Pentakis(methoxycarbonyl)cyclopentadiene Chemistry. Part 6.[1] Some First-row Transition-metal Derivatives: Crystal and Molecular Structures of $[Fe\{C_5(CO_2Me)_5\}_2(MeOH)_2]$, $[Co\{C_5(CO_2Me)_5\}_2(OH_2)_2]$, and $[Cu\{C_5(CO_2Me)_5\}_2(MeOH)_2]$ †

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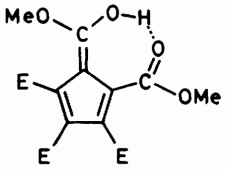
Bivalent transition-metal derivatives of pentakis(methoxycarbonyl)cyclopentadiene have been obtained, which contain Mn, Fe, Co, Ni, or Cu: the latter is the first cyclopentadienyl complex of copper(II). These complexes are soluble in water or alcohols to give solutions containing $[C_5(CO_2Me)_5]^-$ anions and solvated M^{2+} cations. Structural studies of the Fe and Cu complexes show the metal ion to be octahedrally co-ordinated by two solvent molecules, and two pairs of chelating carbonyl oxygens from each $C_5(CO_2Me)_5$ anion; the two salts, *trans*-$[M\{C_5(CO_2Me)_5\}_2(MeOH)_2]$ (M = Fe or Cu) are isomorphous, monoclinic, space group $P2_1/c$ with $a \sim 8.3$, $b \sim 20.2$, $c \sim 11.9$ Å, $\beta \sim 108°$, and $Z = 2$, with the molecule lying on a crystallographic centre of symmetry. For the iron(II) salt, Fe–O$[C_5(CO_2Me)_5]$ are 2.065(3) and 2.050(2) Å and Fe–O(MeOH) 2.151(2) Å, while in the copper(II) salt, Cu–O$[C_5(CO_2Me)_5]$ are 1.946(2) and 1.962(2) Å and Cu–O(MeOH) 2.314(3) Å. The cobalt hydrate analogue, $[Co\{C_5(CO_2Me)_5\}_2(OH_2)_2]$ has also been studied structurally and the molecule lies on a two-fold axis in space group $C2/c$ with $a = 17.151(7)$, $b = 14.722(5)$, $c = 15.026(6)$ Å, $\beta = 108.65(3)°$, and $Z = 4$. The Co–OH_2 bond is 2.054(4) Å; Co–O$[C_5(CO_2Me)_5]$ are 2.043(4) and 2.068(4) Å. Residuals are 0.039, 0.044, and 0.043 respectively for the Fe, Cu, and Co complexes from 2 075, 3 018, and 1 430 'observed' reflections. Unlike the iron and copper derivatives, the cobalt(II) complex is *cis*.

After the discovery of ferrocene was reported in 1951,[2] bis(η^5-cyclopentadienyl) derivatives of the other first-row transition elements except titanium and copper were soon described. The preparation and isolation of vanadocene,[3] chromocene,[4] manganocene,[5] cobaltocene,[6,7] and nickelocene[7,8] were followed by the rationalisation of their properties in terms of their electronic configurations and the now well-known sandwich structure. With the exception of ferrocene, for which a rich organic chemistry was developed, substituted metallocenes were rare, and generally limited to those obtained from the readily-available methylcyclopentadiene, and more recently, from pentamethyl- or ethyltetramethyl-cyclopentadiene.

Previous papers in this series have described some of our investigations into the metal derivatives of the strong organic acid, pentakis(methoxycarbonyl)cyclopentadiene (1).[9-13] The present account describes the synthesis of manganese(II), iron(II), cobalt(II), nickel(II), and copper(II) salts of this acid, and structural determinations of the three title complexes. The iron compound was first described in 1967, and was considered (correctly) not to be a ferrocene derivative, that is, not to contain iron covalently bonded to the C_5 groups.[14] However, no other structure was postulated. We have not yet obtained a chromium(II) derivative, all attempts to do so having afforded $Cr[C_5(CO_2Me)_5]_3$, which has been described earlier.[11] This account amplifies in part a preliminary communication.[15]



(1) E = CO_2Me

Results and Discussion

We have shown previously that diene (1) is sufficiently strong as an acid to displace weaker ones, such as acetic or carbonic, from their salts. Accordingly, we have reacted copper(II) acetate, or the carbonates of manganese(II), cobalt(II), nickel(II), or copper(II), with aqueous solutions of (1) (two equivalents) to give the crystalline transition-metal salts of (1). We have also repeated the earlier synthesis of the iron(II) derivative from the metal and diene (1).

The five compounds so obtained, when dried under vacuum, had elemental microanalyses corresponding to the stoicheiometries $M[C_5(CO_2Me)_5]_2$ [M = Mn (2), Fe (3), Co (4), Ni (5), or Cu (6)], except for (5) which was a dihydrate. As will be shown below, suitable crystals for *X*-ray studies were solvated in water or methanol; as yet, we have not been able to obtain solvent-free crystals of any $M[C_5(CO_2Me)_5]_2$ compound suitable for *X*-ray studies. The compounds, which are variously pale green (2), yellow (3), pink (4), green (5), and orange (6), are all stable in air [contrasting with $M(\eta\text{-}C_5H_5)_2$ where M = Mn, Co, or Ni], soluble in polar solvents, particularly water or the lower alcohols, and are involatile. They have fairly high decomposition points: we have not yet characterised the decomposition products.

In aqueous solution, conductivity measurements on all

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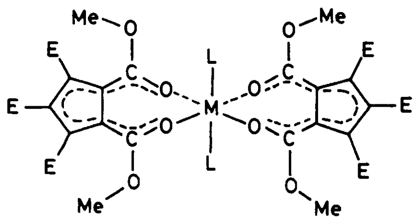
† *Supplementary data available* (No. SUP 23520, 33 pp.): structure factors, thermal parameters, H-atom parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. units employed: B.M. = 0.927×10^{-23} A m^2; mmHg ≈ 13.6×9.8 Pa.

