Pentakis(methoxycarbonyl)cyclopentadiene Chemistry. Part 2.[1] Some Derivatives containing the Alkaline-earth Metals (Mg, Ca, Sr, or Ba) or Group 2 Metals (Zn or Cd). Crystal and Molecular Structure of $Ba[C_5(CO_2Me)_5]_2$ †

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White, air-stable, and water-soluble compounds $M[C_5(CO_2Me)_5]_2$ (M = Mg, Ca, Sr, Ba, Zn, and Cd) are obtained from $HC_5(CO_2Me)_5$ and the metal carbonates or acetates, or from MCl_2 and $Tl[C_5(CO_2Me)_5]$; the i.r., ^1H n.m.r., and mass spectra are reported and briefly discussed. The structure of the barium derivative has been determined at 295 K by single-crystal *X*-ray diffraction methods, and refined to a residual of 0.036 for 8 173 ' observed ' reflections. Crystals are triclinic, space group $P\bar{1}$, with $a = 14.499(4)$, $b = 12.940(4)$, $c = 10.745(2)$ Å, $\alpha = 100.54(2)$, $\beta = 100.02(2)$, $\gamma = 114.23(2)°$, and $Z = 2$. The barium atom is eight-co-ordinate with an environment made up of three pairs of chelating carboxyl-carbonyl oxygen atoms and two others [Ba–O 2.655(3)—2.932(3) Å]; as in the alkali-metal derivatives, there is a tendency for adjacent carboxyl-carbonyl groups to behave as chelate functions.

In the previous paper[1] we described the preparation and properties of alkali-metal and thallium(I) derivatives of the strong organic acid pentakis(methoxycarbonyl)cyclopentadiene, $HC_5(CO_2Me)_5$ (Hpmcp). We showed how the presence of the five strongly electron-withdrawing substituents resulted in the formation of air-stable, water-soluble compounds, and *X*-ray crystal-structure studies of some demonstrated the preference for oxygen co-ordination to the hard metal ions. In this account, we report on some derivatives of bivalent metal ions of Groups 2A and 2B.

Results and Discussion

Ionic complexes of the type $M(pmcp)_2$ [M = Mg (1), Ca (2), Sr (3), Ba (4), Zn (5), or Cd (6)] have been prepared from reactions of the diene with metal carbonates or acetates [equations (i) and (ii)], or from the metal chloride and the thallium(I) salt [equation (iii)]. The compounds so obtained

$$MCO_3 + 2Hpmcp \xrightarrow{H_2O} M(pmcp)_2 + H_2O + CO_2\uparrow \quad \text{(i)}$$

$$M(O_2CMe)_2 + 2Hpmcp \xrightarrow{MeOH} M(pmcp)_2 + 2MeCO_2H \quad \text{(ii)}$$

$$MCl_2 + 2Tl(pmcp) \xrightarrow{MeOH} M(pmcp)_2 + 2TlCl\downarrow \quad \text{(iii)}$$

have been characterised by elemental microanalyses, conductivity measurements, and from their spectroscopic data. The analyses are consistent with the formulation $M(pmcp)_2$ for M = Ca, Ba, or Sr; the magnesium complex is a monohydrate, while the strontium and zinc derivatives are trihydrates. The last two compounds could not be dehydrated by heating at 100 °C *in vacuo* for 8 h. All compounds are air-stable white solids, soluble in water, which if anhydrous melt above 300 °C; the hydrates have considerably lower melting points. In aqueous solution, molar conductances range between 130 and 160 ohm^{-1} cm^2 mol^{-1}, values expected for 2 : 1 electrolytes, and clearly indicating their ionic nature.

The i.r. spectra (Table 1) all show several strong ν(C=O) absorptions above 1 600 cm^{-1}, and ν(CO) bands close to 1 200 cm^{-1}. Although complex, the spectra are similar to that of the potassium salt, in which several of the ester carbonyl groups are involved in weak co-ordination of the metal ion. An additional feature of the spectra of the hydrated derivatives is a broad ν(OH) absorption at *ca.* 3 350 cm^{-1}. The ^1H n.m.r. spectra of solutions in D_2O each contains a single resonance between δ 4.28 and 4.51 assigned to the methoxy-protons of symmetrical $[C_5(CO_2Me)_5]^-$ anions. In $(CD_3)_2CO$ this resonance has shifted to δ 3.68. The mass spectra of $Ca(pmcp)_2$ and $Zn(pmcp)_2$ contain only ions formed by the breakdown of $[C_5(CO_2Me)_5]^+$ (*m*/*e* 355); no molecular ion was observed, as is common for ionic compounds.

