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Antiferromagnetic complexes with the metal–metal bond

XVI *. Synthesis and molecular structure of binuclear dihalogenide cyclopentadienyl-t-butylate chromium(III) complexes

S.E. Nefedov, A.A. Pasynskii*, I.L. Eremenko, B. Orazsakhatov, O.G. Ellert, V.M. Novotortsev, S.B. Katser, A.S. Antsyshkina and M.A. Porai-Koshits

N.S. Kurnakov Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR, Lenin Avenue, 31, Moscow V-71 (U.S.S.R.)

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Abstract

Reactions of $(CpCrOR)_2$ (I) ($R = CMe_3$) with CH_2X_2 in toluene and benzene at room temperature yield the binuclear complexes $Cp_2Cr_2(\mu\text{-}OR)_2X_2$ (X = Cl (II); Br (III); I (IV)) with the X ligands in the *cis*-position with respect to the CpCr–CrCp moiety. The X-ray structural study of complexes II–IV showed that the Cr–X distances (2.28(1), 2.29(1); 2.478(2); 2.716(2), 2.711(2) Å in II–IV) are markedly shortened compared with the sums of the corresponding covalent radii, owing to additional X–Cr π-bonding which involves the half-filled orbitals of the Cr atoms. This shortening is accompanied by the elongation of the Cr–Cr bonds from 2.635 Å in I up to 2.917(7), 2.971(2) and 2.967(2) Å in II–IV and the weakening of the antiferromagnetic exchange interactions ($-2J = 150$, 168 and 148 cm^{-1} for II–IV respectively as compared with $-2J = 246$ cm^{-1} for I). The similarity between the ligand environment of the chromium atom in I and the vanadium atom in Cp_2V is described.

Introduction

The binuclear complex $Cp_2Cr_2(\mu\text{-}OR)_2$ (I) ($Cp = C_5H_5$ and $R = CMe_3$) obtained from the reaction of Cp_2Cr with t-butyl alcohol [1], is a convenient example to use for finding out how the geometry, electronic structure and magnetic properties correlate. From the results of an X-ray diffraction study it was found that the two

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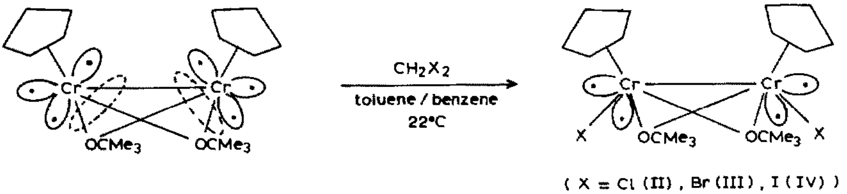
Cr^{II} atoms with d^4 electron configuration in molecule I are bonded directly (Cr–Cr 2.635 Å), and via two bridging μ-$OCMe_3$ ligands, to each other. The Cr_2O_2 group has a butterfly configuration, the dihedral angle formed by its wings being 128.1°. Each of the Cr atoms is coordinated by the η^5-C_5H_5 ligand, the Cr–Cp(centroid) distances being 1.975 and 2.005 Å, and the Cp(centroid)CrCr angles 143.9 and 146.3°, respectively. It is noteworthy that the antiferromagnetic properties of I (μ_{eff} in solution decreases with temperature from 1.88 BM at 333.5 K to 1.49 BM at 214 K [1]) are consistent with the dimeric Heisenberg–Dirac–Van Vleck (HDVV) model [2] having an exchange parameter of $-2J = 246$ cm^{-1} and the spin of each Cr^{II} ion equal to 2 [3]. It means that each Cr^{II} atom, that participates in the direct single Cr–Cr bond still has three half-occupied orbitals.

