Pentakis(methoxycarbonyl)cyclopentadiene Chemistry. Part 3.[1] Synthesis and Crystal Structure of the Trivalent Metal Complex $[Cr\{C_5(CO_2Me)_5\}_3]\cdot$*ca.*$3.75H_2O$ †

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The crystal structure of $[Cr\{C_5(CO_2Me)_5\}_3]\cdot$*ca.*$3.75H_2O$, synthesised by the reaction of chromium(II) acetate with the parent acid in methanol, was determined by single-crystal *X*-ray diffraction methods and refined to a residual of 0.066 for 632 ' observed ' reflections at 295 K. Crystals are rhombohedral, space group $R\bar{3}$, with a = 16.545(20) Å, α = 60.49(7)°, and Z = 3. The molecule lies with the chromium atom situated in a three-fold symmetry axis, chelated by the carbonyl oxygen atoms of adjacent carboxyl groups, to give a tris-chelate complex: mean Cr–O 1.93 Å.

The transition-metal chemistry of pentakis(methoxycarbonyl)cyclopentadiene, $HC_5(CO_2Me)_5$ (1, Hpmcp),[1] shows many interesting differences from that of the parent hydrocarbon, exemplified by the water-soluble, ionic iron(II) derivative,[2] the first copper(II) cyclopentadienide,[3] and the unusual formation of $[Rh\{\eta^5\text{-}C_5H_2(CO_2Me)_3\}_2][C_5(CO_2Me)_5]$ by replacement of CO_2Me by H.[4] The copper and rhodium derivatives were readily obtained from reactions of (1) with $[Cu(O_2CMe)_2]$ and $[Rh_2(O_2CMe)_4]$, respectively.

Extension of this reaction to $[Cr_2(O_2CMe)_4]$ has afforded a novel chromium(III) derivative, which has been characterised as hydrated $[Cr\{C_5(CO_2Me)_5\}_3]$ by single-crystal *X*-ray diffraction described below.

Results and Discussion

The reaction between chromium(II) acetate and Hpmcp in methanol results in an immediate colour change from red to green, and the formation of a green solid, the analysis of which agrees with the formulation as a non-stoicheiometric hydrate of the chromium(III) complex $[Cr\{C_5(CO_2Me)_5\}_3]$ (2), as shown by the structure determination. The complex is soluble in water to give a green solution, which turns blue on heating or standing; the nature of this blue solution has not been elucidated. The electronic spectrum of (2) in aqueous solution is similar to that of $[Cr(OH_2)_6]^{3+}$ ion.

The i.r. spectrum is similar to those of $M(pmcp)_2$ (M = Mn or Mg), suggesting that the pmcp ligands are bonded to chromium *via* carbonyl oxygens. The ^1H n.m.r. spectrum of a solution of (2) shows a single resonance, broadened by the paramagnetic chromium(III) atom, and shifted[5] to an extent consistent with the presence of three unpaired electrons, as expected for $[Cr(OH_2)_6]^{3+}$.

A single-crystal structure determination (Figure, Tables 1—3) confirms the stoicheiometry of the complex to be $[Cr\{C_5(CO_2Me)_5\}_3]$ solvated to the extent of nearly four water molecules, but with considerable disorder evident among these and also among one of the cyclopentadienide ring substituents; in general throughout the ligand, thermal motion is very high also and the resulting structure determination is of poor quality. The complex molecule has crystallographically imposed *3* symmetry with only one of the ligands about the chromium atom (which lies on the three-fold axis) being crystallographically independent. The ligand behaves in the normal way as a chelate towards the metal atom, co-ordinating by way of the carboxyl-carbonyl oxygen atoms [O(11,21)]. The geometry of the ligand is imprecise but within the limits of error conforms to that established previously where it is found in similarly chelating situations. As in copper(II) and iron(II) complexes (to be reported elsewhere), instead of lying on opposite sides of the C_5 ring plane as in the case of the chelate complexes with the alkali- and alkaline-earth metals, O(11,21) lie out of the plane on the same side, together with the chromium atom. As usual, two of the carboxyl substituents