Although the properties of these compounds suggest that the pmcp ligands are *O*-bonded to the metal ions, probably by pairs of ester carbonyl groups acting as chelate functions, the precise structure could not be established. Accordingly we have carried out a single-crystal *X*-ray study of the barium derivative (4).

Structure of $Ba[C_5(CO_2Me)_5]_2$ (4).—The unit-cell contents (Figure) agree with the expected stoicheiometry $Ba[C_5(CO_2Me)_5]_2$, one formula unit comprising the asymmetric unit. The Ba is eight-co-ordinate with Ba–O distances ranging from 2.655(3) to 2.932(3) Å (average 2.76 Å). There are few compounds with which to make any comparisons of similar Ba–O bond lengths, but those in (4) appear to be shorter than most. For example, in four complexes containing macrocyclic polyethers, mean Ba–O distances are found to be in the range 2.82—2.93 Å;[2] other values of 2.82 in $Ba(O_2CH)_2$,[3] 2.87 in $BaC_2O_4{\cdot}2H_2O$,[4] and 2.96 Å in $BaC_2O_4{\cdot}H_2C_2O_4{\cdot}2H_2O$[5] have also been reported. Only those in $Ba(O_2CMe)_2[N(CH_2CH_2OH)_3]_2$[6] [range 2.743—2.805(4), average 2.767 Å] and $Ba(SCN)_2(C_{14}H_{28}N_2O_4)$ ($C_{14}H_{28}N_2O_4$ = 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]icosane)[7] [range 2.747—2.824(7), average 2.783 Å] are similar to those in (4).

All of the eight-co-ordinated oxygen atoms are of type O(*n*1), *i.e.* the carbonyl oxygens. Of these, three pairs are drawn from adjacent substituents in the ligands and thus

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† *Supplementary data available* (No. SUP 23353, 30 pp.): thermal parameters, methyl H-atom parameters, structure-factor amplitudes. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Infrared spectra (cm^{-1}) of M(pmcp)$_2$ obtained from Nujol mulls

Compound	Significant bands	Other bands
1) Mg(pmcp)$_2$·H$_2$O	ν(C=O) 1 750m, 1 729m, 1 703 (sh), 1 696s, 1 674s, 1 646m ν(C–O) 1 315s, 1 288m, 1 266s, 1 203s	1 445w, 1 428m, 1 417w, 1 368m, 1 180m, 1 088m, 1 071m, 1 008m, 987w, 964w, 946 (sh), 941w, 894w, 874vw, 863w, 840w, 818w, 790m, 766m, 751m, 720w, 703w, 678w
(2) Ca(pmcp)$_2$	ν(C=O) 1 733s, 1 704s, 1 684vs, 1 615vs ν(C–O) 1 310s, 1 290s, 1 252s, 1 200s	1 428m, 1 418m, 1 408w, 1 367m, 1 178s, 1 085m, 1 071m, 1 006m, 991m, 960w, 942m, 889m, 866w, 857vw, 848w, 817w, 789m, 768m, 750m, 721w, 703w, 678w
(3) Sr(pmcp)$_2$·3H$_2$O	ν(OH) 3 620m, 3 545m, 3 485m, 3 420m ν(C=O) 1 760—1 650vs (vbr) ν(C–O) 1 297s, 1 220s (br)	1 485 (sh), 1 420w, 1 408w, 1 368 (sh), 1 178s, 1 087m, 1 070m, 1 008m, 987m, 965w, 944m, 885w, 880w, 869vw, 858w, 836m, 810vw, 795 (sh), 791m, 781w, 759m, 750w, 721w, 701w, 678w
(4) Ba(pmcp)$_2$	ν(C=O) 1 705s, 1 700 (sh), 1 689s, 1 664 (sh), 1 657 (sh), 1 653s, 1 646s ν(C–O) 1 293s, 1 230s, 1 209s	1 419w, 1 403w, 1 368w, 1 178s, 1 076m, 1 007m, 984w, 940w, 880w, 860w, 848w, 806vw, 793w, 785w, 763w, 753m, 721w, 695w
(5) Zn(pmcp)$_2$·3H$_2$O	ν(OH) 3 440m, 3 355m (br) ν(C=O) 1 750m, 1 709s, 1 687m, 1 660s ν(C–O) 1 313m, 1 279m, 1 236s, 1 215m, 1 200s	1 460 (sh), 1 430 (sh), 1 420w, 1404w, 1 368 (sh), 1 178m, 1 087m, 1 071m, 1 008m, 988w, 940w, 890w, 862w, 836vw, 815w, 791w, 760w, 751w, 720vw, 705w
(6) Cd(pmcp)$_2$	ν(C=O) 1 732m, 1 707m, 1 688 (sh), 1 674s, 1 657 (sh), 1 650s, 1 635w ν(C–O) 1 312m, 1 289m, 1 254s, 1 202s	1 484 (sh), 1 460 (sh), 1 425w, 1 415w, 1 364m, 1 170m, 1 086m, 1 070m, 1 005m, 989w, 959vw, 940w, 889w, 866vw, 839w, 816w, 789m, 762w, 749w, 720w, 700w