If the molecule is cut by a plane passing through the mid-points of the Cr–O and Cr–Cr bonds (see Scheme 1), it can be seen that the geometry of the ligands about each Cr^{II} atom resembles that of bis-cyclopentadienyl sandwich complexes. Let us regard the complex as a combination of $CpCr^{2+}$ (isoelectronic to CpV^+) and $CpCr(OR)_2{}^{2-}$ moieties. The latter, a three-orbital quasi-ligand, very like the cyclopentadienyl anion, would donate the six electrons to chromium atom (two electrons from each oxygen atom and an electron pair from the Cr–Cr bond). In this case each chromium atom of I is analogous to the V atom in vanadocene Cp_2V. The latter is known to be paramagnetic, since it contains three unpaired electrons and can add π-accepting ligands (CO, $CF_3C{\equiv}CCF_3$) and halogen atoms (X = Cl, Br and I), to give $Cp_2V(CO)$, $CpV(CO)_2{}^+$, $Cp_2V(CF_3C{\equiv}CCF_3)$ and Cp_2VX complexes, respectively [4]. Indeed the formation of the adducts $[(CpCrOR)(CO)_2]_2$ and $(CpCrOR)_2(CF_3C{\equiv}CCF_3)$ by the reaction of $(CpCrOR)_2$ with CO and $CF_3C{\equiv}CCF_3$, respectively has been reported previously [1].

These considerations justify our attempt to carry out the addition of halogen atom X to $(CpCrOR)_2$ by reaction with CH_2X_2 in mild conditions, by analogy with Cp_2V.

Results and discussion

The oxidative addition of CH_2X_2 to I in toluene/benzene at room temperature led to the formation of the binuclear complexes $Cp_2Cr_2(\mu\text{-}OCMe_3)_2X_2$ (X = Cl, Br, I) in yields of 68, 67 and 58%, respectively (Scheme 1).



Scheme 1

Complexes II–IV were isolated as light-blue, blue-green and green crystals, respectively. The IR spectra of the complexes resemble each other closely and contain the bands characteristic of C_5H_5 (815, 1005, 1355 and 3130 cm^{-1}) and CMe_3 groups (1160, 2900–3000 cm^{-1}).

The X-ray diffraction study of II–IV (Tables 1–10, Fig. 1) has shown that the addition of two halogen atoms occurs in *cis*-position with respect to the CpCr–CrCp

Table 1

Crystal data for complexes II, III and IV

	II	III	IV
Crystal system	trigonal	rhombic	monoclinic
Space group	$P3_121$	*Pccn*	$P2_1/n$
a (Å)	14.608(3)	13.271(2)	9.864(3)
b (Å)	14.608(3)	13.879(3)	16.797(5)
c (Å)	19.444(3)	14.266(2)	13.602(4)
α (°)	90	90	90
β (°)	90	90	102.16(2)
γ (°)	120	90	90
Z	6	4	4
V $(Å)^3$	3593(1)	2627.6(8)	2203(1)

moiety and is accompanied by a substantial decrease in the Cp(centroid)CrCr angle (average values are 126.6, 131.6 and 131.7° for II–IV respectively) compared with 145° (average) for I. This difference is analogous to the change of the Cp(centroid)VCp(centroid) angle from 180° in Cp_2V to 139.5° in Cp_2VCl [5].

The Cr–X bond lengths increase in the series X = Cl, Br, I (2.29(1) and 2.28(1) in II, 2.478(2) and 2.478(2) in III, 2.716(2) and 2.711(2) Å in IV) owing to an increase

Table 2

Atomic coordinates ($\times 10^3$) (for Cr and Cl, $\times 10^4$) and isotropic temperature factors ($\times 10^3$) ($Å^2$) (anisotropic for Cr and Cl) for $(C_5H_5)_2Cr_2(\mu\text{-}OCMe_3)_2Cl_2$ (II)