Table 1. Infrared spectra (Nujol mulls) (cm^{-1}) of M[$C_5(CO_2Me)_5$]$_2$

Complex	M	ν(CO)	Other bands
(2)	Mn	ν(C=O) 1 725s, 1 705m, 1 680s, 1 648vs ν(C–O) 1 312s, 1 285s, 1 250vs, 1 205s	1 425m, 1 415m, 1 365m, 1 085m, 1 068m, 1 005m, 985w, 935w, 885w, 788m, 763w, 745m, 660w
(3)	Fe	ν(C=O) 1 725s, 1 700m, 1 685 (sh), 1 677s, 1 650 (sh), 1 645s ν(C–O) 1 312s, 1 280s, 1 245s, 1 210 (sh), 1 200s	1 485 (sh), 1 480 (sh), 1 455 (sh), 1 445 (sh), 1 430 (sh), 1 420m, 1 410w, 1 360m, 1 180 (sh), 1 170 (sh), 1 082s, 1 063m, 1 000s, 980w, 954w, 932w, 884w, 860vw, 835vw, 810vw, 782s, 755m, 742m, 710w
(4)	Co	ν(C=O) 1 745m, 1 703vs, 1 655vs ν(C–O) 1 325s, 1 275m, 1 235vs, 1 200vs, 1 175s	1 405m, 1 085m, 1 065m, 1 015m, 1 005s, 990m, 935w, 885w, 788m, 760m, 660w
(5)	Ni	ν(C=O) 1 745s, 1 740 (sh), 1 706s, 1 700 (sh), 1 680w, 1 656s ν(C–O) 1 310s, 1 270m, 1 230s, 1 210w ν(OH) 3 420s, 3 350s	1 645 (sh), 1 635 (sh), 1 620w, 1 403w, 1 195w, 1 170w, 1 165 (sh), 1 080s, 1 065s, 1 000s, 980w, 935w, 885w, 860w, 810w, 785m, 755m, 745m
(6)	Cu	ν(C=O) 1 740s, 1 735 (sh), 1 705 (sh), 1 700s, 1 685 (sh), 1 655 (sh), 1 645 (sh), 1 635 (sh), 1 630s, 1 620 (sh) ν(C–O) 1 327s, 1 242s, 1 225s, 1 198s	1 490 (sh), 1 474 (sh), 1 450 (sh), 1 438 (sh), 1 425 (sh), 1 414w, 1 385m, 1 179m, 1 169w, 1 155m, 1 089m, 1 010 (sh), 1 000m, 985w, 950 (sh), 932w, 895w, 868w, 831vw, 814w, 789m, 757m, 746m, 715w, 698w



	M	L
(3)	Fe	MeOH
(4)	Co*	H_2O
(6)	Cu	MeOH

E = CO_2Me
* *cis* complex

compounds indicate that they are 1 : 2 electrolytes; the solutions have the colour of the corresponding aquo-cations, and the magnetic susceptibilities, determined by the Evans n.m.r. method, show that these complexes have the same number of unpaired electrons as the well known [$M(OH_2)_6$]$^{2+}$ cations. In this connection we note that the ^{1}H n.m.r. spectra of aqueous solutions always contained the CO_2Me resonance for the symmetrical anion in the region δ 3.25—3.65; the signal was a singlet, more or less broadened by the paramagnetic cation. The u.v.–visible spectra are also consistent with the presence of these cations in solution, being the same as aqueous solutions of simple salts of the metal concerned; absorptions due to the [$C_5(CO_2Me)_5$]$^-$ anion were also present. This observation is in accord with the previous results obtained with the iron(II) complex.[14]

Compound (6) is notable as being the only cyclopentadienyl complex of copper(II) so far described. The orange colour is also unusual for this metal, and is the result of some Cu^{II}–$C_5(CO_2Me)_5$ interaction; in water, where the compound is fully ionised, blue solutions are obtained. In methanol, however, (6) dissolves to form an orange solution. Most copper(II) compounds are blue or green, exceptions generally resulting from strong u.v. bands which may tail off into the blue end of the spectrum. The anion has strong absorptions at 261 and 295 nm; the spectrum of the complex (in methanol) did not show any of the expected charge-transfer bands, but these may have been obscured.

Table 2. Ligand least-squares planes. Planes are given in the form $pX + qY + rZ = s$, where the right hand orthogonal Å frame (X,Y,Z) is defined with X parallel to a,Z in the ac plane. σ (defining atoms) and atom deviations δ are in Å. Defining atoms are C(1)—C(5). $\theta(n)$° is the dihedral angle to the plane of the atoms defined by C(n,n1)–O(n1,2)