effectively act as chelates, while the other two contacts arise from the remaining substituents in symmetry-related ligands. Empirical bond valences, calculated from the relationship $S = (R/R_1)^{-N}$ (where R = observed Ba–O distance, R_1 = 2.297, and N = 7.0), fall in the range 0.18—0.36, total 2.28; a value of *ca.* 2.3 is often found for barium compounds, rather than the ideal value of 2.0.[8]

As in most of the alkali-metal complexes reported in the previous paper, we find that for each of the ligands two of the substituents lie pseudo-perpendicular to the ring plane, while the others are more nearly parallel; in each ligand two of the latter form the chelating pair of substituents. In ligand b, however, two chelating pairs are used, as was the case in the potassium salt, and in both of these salts we find that in one of the chelate pairs a pseudo-normal substituent is necessarily employed.

In contrast with the cyclopentadienide analogues, the anion in (4), as also in the compounds studied previously, interacts with the metal by way of the carbonyl oxygen atoms of one or more of the carboxylate groups, and where the ratio of potentially co-ordinating carbonyl oxygen atoms is sufficiently high relative to the number of co-ordination sites about the metal a strong tendency to chelation is observed. In this situation, chelation tends to occur *via* the carbonyl oxygen atoms of a pair of CO$_2$Me substituents in which the carboxyl plane is quasi-parallel to the C$_5$ ring plane. Where the metal ion is small, as is the case in the extreme example of hydrogen, the two carboxyl groups are closely coplanar with the C$_5$ ring; in the hydrogen case the dihedral angles are (Table 6) 3.3 and 0.7°, and a significant related feature appears to be that the O $\cdots$ O distance in this case is less than the van der Waals sum [2.431(4) Å] with the hydrogen atom being almost collinear. As the metal-atom size increases, the metal rapidly moves out of the O $\cdots$ O line [O–Li–O for example is 95.1(3)°] and the two oxygen atoms more directly confront each other; the tendency for the associated carboxyl groups to remain coplanar with the C$_5$ ring is greatly reduced. In those ligands which do not behave in a bis(chelate) capacity but which are monochelating, *i.e.* in the lithium and thallium salts, and ligand a of the barium salt, we find dihedral angles remaining

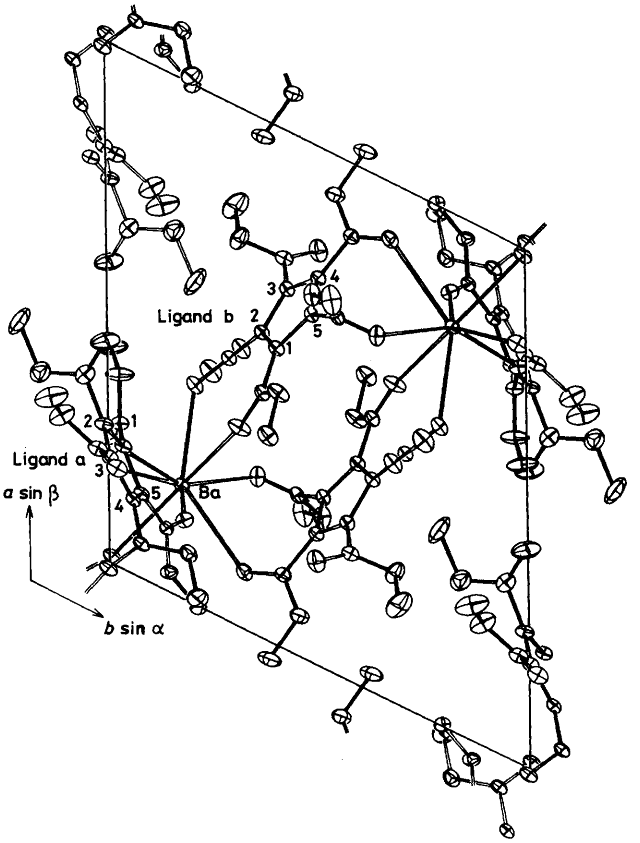


Figure. Unit-cell contents of Ba[C$_5$(CO$_2$Me)$_5$)]$_2$ projected down *c*; 20% thermal ellipsoids are shown of the non-hydrogen atoms. Atom labelling within each of the C$_5$ rings is given

