2995m, 3130w.

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