Atom	x	y	z	U_{11}/U_i	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr(1)	111(5)	4705(6)	3675(2)	35(4)	83(5)	35(3)	−16(3)	−9(3)	19(4)
Cr(2)	9564(4)	5328(5)	4968(2)	33(4)	59(5)	37(3)	−3(3)	11(3)	18(3)
Cl(1)	1848(8)	5658(10)	3352(5)	46(7)	130(12)	73(7)	8(8)	21(6)	15(3)
Cl(2)	907(10)	6693(10)	5552(5)	85(10)	96(9)	64(6)	−37(4)	−22(7)	24(9)
O(1)	28(2)	456(2)	467(1)	41(6)					
O(2)	989(2)	583(2)	401(1)	39(6)					
C(1)	89(3)	424(3)	506(2)	59(11)					
C(2)	88(4)	335(4)	468(2)	109(18)					
C(3)	43(3)	387(3)	579(2)	79(13)					
C(4)	211(5)	520(5)	505(3)	119(19)					
C(5)	11(3)	682(3)	369(2)	67(12)					
C(6)	6(3)	671(4)	291(2)	82(14)					
C(7)	126(4)	762(4)	389(2)	88(13)					
C(8)	−64(4)	710(4)	396(2)	102(16)					
C(10)	919(3)	427(3)	264(2)	66(11)					
C(11)	983(3)	383(3)	270(2)	66(12)					
C(12)	958(4)	312(5)	321(3)	111(19)					
C(13)	866(4)	321(4)	355(2)	76(13)					
C(14)	849(4)	380(4)	313(2)	91(15)					
C(20)	835(4)	419(4)	580(2)	83(14)					
C(21)	856(4)	521(4)	589(2)	80(14)					
C(22)	817(4)	545(4)	535(2)	85(14)					
C(23)	776(3)	462(3)	484(2)	59(11)					
C(24)	790(3)	383(3)	517(2)	70(12)					

Table 3

Atomic coordinates ($\times 10^4$) and anisotropic temperature factors ($\times 10^3$, and $\times 10^4$ for Cr and Br) ($Å^2$) for $(C_5H_5)_2Cr_2(\mu\text{-}OCMe_3)_2Br_2 \cdot C_6H_6$ (III)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr(1)	3329(1)	3218(1)	3590(1)	428(12)	345(10)	274(8)	−20(9)	−23(10)	−26(11)
Br(1)	3826(1)	3693(1)	1980(1)	674(9)	544(7)	321(5)	28(7)	47(7)	−99(9)
O(1)	1861(5)	3178(5)	3405(4)	37(5)	31(4)	31(4)	4(4)	1(4)	−2(4)
C(1)	1091(9)	3963(7)	3258(7)	48(8)	40(8)	40(7)	0(5)	2(6)	27(7)
C(2)	228(8)	3566(8)	2662(7)	33(8)	44(8)	71(8)	−3(7)	−27(7)	4(7)
C(3)	1615(9)	4808(7)	2746(8)	67(10)	24(7)	91(10)	28(6)	5(8)	5(7)
C(4)	717(10)	4301(9)	4239(7)	107(12)	75(10)	32(7)	−13(7)	9(8)	58(9)
C(10)	3267(12)	3900(23)	5023(12)	54(11)	178(22)	45(10)	−65(12)	11(9)	−24(14)
C(11)	3965(23)	3111(12)	5043(11)	187(22)	59(12)	32(8)	9(8)	−61(12)	−59(14)
C(12)	4780(13)	3368(17)	4430(15)	63(13)	99(15)	79(13)	−51(11)	−51(11)	8(12)
C(13)	4561(18)	4249(19)	4086(9)	99(17)	117(17)	35(8)	−4(11)	−25(10)	−64(14)
C(14)	3648(19)	4568(11)	4416(15)	99(18)	69(12)	84(13)	−44(11)	−62(12)	8(13)
C(30)	−2313(14)	2989(12)	3538(16)	49(14)	99(18)	267(25)	24(15)	22(18)	26(14)
C(31)	−2121(18)	3382(18)	4396(19)	75(16)	114(22)	253(35)	−88(23)	−15(23)	19(13)
C(32)	−2244(28)	2994(19)	5260(16)	211(38)	188(36)	223(25)	−51(21)	1(30)	125(34)

in the covalent radii of the halogen atoms. At the same time their bonds are shortened relative to the sums of the covalent radii of Cr (1.46 Å in the cyclopentadienyl complexes [6]) and corresponding X atoms (0.99, 1.14 and 1.33 Å for Cl, Br