Compound	(3)	(6)	(4)
10^4p	−7 859	−7 915	−1 071
10^4q	−2 088	−1 967	2 359
10^4r	5 821	5 786	9 659
s	−1.485	−1.395	3.612
σ	0.006	0.006	0.003
δM	1.485	1.395	1.223
δC(1)	0.000	−0.004	−0.003
δC(2)	−0.004	0.000	0.002
δC(3)	0.007	0.004	0.000
δC(4)	−0.008	−0.007	−0.002
δC(5)	0.005	0.007	0.003
δC(11)	0.268	0.238	0.171
δC(21)	−0.044	−0.058	−0.071
δC(31)	0.065	0.030	0.007
δC(41)	−0.038	−0.040	−0.075
δC(51)	0.158	0.151	0.073
δO(11)	1.354	1.326	−0.705
δO(21)	0.344	0.320	0.261
δO(31)	0.370	0.328	0.282
δO(41)	−1.015	−1.018	−1.070
δO(51)	0.138	0.109	−0.012
δO(12)	−0.817	−0.857	1.469
δO(22)	−0.542	−0.572	−0.563
δO(32)	−0.227	−0.294	−0.316
δO(42)	1.168	1.171	1.095
δO(52)	0.351	0.353	0.242
δC(12)	−0.602	−0.661	1.764
δC(22)	−0.655	−0.702	−0.776
δC(32)	−0.001	−0.113	−0.150
δC(42)	1.253	1.256	1.114
δC(52)	0.597	0.571	0.297
θ(1)	80.1	81.2	85.0
θ(2)	24.1	24.4	22.7
θ(3)	15.7	16.4	15.7
θ(4)	79.1	79.6	75.8
θ(5)	8.7	8.9	7.3

In view of the pronounced differences in behaviour between these compounds and the corresponding M(η-C_5H_5)$_2$ complexes, we decided to determine the solid-state structures, and hence the co-ordination about the metal atom, of these complexes. We describe below the results obtained with the iron, cobalt, and copper compounds.

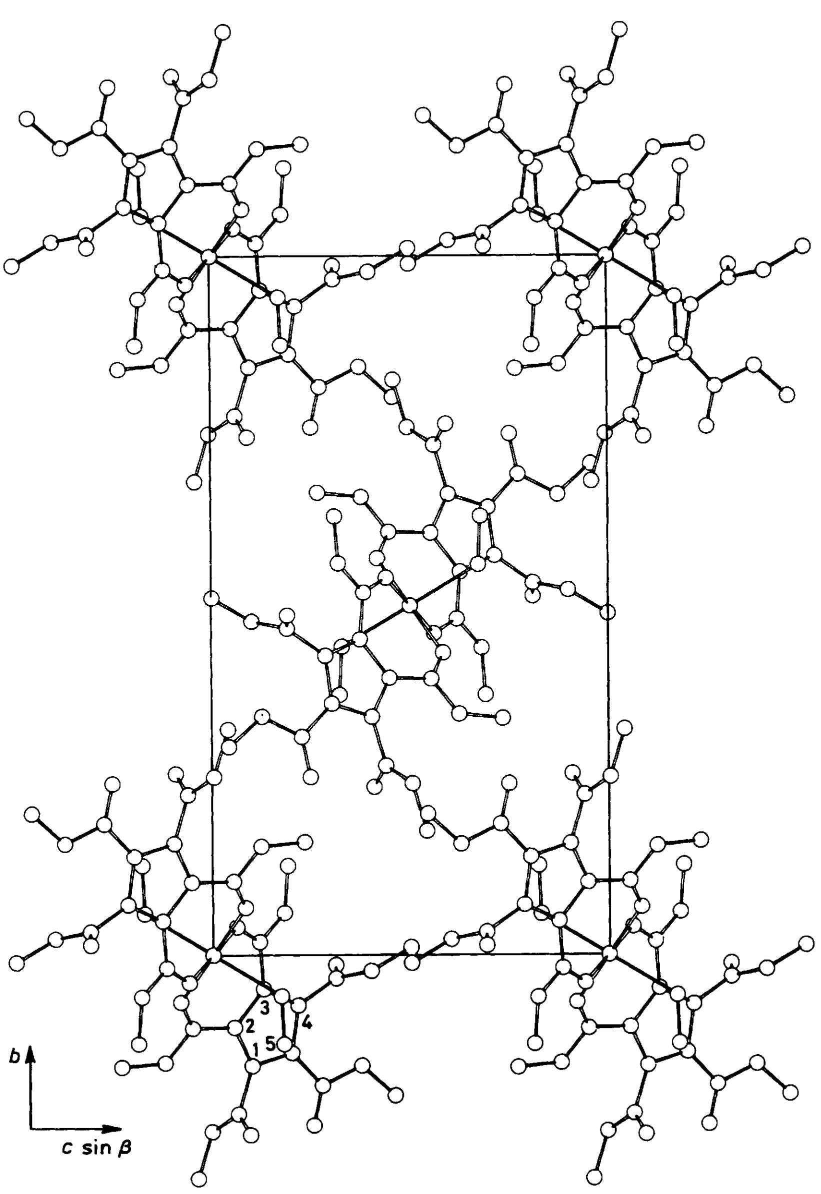


Figure 1. Unit-cell contents projected down *a* for $[Cu\{C_5(CO_2Me)_5\}_2(MeOH)_2]$. The iron(II) analogue is isostructural

Crystal Structures.—(*a*) $[M\{C_5(CO_2Me)_5\}_2(MeOH)_2]$ (M = Fe *or* Cu) (3) *and* (6). The iron and copper complexes are isomorphous. The unit-cell contents confirm the stoicheiometry of the complexes to be $[M\{C_5(CO_2Me)_5\}_2(MeOH)_2]$ (see Figures 1 and 2). The Fe^{II} and Cu^{II} derivatives are isostructural. All species are co-ordinated to the metal atom which lies on a centre of symmetry so that only one ligand and one solvent molecule are crystallographically independent. The methanol molecules are *trans* in the co-ordination sphere of the metal. The $[C_5(CO_2Me)_5]^-$ ligand is co-ordinated by way of O(21,31) in chelate fashion in the manner previously found, for example, for $Cr[C_5(CO_2Me)_5]_3$.[11] A pair of non-chelating carboxylate groups lie pseudo-normal to the C_5 ring plane, with the other three pseudo-parallel. Deviations of C(*n*1) from the C_5 plane are erratic (Table 2); deviations of the metal atoms from the C_5 plane are 1.485 Å (Fe); 1.395 Å (Cu). As usual, the C–C distance in the ring (Table 3) between the chelating carboxylate groups is lengthened relative to the remainder, as are the C(*n*1)–O(*n*1) distances (*n* = 2 and 3). The O–C–O angle in substituents 2 and 3 are also diminished relative to the remainder as is usual; O(21) · · · O(31) is 2.814(3), (Fe) 2.794(3) Å (Cu).