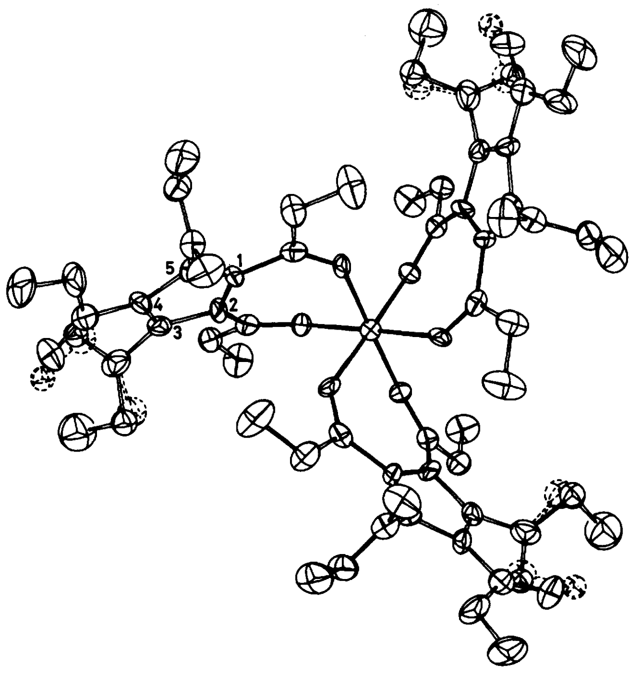

Figure. Molecular projection down the three-fold crystallographic axis. 20% Probability thermal ellipsoids are shown for the non-hydrogen atoms

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† *Supplementary data available* (No SUP 23354, 10 pp.): thermal parameters, H-atom parameters, least-squares planes, structure-factor amplitudes. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Non-hydrogen atom co-ordinates for $[\mathrm{Cr}\{\mathrm{C_5(CO_2Me)_5}\}_3]$

Atom	*x*	*y*	*z*
Cr	0.134 8(1)	0.134 8(—) [a]	0.134 8(—) [a]
C(1)	−0.005(2)	−0.025(2)	0.330(2)
C(11)	0.086(2)	−0.050(2)	0.249(2)
O(11)	0.141(1)	0.001(1)	0.183(1)
O(12)	0.105(1)	−0.137(2)	0.247(1)
C(12)	0.189(2)	−0.165(2)	0.164(2)
C(2)	−0.031(2)	0.051(2)	0.364(2)
C(21)	0.020(2)	0.114(2)	0.346(2)
O(21)	0.087(1)	0.133(1)	0.269(1)
O(22)	−0.016(1)	0.149(1)	0.416(1)
C(22)	0.026(2)	0.220(2)	0.396(2)
C(3)	−0.124(2)	0.049(1)	0.437(2)
C(31)	−0.193(2)	0.114(2)	0.503(2)
O(31) [b]	−0.198(4)	0.071(4)	0.591(4)
O(31′) [b]	−0.215(3)	0.204(4)	0.464(3)
O(32) [b]	−0.249(3)	0.204(3)	0.457(3)
O(32′) [b]	−0.189(5)	0.085(5)	0.588(5)
C(32) [b]	−0.283(4)	0.236(4)	0.553(5)
C(32′) [b]	−0.259(2)	0.152(3)	0.641(3)
C(4)	−0.154(2)	−0.023(1)	0.445(2)
C(41)	−0.249(2)	−0.033(2)	0.506(2)
O(41)	−0.322(1)	0.020(1)	0.544(1)
O(42)	−0.248(1)	−0.120(2)	0.515(1)
C(42)	−0.339(2)	−0.143(2)	0.571(2)
C(5)	−0.076(2)	−0.073(2)	0.376(2)
C(51)	−0.080(2)	−0.145(2)	0.349(2)
O(51)	−0.116(2)	−0.124(2)	0.293(1)
O(52)	−0.035(1)	−0.236(2)	0.404(1)
C(52)	−0.029(2)	−0.312(2)	0.380(2)
Solvent			
O(A) [b]	0.474(7)	0.239(6)	0.511(7)
O(B) [b]	0.524(6)	0.318(8)	0.364(9)
O(C) [c]	0.022(4)	0.022(—) [a]	0.022(—) [a]

[a] Constrained by symmetry. [b] Population: 0.5 (disordered). [c] Population: 0.25 (disordered).