Table 4

Atomic coordinates ($\times 10^4$) and anisotropic temperature factors ($\times 10^3$, and $\times 10^4$ for Cr and I) ($Å^2$) for $(C_5H_5)_2Cr_2(\mu\text{-}OCMe_3)_2I_2$ (IV)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr(1)	999(2)	1837(1)	6178(1)	305(8)	294(8)	293(8)	−23(6)	32(6)	63(7)
Cr(2)	−521(2)	3087(1)	7048(1)	363(9)	316(8)	276(8)	−45(6)	93(7)	15(7)
I(1)	−70(1)	1557(1)	4200(1)	487(4)	503(4)	335(3)	−62(3)	21(3)	−22(4)
I(2)	−2641(1)	3699(1)	5655(1)	466(4)	540(5)	514(5)	12(4)	−5(4)	98(4)
O(1)	903(7)	3018(4)	6221(5)	38(4)	30(4)	33(3)	−4(3)	13(3)	0(3)
O(2)	−733(7)	1947(4)	6684(5)	33(4)	30(4)	44(4)	0(3)	10(3)	−5(3)
C(1)	1550(12)	3644(7)	5718(8)	60(7)	36(6)	44(6)	8(5)	21(5)	−11(5)
C(2)	1265(20)	4457(8)	6111(12)	155(17)	36(7)	81(11)	−7(7)	55(11)	−15(9)
C(3)	881(19)	3638(8)	4593(9)	152(16)	52(8)	36(6)	15(6)	21(8)	−22(9)
C(4)	3114(15)	3491(12)	5908(18)	42(8)	130(17)	216(23)	109(17)	46(11)	13(10)
C(5)	−1735(13)	1353(6)	6883(8)	69(8)	33(6)	37(6)	2(5)	13(5)	−5(6)
C(6)	−1952(14)	731(7)	6023(10)	74(9)	39(7)	63(8)	−10(6)	19(7)	−28(6)
C(7)	−3122(14)	1758(9)	6866(13)	48(8)	67(9)	111(12)	−5(9)	40(8)	−13(7)
C(8)	−1152(16)	940(9)	7899(10)	96(11)	65(9)	47(7)	28(7)	14(7)	−6(8)
C(10)	3152(13)	1778(8)	7158(10)	45(7)	57(8)	64(8)	1(7)	−14(6)	46(6)
C(11)	3194(14)	1474(10)	6193(11)	44(7)	99(13)	72(9)	−7(9)	−6(7)	13(8)
C(12)	2370(18)	774(11)	6036(12)	79(11)	87(12)	70(10)	−31(9)	−20(9)	55(10)
C(13)	1801(16)	655(8)	6856(14)	74(10)	33(7)	111(13)	10(8)	−26(10)	32(7)
C(14)	2263(14)	1270(10)	7566(10)	58(9)	80(10)	59(8)	12(8)	−10(7)	43(8)
C(20)	−1433(14)	3722(10)	8217(10)	63(8)	89(11)	54(8)	−14(8)	29(7)	−8(8)
C(21)	−315(14)	4184(8)	8037(9)	63(8)	61(8)	47(7)	−27(6)	13(6)	−2(7)
C(22)	897(13)	3736(9)	8336(9)	46(7)	75(9)	46(7)	−29(7)	−6(6)	7(7)
C(23)	549(19)	2985(9)	8691(8)	129(14)	63(10)	22(6)	−5(6)	6(7)	28(9)
C(24)	−969(20)	3003(10)	8624(10)	119(14)	73(11)	37(7)	−25(7)	32(8)	−16(10)

Table 5

Bond lengths (Å) for $(C_5H_5)_2Cr_2(\mu\text{-}OCMe_3)_2Cl_2$ (II)

Cr(1)–Cr(2)	2.917(7)	Cr(2)–O(2)	1.97(2)
Cr(1)–Cl(1)	2.29(1)	Cr–C(C_5H_5)(av.)	2.28(6)
Cr(2)–Cl(2)	2.28(1)	O(1)–C(1)	1.42(4)
Cr(1)–O(1)	1.97(2)	O(2)–C(5)	1.46(4)
Cr(1)–O(2)	1.94(2)	C–C(C_4H_9)(av.)	1.53(6)
Cr(2)–O(1)	1.96(2)	C–C(C_5H_5)(av.)	1.38(6)

Table 6

Bond angles (°) for $(C_5H_5)_2Cr_2(\mu\text{-}OCMe_3)_2Cl_2$ (II)