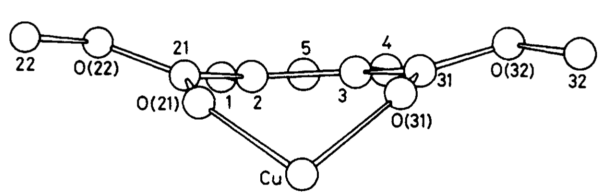


Figure 2. A projection of the copper environment through the bisector of C(2)–C(3) in the C_5 ring plane

About the metal atoms, the M–O(*n*1) distances are shorter (Table 4) than the usual values observed in σ-bonded oxygen-ligand complexes, *e.g.*, Fe–O, 2.086(7)—2.156(7) Å in $[NH_4]_2[Fe(SO_4)_2]\cdot 6H_2O$.[16] However, it is interesting to observe the longer metal–methanol distance relative to these in each of the present cases. While this is not surprising in the copper complex, since the two methanol groups are *trans* and likely

Table 3. Ligand non-hydrogen geometry: distances (Å), angles (°)

Compound	(3)	(6)	(4)
C(1)-C(2)	1.389(4)	1.392(4)	1.404(8)
C(2)-C(3)	1.438(4)	1.439(4)	1.443(7)
C(3)-C(4)	1.398(4)	1.392(3)	1.406(7)
C(4)-C(5)	1.409(5)	1.416(4)	1.408(8)
C(5)-C(1)	1.408(4)	1.404(3)	1.424(7)
C(1)-C(11)	1.492(5)	1.486(4)	1.484(7)
C(2)-C(21)	1.451(4)	1.448(3)	1.458(7)
C(3)-C(31)	1.443(4)	1.439(4)	1.453(8)
C(4)-C(41)	1.491(4)	1.493(4)	1.486(7)
C(5)-C(51)	1.451(4)	1.459(4)	1.445(8)
C(11)-O(11)	1.191(5)	1.198(4)	1.205(9)
C(21)-O(21)	1.224(4)	1.231(3)	1.221(7)
C(31)-O(31)	1.227(4)	1.236(3)	1.223(7)
C(5)-C(1)-C(2)	108.8(3)	108.6(2)	108.0(4)
C(1)-C(2)-C(3)	107.8(2)	107.9(2)	108.2(4)
C(2)-C(3)-C(4)	107.1(3)	107.1(2)	106.8(4)
C(3)-C(4)-C(5)	108.8(3)	108.7(2)	109.2(4)
C(4)-C(5)-C(1)	107.6(3)	107.7(2)	107.8(5)
C(5)-C(1)-C(11)	124.5(3)	124.3(2)	122.9(5)
C(2)-C(1)-C(11)	125.4(3)	125.9(2)	128.4(5)
C(1)-C(2)-C(21)	122.3(3)	123.0(2)	122.8(5)
C(3)-C(2)-C(21)	129.9(3)	129.0(2)	128.9(5)
C(2)-C(3)-C(31)	128.9(3)	128.7(2)	129.4(5)
C(4)-C(3)-C(31)	124.0(3)	124.2(2)	123.7(5)
C(3)-C(4)-C(41)	127.1(3)	127.4(3)	126.6(5)
C(5)-C(4)-C(41)	124.1(3)	123.9(2)	124.1(5)
C(4)-C(5)-C(51)	128.6(3)	128.6(2)	128.5(5)
C(1)-C(5)-C(51)	123.4(3)	123.4(3)	123.7(5)
C(1)-C(11)-O(11)	122.7(3)	122.7(3)	126.4(5)
C(2)-C(21)-O(21)	128.0(3)	128.5(3)	128.0(5)
C(3)-C(31)-O(31)	126.8(3)	127.3(2)	128.2(5)

Compound	(3)	(6)	(4)
C(41)-O(41)	1.201(4)	1.201(4)	1.216(7)
C(51)-O(51)	1.203(4)	1.198(4)	1.218(8)
C(11)-O(12)	1.324(5)	1.324(4)	1.339(7)
C(21)-O(22)	1.321(4)	1.325(4)	1.323(7)
C(31)-O(32)	1.324(4)	1.321(3)	1.336(6)
C(41)-O(42)	1.330(5)	1.334(4)	1.331(8)
C(51)-O(52)	1.347(4)	1.347(4)	1.327(7)
O(12)-C(12)	1.441(5)	1.441(5)	1.457(7)
O(22)-C(22)	1.446(4)	1.443(4)	1.450(7)
O(32)-C(32)	1.446(5)	1.449(4)	1.448(7)
O(42)-C(42)	1.443(5)	1.440(5)	1.443(8)
O(52)-C(52)	1.444(5)	1.443(5)	1.455(8)
C(4)-C(41)-O(41)	125.1(3)	125.2(3)	125.3(7)
C(5)-C(51)-O(51)	125.6(3)	125.0(3)	123.7(5)
C(1)-C(11)-O(12)	113.3(3)	113.7(3)	109.9(5)
C(2)-C(21)-O(22)	112.3(3)	112.3(2)	111.8(5)
C(3)-C(31)-O(32)	113.7(2)	113.4(2)	111.9(5)
C(4)-C(41)-O(42)	111.6(3)	111.6(3)	112.1(5)
C(5)-C(51)-O(52)	112.1(3)	111.8(3)	113.1(5)
O(11)-C(11)-O(12)	124.0(3)	123.6(3)	123.7(5)
O(21)-C(21)-O(22)	119.6(3)	119.3(2)	120.3(5)
O(31)-C(31)-O(32)	119.5(3)	119.3(3)	119.8(5)
O(41)-C(41)-O(42)	123.3(3)	123.2(3)	122.6(5)
O(51)-C(51)-O(52)	122.3(3)	123.2(3)	123.2(5)
C(11)-O(12)-C(12)	114.8(4)	115.3(3)	115.5(5)
C(21)-O(22)-C(22)	117.1(3)	117.6(2)	117.4(5)
C(31)-O(32)-C(32)	116.7(3)	116.9(2)	116.3(4)
C(41)-O(42)-C(42)	115.8(3)	115.7(3)	116.4(4)
C(51)-O(52)-C(52)	116.8(3)	116.0(3)	117.3(5)