Table 2. Molecular geometry of $[\mathrm{Cr}\{\mathrm{C_5(CO_2Me)_5}\}_3]$: distances (Å), angles (°)

C(1)–C(2)	1.42(5)	C(41)–O(41)	1.18(3)
C(2)–C(3)	1.42(4)	C(51)–O(51)	1.18(5)
C(3)–C(4)	1.42(5)	C(11)–O(12)	1.33(5)
C(4)–C(5)	1.44(4)	C(21)–O(22)	1.30(4)
C(5)–C(1)	1.43(5)	C(31)–O(32)	1.37(4), 1.27(9)
C(1)–C(11)	1.48(3)		
C(2)–C(21)	1.48(6)	C(41)–O(42)	1.37(5)
C(3)–C(31)	1.54(4)	C(51)–O(52)	1.36(3)
C(4)–C(41)	1.43(5)	O(12)–C(12)	1.47(3)
C(5)–C(51)	1.50(7)	O(22)–C(22)	1.46(4)
C(11)–O(11)	1.25(3)	O(32)–C(32)	1.66(10), 1.42(8)
C(21)–O(21)	1.23(3)		
C(31)–O(31)	1.24(6), 1.22(6)	O(42)–C(42)	1.45(4)
		O(52)–C(52)	1.43(5)
C(5)–C(1)–C(2)	115(2)	C(4)–C(41)–O(41)	131(4)
C(1)–C(2)–C(3)	101(3)	C(5)–C(51)–O(51)	125(3)
C(2)–C(3)–C(4)	113(3)	O(12)–C(11)–O(11)	120(2)
C(3)–C(4)–C(5)	108(3)	O(22)–C(21)–O(21)	125(3)
C(4)–C(5)–C(1)	103(3)	O(32)–C(31)–O(31)	127(4), 114(6)
C(5)–C(1)–C(11)	122(3)		
C(2)–C(1)–C(11)	123(3)	O(42)–C(41)–O(41)	120(3)
C(1)–C(2)–C(21)	135(2)	O(52)–C(51)–O(51)	129(4)
C(3)–C(2)–C(21)	123(3)	C(1)–C(11)–O(12)	111(3)
C(2)–C(3)–C(31)	128(3)	C(2)–C(21)–O(22)	114(2)
C(4)–C(3)–C(31)	120(2)	C(3)–C(31)–O(32)	113(3), 120(3)
C(3)–C(4)–C(41)	123(3)		
C(5)–C(4)–C(41)	129(4)	C(4)–C(41)–O(42)	109(2)
C(4)–C(5)–C(51)	127(3)	C(5)–C(51)–O(52)	106(3)
C(1)–C(5)–C(51)	129(2)	C(11)–O(12)–C(12)	115(2)
C(1)–C(11)–O(11)	129(3)	C(21)–O(22)–C(22)	115(2)
C(2)–C(21)–O(21)	121(3)	C(31)–O(32)–C(32)	87(3), 113(5)
C(3)–C(31)–O(31)	114(3), 118(3)		
		C(41)–O(42)–C(42)	119(2)
		C(51)–O(52)–C(52)	111(3)

Table 3. Chromium geometry: distances (Å), angles (°); independent values only are given

Cr–O(11)	1.92(2)	O(11)–Cr–O(21)	90.3(7)
Cr–O(21)	1.94(2)	O(11)–Cr–O(11$^{\mathrm{I}}$)	91.9(7)
O(11) ··· O(21)	2.74(3)	O(11)–Cr–O(21$^{\mathrm{I}}$)	88.8(7)
		O(11)–Cr–O(21$^{\mathrm{II}}$)	177.7(12)

Transformation of the asymmetric unit (*x*, *y*, *z*): I *z*, *x*, *y*; II *y*, *z*, *x*.

about the ring lie quasi-normal to the plane, those being necessarily on either side of the chelating substituents. In these cases, in consequence, a snug disposition of chelating groups and carboxyl substituents about the central metal atom results; for smaller metal atoms, the steric requirements of the ligand may become incompatible with the co-ordination of three chelating groups. Similar considerations, as well as the potential for forming a chelate on account of an amenable ligand bite, may be involved in the fact that a stable *tris* chelate is produced here rather than an oligonuclear basic complex.