Cr(2)Cr(1)Cl(1)	116.1(4)	O(1)Cr(2)O(2)	80.3(9)
Cr(2)Cr(1)O(1)	42.0(6)	Cr(1)O(1)Cr(2)	95.8(9)
Cr(2)Cr(1)O(2)	42.0(6)	Cr(1)O(1)C(1)	134(2)
Cl(1)Cr(1)O(1)	100.1(8)	Cr(2)O(1)C(1)	129(2)
Cl(1)Cr(1)O(2)	100.4(7)	Cr(1)O(2)Cr(2)	97(1)
O(1)Cr(1)O(2)	80.9(8)	Cr(1)O(2)C(5)	131(2)
Cr(1)Cr(2)Cl(2)	116.9(4)	Cr(2)O(2)C(5)	132(2)
Cr(1)Cr(2)O(1)	42.2(6)	OCC(av.)	109(3)
Cr(1)Cr(2)O(2)	41.2(7)	CCC(C_4H_9)(av.)	110(4)
Cl(2)Cr(2)O(1)	100.3(8)	CCC(C_5H_5)(av.)	108(5)
Cl(2)Cr(2)O(2)	101.6(7)		

Table 7

Bond lengths (Å) for $(C_5H_5)_2Cr_2(\mu\text{-}OCMe_3)_2Br_2 \cdot C_6H_6$ (III)

Cr(1)–C(2)	2.971(3)	O(1)–C(1)	1.51(1)
Cr(1)–Br(1)	2.478(2)	C–C(C_4H_9)(av.)	1.54(1)
Cr(1)–O(1)	1.968(6)	C–C(C_5H_5)(av.)	1.39(2)
Cr(1)–O(2)	1.973(6)	C–C(C_6H_6)(av.)	1.39(3)
Cr–C(C_5H_5)(av.)	2.26(1)		

Table 8

Bond angles (°) for $(C_5H_5)_2Cr_2(\mu\text{-}OCMe_3)_2Br_2 \cdot C_6H_6$ (II)

Cr(2)Cr(1)Be(1)	112.0(1)	Cr(1)O(1)C(1)	132.1(6)
Cr(2)Cr(1)O(1)	41.1(2)	Cr(2)O(1)C(1)	129.9(6)
Cr(2)Cr(1)O(2)	41.0(2)	OCC(av.)	108.3(9)
Br(1)Cr(1)O(1)	98.4(2)	CCC(C_4H_9)(av.)	111(1)
Br(1)Cr(1)O(2)	99.8(2)	CCC(C_5H_5)(av.)	108(2)
O(1)Cr(1)O(2)	80.1(4)	CCC(C_6H_6)(av.)	120(3)
Cr(1)O(1)Cr(2)	97.8(4)		

Table 9

Bond lengths (Å) for $(C_5H_5)_2Cr_2(\mu\text{-}OCMe_3)_2I_2$ (IV)

Cr(1)–Cr(2)	2.967(2)	Cr(2)–O(2)	1.977(7)
Cr(1)–I(1)	2.716(2)	Cr–C(C_5H_5)(av.)	2.26(1)
Cr(2)–I(2)	2.711(2)	O(1)–C(1)	1.47(1)
Cr(1)–O(1)	1.987(7)	O(2)–C(50	1.47(1)
Cr(1)–O(2)	1.980(7)	C–C(C_4H_9)(av.)	1.53(2)
Cr(2)–O(1)	1.979(7)	C–C(C_5H_5)(av.)	1.41(2)

Table 10

Bond angles (°) for $(C_5H_5)_2Cr_2(\mu\text{-}OCMe_3)_2I_2$ (IV)

Cr(1)Cr(1)I(1)	113.2(1)	O(1)Cr(2)O(2)	81.4(3)
Cr(2)Cr(1)O(1)	41.5(2)	Cr(1)O(1)Cr(2)	96.8(3)
Cr(2)Cr(1)O(2)	41.4(2)	Cr(1)O(1)C(1)	132.2(6)
I(1)Cr(1)O(1)	101.0(2)	Cr(2)O(1)C(1)	130.7(6)
I(1)Cr(1)O(2)	100.2(2)	Cr(1)O(2)Cr(2)	97.1(3)
O(1)Cr(1)O(2)	81.2(3)	Cr(1)O(2)C(5)	131.6(6)
Cr(1)Cr(2)I(2)	111.7(1)	Cr(2)O(2)C(5)	130.6(6)
Cr(1)Cr(2)O(1)	41.7(2)	OCC(av.)	109(1)
Cr(1)Cr(2)O(2)	41.5(2)	$CCC(C_4H_9)$(av.)	110(1)
I(2)Cr(2)O(1)	99.2(2)	$CCC(C_5H_5)$(av.)	108(2)
I(2)Cr(2)O(2)	99.6(2)		

and I respectively [7]), which is apparently the result of additional π-bonding due to the lone electron pairs of the terminal X atoms and the half-occupied orbitals of the Cr atom. An analogous situation is observed in the case of Cp_2VCl where the bond length V–Cl (2.39 Å) [5] is shortened by 0.09 Å as compared with the sum of the covalent radii of V and Cl (2.48 Å).