Table 4. Metal atom environments in (3), (6), and (4). The first column in the matrix is the metal–oxygen distance (Å); the other entries are the angles subtended at the metal by the two relevant oxygen atoms. Primed atoms are generated by the two-fold rotor ($\bar{x},y,\frac{1}{2} - z$) in (4)

(3)	r_{Fe-O}	O(31)	O(A)
O(21)	2.065(3)	86.3(1)	96.7(1)
O(31)	2.050(2)		91.4(1)
O(A)	2.151(2)		

(6)	r_{Cu-O}	O(31)	O(A)
O(21)	1.946(2)	91.3(1)	96.7(1)
O(31)	1.962(2)		91.8(1)
O(A)	2.314(3)		

(4)	r_{Co-O}	O(31)	O	O(21′)	O(31′)	O
O(21)	2.043(4)	87.4(2)	90.4(1)	175.9(2)	95.6(2)	86.8(1)
O(31)	2.068(4)		176.7(4)	95.6(2)	88.2(1)	89.6(1)
O	2.054(4)			86.8(1)	89.6(1)	92.7(1)

Associated M–O–C angles

Fe–O(21,31)–C	136.8(2), 138.0(2)	Fe–O(A)–C(A)	125.6(3)
Cu–O(21,31)–C	133.5(2), 134.0(2)	Cu–O(A)–C(A)	124.0(3)
Co–O(21,31)–C	140.7(4), 139.7(3)		

candidates for Jahn-Teller distortions, it is interesting to note that in the Fe^{II} derivative Fe–O(A) 2.151(2) Å is much longer than the Fe–O(21,31) distance (see above) and indicative of weaker σ-bonding capacity.

(*b*) $[Co\{C_5(CO_2Me)_5\}_2(OH_2)_2]$ (4). The structure determination shows the stoicheiometry of the cobalt complex to be $[Co\{C_5(CO_2Me)_5\}_2(OH_2)_2]$ (see Figures 3 and 4). Although the unit cell is not isostructural with that of the methanol analogues [(3), (6)] we find that in the present case the asymmetric unit of the structure is also one half of the above molecular unit. In (4) however, the symmetry operation generating the second half of the molecule is a two-fold rotor, consistent with the interesting feature that, whereas the molecules of (3) and (6) are *trans* isomers and centrosymmetric, that in (4) is *cis*. The $C_5(CO_2Me)_5$ ligand dispositions in (4) correlate remarkably well with those observed in (3) and (6) (Tables 3 and 4). The metal–oxygen distance range is much closer [2.043(4)—2.068(4) Å] than in the iron derivative, reflecting the stronger donor capacity of water *versus* methanol; Co–OH_2 [2.054(4) Å] is shorter than the value observed in ammonium cobalt(II) sulphate Tutton salt [2.070(4)—2.107(4) Å].[16]

Of interest in all three structures is the metal atom disposition relative to the chelate ligand. The carboxylate planes are distorted slightly out of coplanarity with the C_5 ring by consistent amounts (Table 2), with the metal atom well out of the C_5 plane (Table 2, Figure 2).

Conclusions

The first-row transition-metal (Mn ⟶ Cu) derivatives of diene (1) behave as typical salts of a strong acid, $M^{2+}[C_5(CO_2Me)_5]^-_2$. In water, ionisation to $[M(OH_2)_6]^{2+}$ and $[C_5(CO_2Me)_5]^-$ occurs, and similar solvated cations are formed in the lower alcohols. In the solid state, four of the solvent molecules are replaced by two $C_5(CO_2Me)_5$ ligands, each chelating the metal ion *via* two adjacent ester carbonyl groups. In addition to their solution properties, these complexes differ from the analogous $M(\eta\text{-}C_5H_5)_2$ derivatives in being involatile, generally air-stable, and insoluble in non-polar solvents. The orange copper(II) derivative has no known C_5H_5 analogue.