The compound is of interest in providing an addition to the rather meagre collection of tris(symmetrical bidentate ligand-*OO′*)metal systems available; for chromium it provides the only example of such a system with a seven-membered chelate ring. As noted above, O(11,21) lie out of the C_5 ring plane on the same side by 0.44, 0.23 Å; Cr is further out on the same side (1.36 Å) and is clearly the strain-relieving element. The Cr–O bond length [1.92(2) Å] is somewhat shorter than values found for other tris(bidentate ligand-*OO′*)chromium(III) complexes: 1.951(7) in *rac*-$[\mathrm{Cr(acac)_3}]$ (acac = acetylacetonate),[6] 1.953(7) in $[(-)\mathrm{Co}\{(-)\text{-}\mathrm{pn}\}_3][(+)\mathrm{Cr(mal)_3}]$ (pn = propane-1,2-diamine, mal = malonate),[7] 1.962(5) in (−)-$[\mathrm{Cr(acac)_3}]$,[8] 1.969(13) in $\mathrm{K_3[Cr(C_2O_4)_3]}$,[9] or 1.986(4) Å in $\mathrm{K_3[Cr(O_2C_6H_4)_3]}$.[10] The co-ordination about chromium is distorted from octahedral to *D*3 symmetry, as expected for this ligand, which has a bite of 2.74(3) Å; the twist angle is 30.6° {*cf.* $[\mathrm{Cr(C_2O_4)_3}]^{3-}$, 23.9°; $[\mathrm{Cr(O_2C_6H_4)_3}]^{3-}$, 25.5°}.

Conclusion

Once again the effect of the strongly electron-withdrawing $\mathrm{CO_2Me}$ groups is to allow the anion to bond to the transition metal *via* carbonyl oxygen atoms with formation of a classical co-ordination complex; a π-type interaction of ring orbitals with the metal, as found with $\mathrm{C_5H_5}^-$ anion in $[\mathrm{Cr}(\eta\text{-}\mathrm{C_5H_5})_2]$, is not found.

Experimental

General experimental details have been given in earlier parts of this series. Chromium(II) acetate was made by a literature method.[11] Reactions were carried out in inert atmospheres using standard Schlenk techniques.

Reaction between $[Cr_2(O_2CMe)_4]$ *and* Hpmcp.—Solid chromium(II) acetate (250 mg, 1.45 mmol) was added to a solution of Hpmcp (1.0 g, 2.81 mmol) in methanol (30 cm^3). The colour changed immediately from maroon to green, and after 5 min a light green flocculent precipitate had separated. This material was filtered off, washed with methanol (2 × 10 cm^3), and dried to give a light green solid (297 mg, 18%), m.p. >300 °C, shown to be $[Cr\{C_5(CO_2Me)_5\}_3]\cdot 3.75H_2O$ (Found: C, 45.6; H, 3.75. $C_{45}H_{45}CrO_{30}\cdot 3.75H_2O$ requires C, 45.6; H, 4.45%). Recrystallisation afforded a more coarsely crystalline product, from which a poorly developed hexagonal plate was chosen for the structural study. Infrared (Nujol mull): ν(CO) at 1 725s, 1 695s, 1 640vs, other bands at 1 425m, 1 415m, 1 365m, 1 320s, 1 240vs, 1 225s, 1 210s, 1 190m, 1 168m, 1 005m, 985w, 938w, 790m, 760w, and 660w cm^{-1}. Electronic spectrum (aqueous solution): $\lambda_{max.}$ 579 (ε 58 dm^3 mol^{-1} cm^{-1}) and 648 (sh) nm. ^{1}H N.m.r.: δ (D_2O, external $SiMe_4$) 4.45 (s, br).

Crystallography.—General details of procedure are given in Part 1.[12]

Crystal data. $[Cr\{C_5(CO_2Me)_5\}_3]\cdot$*ca.*$3.75H_2O$, $C_{45}H_{52.5}CrO_{33.75}$, M = 1 185.4, Rhombohedral, space group $R\bar{3}$ (C_{3i}, no. 148), a = 16.545(20) Å, α = 60.49(7)°, U = 3 238(5) Å^3, Z = 3, D_c = 1.82 g cm^{-3}, $F(000)$ = 1 849.5, specimen 0.28 × 0.25 × 0.10 mm (hexagonal plate enclosed in capillary), μ_{Mo} = 4.1 cm^{-1}, $2\theta_{max.}$ = 35°, N = 1 366, N_o = 632, R,R',S = 0.066, 0.073, 2.1.

Data were of poor quality, limiting both the range available and the precision of the structure determination and cell calibration. One of the carboxylate groups and the solvent molecule are disordered and were refined with isotropic thermal parameters and appropriate fractional populations.

Acknowledgements

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