The bridging OR groups are disposed symmetrically over and below the plane passing through the centroids of the Cp rings, the Cr and the X atoms. The dihedral angle between the Cr_2O wings in Cr_2O_2 butterfly increases markedly in II–IV (151.3 or 156.4 and to 158.9°, respectively) compared with 128.1° in I. This increase in dihedral angle is evidently caused by the repulsion between the O and X atoms (the

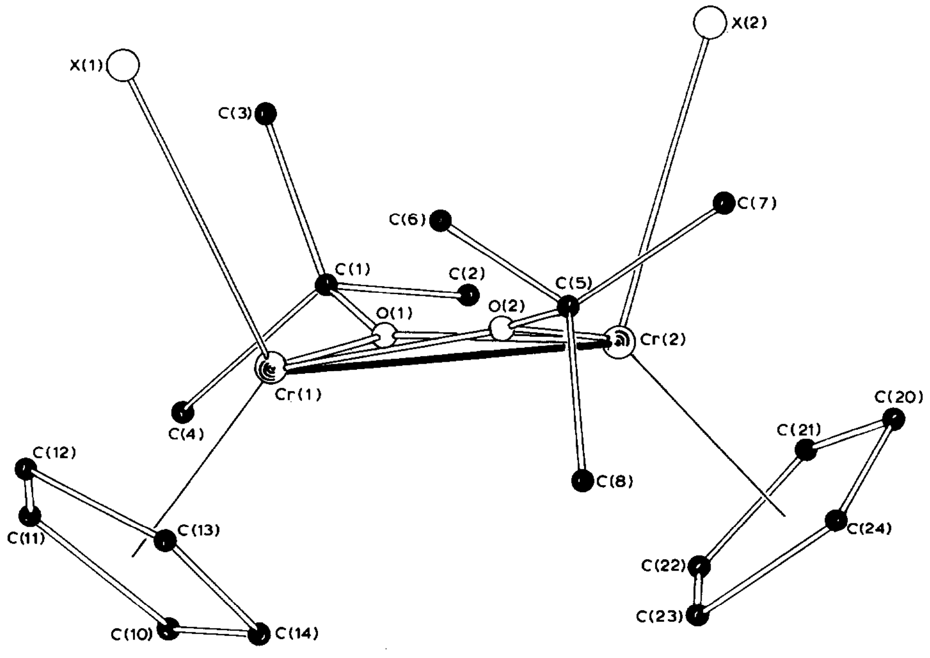


Fig. 1. The molecular structure of the complexes $Cp_2Cr_2(\mu\text{-}OCMe_3)_2X_2$.

XCrCr bond angles are 116.5, 112.0 and 112.5° in II–IV, respectively). At the same time the Cr–O bonds in II–IV (average lengths 1.964, 1.970, 1.977 Å, respectively) shortened for the same reason as for the Cr–X bonds, and do not differ from that in I (1.967 Å). On the other hand the Cr–Cr bonds in II–IV (2.917(7), 2.971(2) and 2.967(2) Å, respectively) are essentially longer than that in I (2.635 Å) which is evidently the result of more significant steric crowding in the ligand environment of the Cr atoms in II–IV compared with I. It is noteworthy that the geometry of the ligand environment of each chromium atom in II–IV is rather close to that found in the $CpCrCl_3^-$ [8] or $CH_3C_5H_4CrBr_3^-$ [9] anions with three unpaired electrons on the three half-filled orbitals.