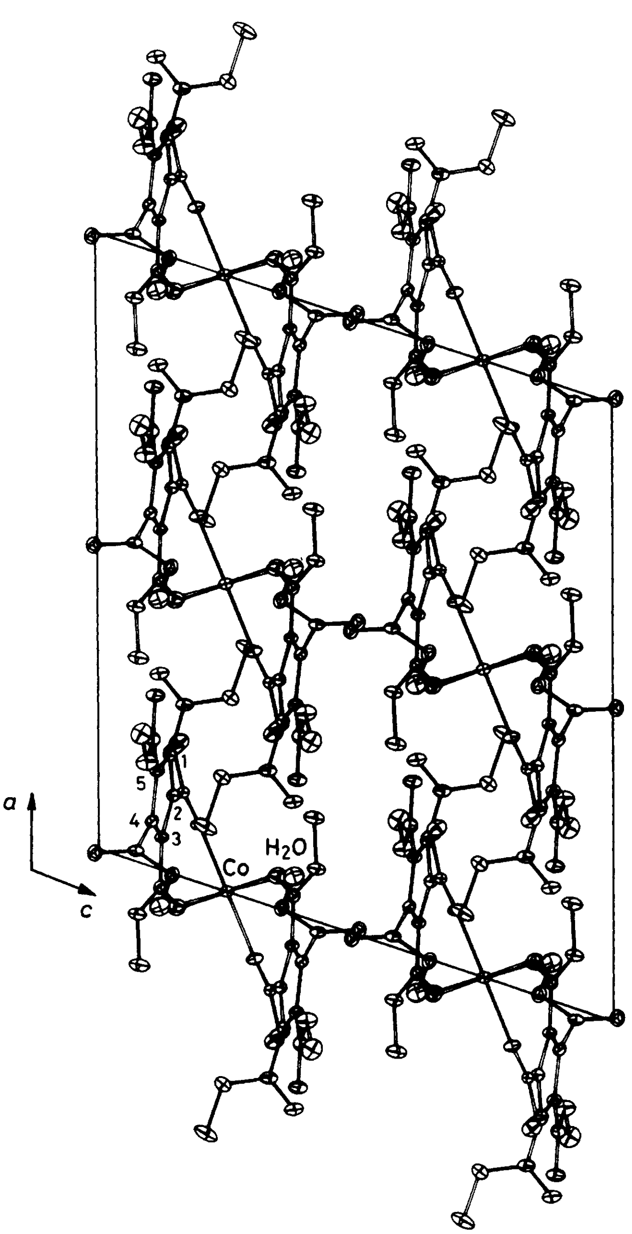


Figure 3. Unit-cell contents of (4) projected down *b*

Experimental

General experimental conditions and intrumental facilities have been described previously. Diene (1) was made by the published method, and transition-metal salts were commerical samples used as received. Infrared spectra are collected in Table 1.

Preparation of Complexes $M[C_5(CO_2Me)_5]$ (M = Mn, Fe, Co, Ni, *or* Cu).—(*a*) M = Mn. Manganese(II) carbonate (81 mg, 0.71 mmol) was added to an aqueous solution of $HC_5(CO_2Me)_5$ (500 mg, 1.4 mmol, in 5 cm^3). After evolution of CO had ceased, the solution was filtered and evaporated to dryness to give a pale green *solid*; recrystallisation (methanol) gave pure $Mn[C_5(CO_2Me)_5]_2$ (2) (185 mg, 34%), m.p. >300 °C (Found: C, 47.00; H, 3.90. $C_{30}H_{30}MnO_{20}$ requires C, 47.10; H, 3.90%). Conductivity (H_2O) 124 ohm^{-1} cm^2 mol^{-1}. ^1H N.m.r.: δ (D_2O, external $SiMe_4$ reference) 3.5 (s br, CO_2*Me*); $\mu_{obs.}$ 6.01 B.M.

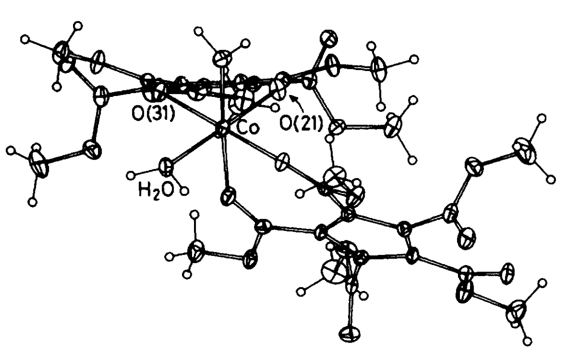


Figure 4. A single molecule of (4) projected normal to one of the faces of the co-ordination polyhedron containing the two water molecules. The relative disposition of the cobalt and the C_5 ligand plane are seen in the upper ligand

(*b*) M = Fe. A mixture of iron powder (3 g) and $HC_5(CO_2Me)_5$ (1 g, 2.8 mmol) in water (10 cm^3) was stirred at 80 °C for 5 h, then filtered; the filtrate was taken to dryness under vacuum, and the resulting yellow solid was washed with boiling acetone (3 × 50 cm^3) and dried. Recrystallisation (methanol) gave yellow crystals of $Fe[C_5(CO_2Me)_5]_2$ (3) (900 mg, 85%) which were dried at 80 °C, 10^{-2} mmHg (Found: C, 47.00; H, 3.80. $C_{30}H_{30}FeO_{20}$ requires C, 47.00; H, 3.95%). Conductivity (H_2O) 133 ohm^{-1} cm^2 mol^{-1}. ^1H N.m.r.: δ (D_2O, external $SiMe_4$ reference) 3.57 (s br, CO_2*Me*); $\mu_{obs.}$ 5.10 B.M

(*c*) M = Co. A similar reaction to (*a*) used $CoCO_3$ (334 mg, 2.81 mmol) and $HC_5(CO_2Me)_5$ (2.0 g, 5.6 mmol) in water (10 cm^3). The pink filtrate was evaporated, and the residue recrystallised (methanol) to give small *crystals* of $Co[C_5(CO_2Me)_5]_2$ (4) (1.88 g, 87%), m.p. 210 °C (decomp.) (Found: C, 45.95; H, 3.80. $C_{30}H_{30}CoO_{20}$ requires C, 46.80; H, 3.90%). Conductivity (H_2O) 121 ohm^{-1} cm^2 mol^{-1}. ^1H N.m.r.: δ (D_2O, external $SiMe_4$ reference) 3.50 (s br, CO_2*Me*); $\mu_{obs.}$ 4.67 B.M.

(*d*) M = Ni. Similarly, a pale green solid was obtained by evaporating the filtered solution from $NiCO_3$ (20 mg, 0.8 mmol) and an aqueous solution of $HC_5(CO_2Me)_5$ (500 mg, 1.4 mmol, in 20 cm^3). Recrystallisation (methanol–diethyl ether) gave green *crystals* of $Ni[C_5(CO_2Me)_5]_2 \cdot 2H_2O$ (5) (430 mg, 80%), m.p. 210 °C (decomp.) (Found: C, 44.90; H, 4.25; O, 42.10. $C_{30}H_{34}NiO_{22}$ requires C, 44.75; H, 4.25; O, 43.75%). Conductivity (H_2O) 140 ohm^{-1} cm^2 mol^{-1}.^{1} H N.m.r.: δ (D_2O, external $SiMe_4$ reference) 3.25, (s br, CO_2*Me*). U.v.–visible $\lambda_{max.}$ (H_2O) 261 (log ε, 5.00), 295 (4.40), 390 (3.02), 695 (weak), 710 nm (weak).

(*e*) M = Cu. Solutions of copper(II) acetate (140 mg, 0.7 mmol) and $HC_5(CO_2Me)_5$ (500 mg, 1.4 mmol) in methanol (total volume 10 cm^3) were mixed, with an immediate colour change from blue-green to orange. Small crystals of $Cu[C_5(CO_2Me)_5]_2$ (6) (300 mg, 56%), m.p. 280—290 °C (decomp.), darkens >245 °C, precipitated from the reaction mixture, and were collected, washed with methanol (3 × 5 cm^3) and dried. A similar product was obtained from $CuCO_3$ and $HC_5(CO_2Me)_5$, the product being recrystallised from methanol–diethyl ether (Found: C, 46.45, H, 3.95. $C_{30}H_{30}CuO_{20}$ requires C, 46.55; H, 3.90%). Conductivity (H_2O) 140 ohm^{-1} cm^2 mol^{-1}. ^1H N.m.r.: δ (D_2O, external $SiMe_4$ reference) 3.63 (s br, CO_2*Me*). U.v.–visible: $\lambda_{max.}$ (MeOH) 261 (log ε, 5.04), 295 nm (4.44); $\lambda_{max.}$ (H_2O) 805 nm (1.00); $\mu_{obs.}$ 2.62 B.M.

Crystallography.—For general details, see ref. 1. Atom coordinates for (3), (4), and (6) are given in Table 5.

Table 5. Non-hydrogen atom co-ordinates

Atom	(3) (M = Fe)			(6) (M = Cu)			(4) * (M = Co)		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Ligand									
C(1)	0.468 8(4)	−0.161.4(2)	0.095 0(3)	0.455 5(3)	−0.159 5(1)	0.097 1(2)	0.191 5(3)	0.563 8(3)	0.140 4(3)
C(11)	0.421 0(4)	−0.231 4(2)	0.059 1(3)	0.409 0(4)	−0.229 2(1)	0.061 8(2)	0.280 9(3)	0.543 5(4)	0.169 1(5)
O(11)	0.315 6(3)	−0.260 6(1)	0.088 3(2)	0.303 9(3)	−0.259 3(1)	0.091 8(2)	0.317 7(2)	0.512 4(3)	0.120 0(3)
O(12)	0.506 9(3)	−0.256 9(1)	−0.008 0(2)	0.495 2(3)	−0.254 6(1)	−0.004 9(2)	0.316 9(2)	0.567 7(3)	0.258 8(3)
C(12)	0.460 1(8)	−0.323 8(2)	−0.047 5(5)	0.454 7(7)	−0.322 3(2)	−0.040 3(5)	0.406 4(4)	0.563 6(6)	0.292 0(5)
C(2)	0.370 5(4)	−0.106 0(2)	0.051 3(3)	0.355 9(3)	−0.104 0(1)	0.052 8(2)	0.127 2(3)	0.507 5(3)	0.146 2(3)
C(21)	0.225 9(4)	−0.108 4(2)	−0.054 2(3)	0.210 2(3)	−0.105 5(1)	−0.053 1(2)	0.137 8(3)	0.410 5(4)	0.166 1(3)
O(21)	0.103 0(3)	−0.071 6(1)	−0.081 8(2)	0.086 1(2)	−0.067 9(1)	−0.082 4(2)	0.095 2(2)	0.360 5(2)	0.196 0(2)
O(22)	0.234 4(3)	−0.158 6(1)	−0.123 8(2)	0.217 9(3)	−0.155 5(1)	−0.122 8(2)	0.203 0(2)	0.377 9(2)	0.147 9(3)
C(22)	0.098 3(5)	−0.165 1(2)	−0.233 0(3)	0.081 0(5)	−0.161 8(2)	−0.232 3(3)	0.217 4(4)	0.280 9(4)	0.158 4(5)
C(3)	0.441 8(4)	−0.050 8(2)	0.126 6(3)	0.429 8(3)	−0.048 6(1)	0.126 7(2)	0.053 0(3)	0.561 1(3)	0.123 5(3)
C(31)	0.381 3(4)	0.016 6(2)	0.121 0(3)	0.371 3(4)	0.081 9(1)	0.117 7(3)	−0.029 5(3)	0.534 3(4)	0.119 9(4)
O(31)	0.240 5(3)	0.036 8(1)	0.064 9(2)	0.228 4(3)	0.040 1(1)	0.060 4(2)	−0.050 6(2)	0.466 4(3)	0.153 0(3)
O(32)	0.493 5(3)	0.058 6(1)	0.186 6(2)	0.487 8(3)	0.060 7(1)	0.180 5(2)	−0.085 8(2)	0.595 7(2)	0.075 0(3)
C(32)	0.434 0(5)	0.124 7(2)	0.198 9(4)	0.432 0(5)	0.127 9(2)	0.189 5(4)	−0.168 1(3)	0.582 3(4)	0.079 4(4)
C(4)	0.584 5(4)	−0.074 4(2)	0.213 4(3)	0.573 6(3)	−0.071 9(1)	0.213 8(2)	0.074 2(3)	0.649 6(3)	0.104 5(3)
C(41)	0.703 1(4)	−0.035 3(2)	0.309 9(3)	0.695 5(4)	−0.032 9(1)	0.309 7(3)	0.017 2(3)	0.727 8(3)	0.073 0(4)
O(41)	0.839 6(3)	−0.015 8(1)	0.309 4(2)	0.833 8(3)	−0.013 8(1)	0.309 3(2)	−0.008 7(2)	0.756 4(3)	−0.007 0(3)
O(42)	0.640 6(3)	−0.025 2(1)	0.399 2(2)	0.633 5(3)	−0.022 5(1)	0.398 9(2)	−0.003 1(2)	0.764 9(3)	0.143 4(2)
C(42)	0.749 1(6)	0.010 1(3)	0.499 3(4)	0.746 5(5)	0.011 4(2)	0.498 9(3)	−0.061 4(4)	0.838 8(5)	0.119 2(5)
C(5)	0.601 1(4)	−0.142 8(2)	0.195 7(3)	0.589 3(3)	−0.140 7(1)	0.197 3(2)	0.158 8(3)	0.652 5(3)	0.115 1(4)
C(51)	0.716 8(4)	−0.189 8(2)	0.271 1(3)	0.707 7(4)	−0.187 8(2)	0.273 5(3)	0.208 0(4)	0.729 9(4)	0.107 5(4)
O(51)	0.727 1(3)	−0.247 7(1)	0.250 1(3)	0.717 7(3)	−0.245 3(1)	0.251 9(2)	0.280 1(2)	0.724 7(3)	0.112 1(3)
O(52)	0.813 7(3)	−0.161 5(1)	0.371 4(2)	0.805 5(3)	−0.159 0(1)	0.373 3(2)	0.166 8(2)	0.807 6(3)	0.095 1(3)
C(52)	0.926 5(6)	−0.204 7(3)	0.456 5(4)	0.921 4(6)	−0.202 3(2)	0.457 1(4)	0.210 6(4)	0.889 5(4)	0.084 7(5)
Metal									
M	0	0	0	0	0	0	0.000 0(−)	0.365 50(7)	0.250 0(−)
Solvent									
O(A)	0.026 3(3)	−0.054 2(1)	0.160 6(2)	0.039 1(3)	−0.058 9(1)	0.172 1(2)	0.056 6(2)	0.269 2(3)	0.348 3(2)
C(A)	0.035 2(8)	−0.123 1(3)	0.172 3(5)	0.033 2(8)	−0.128 0(3)	0.177 7(5)			