This observation is consistent with the fact that complexes II–IV are paramagnetic, their effective magnetic moments decrease with temperature in the range 289–77 K from 2.17, 2.07 and 2.245 to 0.95, 0.83 and 1.08 BM for II–IV respectively. The temperature dependence of the static magnetic susceptibility may be described in terms of the dimeric HDVV model [2] for interaction of the Cr^{III} ions with 3/2 spins and antiferromagnetic exchange parameters of $-2J = 150$, 168 and 148 cm^{-1} for II–IV, respectively. The decrease of the $-2J$ value compared with 246 cm^{-1} for I [3] is probably the result of weakening the direct Cr–Cr bond mentioned earlier.

Experimental

Synthesis and isolation of the complexes was carried out under pure argon in absolute solvents. Cp_2Cr was synthesized by a published procedure [10]. $(CpCrOR)_2$ was synthesized [1] by heating a mixture of Cp_2Cr and t-BuOH in toluene under reflux, for 3 h. To this mixture was added CH_2X_2 dried by distillation over P_2O_5 without prior isolation of $(CpCrOR)_2$.

IR spectra in the region 400–4000 cm^{-1} were recorded with a Specord-75IR instrument in KBr pellets.

The X-ray diffraction data were collected with an automatic Syntex $P2_1$ diffractometer (Mo-K_α, $\theta/2\theta$-scan, $2\theta_{max} = 60°$). The structures II–IV were solved by direct methods and refined anisotropically by full-matrix least squares for III–IV; for II the Cr and Cl atoms were refined anisotropically, all the other atoms were refined isotropically. The discrepancy factors are: $R = 0.133$, 0.088, 0.051 (R_w = –, 0.053, 0.040) for 1733, 1396, 3039 reflections with $I \geqslant 2\sigma(I)$ for II–IV, respectively.

Synthesis of $Cp_2Cr_2(\mu\text{-}OCMe_3)_2Cl_2$ (II)

The red-brown solution of $(CpCrOR)_2$ (I) obtained from 0.52 g (2.8 mmol) of Cp_2Cr in 10 ml of benzene was treated with CH_2Cl_2 (0.12 g, 1.5 mmol). The dark-blue solution formed instantly, and large dark-blue needles were precipitated from solution after the addition of 3 ml of heptane and the solution had been cooled to −5°C. The crystals were separated from the solution by decantation, washed first with the cold benzene/heptane (1/5) mixture, then with pentane and dried under a stream of argon. Yield 0.43 g (68%).

IR spectrum (cm^{-1}): 600s, 760m, 810s, 885s, 1005m, 1160s, 1350m, 1385w, 2935w br.

Synthesis of $Cp_2Cr_2(\mu\text{-}OCMe_3)_2Br_2$ (III)

0.37 g (1.94 mmol) of CH_2Br_2 was added to the red-brown solution of I obtained from 0.6 g (3.2 mmol) of Cp_2Cr in 20 ml of toluene. The violet solution that formed immediately was evaporated to dryness under a stream of argon at 110 °C. The residue was extracted with 30 ml of boiling benzene. The blue extract was concentrated at 60 °C/0.1 torr to 5 ml and cooled to +5 °C. The large, dark-blue-green needles that precipitated were separated from the solution by decantation, washed first with cold benzene/heptane (1/5) mixture, then with pentane and dried under a stream of argon. Yield 0.57 g (67%).

IR spectrum (cm^{-1}): 610m, 765m, 815s, 865m, 1005m, 1160s, 1355m, 2920w, 2970w br, 3130w.

Synthesis of $Cp_2Cr_2(\mu\text{-}OCMe_3)_2I_2$ (IV)

0.43 g (1.61 mmol) of CH_2I_2 was added to the solution of I obtained from 0.55 g (3.0 mmol) of Cp_2Cr in 20 ml of toluene. The violet-green solution that formed immediately was evaporated to dryness under a stream of argon at 110 °C. The green residue was extracted by a boiling THF/hexane (1/2) mixture and concentrated to the 1/3 volume in the argon flow at 70 °C. The green prisms, which precipitated upon cooling, were separated from the solution by decantation, washed with cold benzene and pentane and dried in a gentle stream of argon at room temperature. Yield 0.75 g (57%).

IR spectrum (cm^{-1}): 615m, 760m, 815s, 840m, 860m, 1010m, 1160s, 1235w, 1355m, 1375m, 2935m br.

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