* Water hydrogens for (4) (x,y,z; 10^3U Å^2) (0.026, 0.260, 0.391; 66) (0.108, 0.249, 0.373; 66).

Crystal data. $[Fe\{C_5(CO_2Me)_5\}_2(MeOH)_2]$ (3), $C_{32}H_{38}FeO_{22}$, M = 830.5, Monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), a = 8.304(3), b = 20.168(4), c = 11.878(3) Å, β = 107.60(2)°, U = 1 896.2(8) Å^3, Z = 2, D_c = 1.45 g cm^{-3}, $F(000)$ = 864, μ(Mo-K_α) = 4.7 cm^{-1}, λ = 0.710 69 Å, $2\theta_{max.}$ = 50°, N = 3 161, N_o = 2 075; R,R',S = 0.039, 0.049, 1.4, specimen size 0.40 × 0.12 × 0.18 mm (specimen enclosed in capillary).

$[Cu\{C_5(CO_2Me)_5\}_2(MeOH)_2]$ (6), $C_{32}H_{38}CuO_{22}$, M = 838.2, Monoclinic, space group $P2_1/c$, a = 8.205(5), b = 20.204(9), c = 11.975(5) Å, β = 108.09(4)°, U = 1 887(2) Å^3, Z = 2, D_c = 1.48 g cm^{-3}, $F(000)$ = 870, μ(Mo-K_α) = 6.5 cm^{-1}, λ = 0.710 69 Å, $2\theta_{max.}$ = 60°, N = 5 407, N_o = 3 018; R,R',S = 0.044, 0.053, 1.4, specimen size 0.50 × 0.10 × 0.30 mm (specimen enclosed in capillary).

$[Co\{C_5(CO_2Me)_5\}_2(OH_2)_2]$ (4), $C_{30}H_{34}CoO_{22}$, M = 805.5, Monoclinic, space group $C2/c$ (C^6_{2h}, no. 15), a = 17.151(7), b = 14.722(5), c = 15.026(6) Å, β = 108.65(3)°, U = 3 595(2) Å^3, D_m = 1.48(1), Z = 4, D_c = 1.49 g cm^{-3}, $F(000)$ = 1 668, μ(Mo-K_α) = 5.6 cm^{-1}, λ = 0.710 69 Å, $2\theta_{max.}$ = 45°, N = 2 255, N_o = 1 430; R,R',S = 0.043, 0.049, 1.4, specimen: spheroid, ~0.2 mm diameter (no absorption correction).

The $C_5(CO_2Me)_5$ ligand numbering follows that employed previously [11] with ring atoms designated C(n), n = 1—5 and attached carbon and oxygen atoms designated C,O(n1,n2) in order from the point of attachment. For clarity in presentation of the Figures only the numbering of the $C_5(CO_2Me)_5$ ring atoms is shown.

Acknowledgements

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