Table 2. Non-hydrogen atom co-ordinates for Ba[$C_5(CO_2Me)_5$]$_2$

	Ligand a			Ligand b		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Ba	0.218 62(1)	0.174 01(1)	0.424 44(1)			
C(1)	0.238 1(2)	0.035 1(3)	0.015 7(2)	0.571 7(2)	0.404 7(3)	0.447 7(3)
C(11)	0.278 2(2)	0.028 0(3)	0.146 7(2)	0.472 2(2)	0.369 2(3)	0.351 1(3)
O(11)	0.233 7(2)	0.018 0(2)	0.233 7(2)	0.384 4(2)	0.313 9(3)	0.358 5(3)
O(12)	0.371 5(2)	0.028 5(3)	0.161 7(2)	0.487 8(2)	0.407 8(2)	0.245 6(2)
C(12)	0.416 2(4)	0.010 8(6)	0.283 4(4)	0.395 9(3)	0.381 7(4)	0.144 4(3)
C(2)	0.260 9(2)	−0.010 5(3)	−0.096 3(3)	0.588 1(2)	0.369 9(3)	0.565 9(3)
C(21)	0.338 3(3)	−0.054 7(4)	−0.104 1(3)	0.507 4(2)	0.290 6(3)	0.616 6(3)
O(21)	0.421 5(3)	−0.005 1(4)	−0.124 9(4)	0.422 9(2)	0.208 3(2)	0.553 2(2)
O(22)	0.299 8(3)	−0.162 5(3)	−0.092 6(3)	0.537 4(2)	0.320 4(2)	0.749 2(2)
C(22)	0.377 8(7)	−0.211 7(6)	−0.118 2(8)	0.465 2(4)	0.247 0(4)	0.810 1(4)
C(3)	0.203 3(2)	0.003 2(3)	−0.206 3(2)	0.696 0(2)	0.431 3(3)	0.630 5(3)
C(31)	0.208 8(2)	−0.025 8(3)	−0.341 9(3)	0.752 3(2)	0.424 9(3)	0.756 3(3)
O(31)	0.189 3(2)	0.019 8(2)	−0.424 4(2)	0.799 7(2)	0.506 8(2)	0.854 4(2)
O(32)	0.238 1(3)	−0.111 2(3)	−0.366 3(2)	0.747 4(3)	0.318 9(3)	0.747 3(3)
C(32)	0.262 5(5)	−0.136 3(7)	−0.488 9(4)	0.806 3(6)	0.310 5(6)	0.863 6(6)
C(4)	0.144 7(2)	0.057 5(2)	−0.162 7(2)	0.746 8(2)	0.505 8(3)	0.556 5(3)
C(41)	0.066 5(2)	0.075 7(3)	−0.252 6(3)	0.858 0(2)	0.586 2(3)	0.582 0(3)
O(41)	−0.013 7(2)	−0.004 7(2)	−0.327 4(2)	0.889 6(2)	0.678 4(2)	0.551 3(3)
O(42)	0.092 9(2)	0.188 2(2)	−0.245 5(3)	0.922 6(2)	0.549 0(2)	0.639 8(3)
C(42)	0.014 6(4)	0.208 7(4)	−0.322 8(5)	1.034 5(3)	0.621 9(5)	0.666 3(5)
C(5)	0.164 0(2)	0.077 7(2)	−0.025 3(2)	0.669 6(2)	0.488 3(2)	0.444 7(3)
C(51)	0.120 8(2)	0.136 0(2)	0.057 9(3)	0.690 3(2)	0.550 3(3)	0.340 8(3)
O(51)	0.154 0(2)	0.179 6(2)	0.176 1(2)	0.692 0(2)	0.644 4(2)	0.344 4(2)
O(52)	0.037 4(2)	0.140 9(2)	−0.012 8(2)	0.708 7(2)	0.490 5(2)	0.242 9(2)
C(52)	−0.003 3(3)	0.210 0(3)	0.059 5(4)	0.716 7(5)	0.536 4(4)	0.129 0(4)

Table 3. Metal-atom environment: *r* is the metal–ligand distance (Å); the other entries are the angles (°) subtended at the metal by the ligand atoms in question. Atoms derived from ligand b are italicised

	r	O(51)	*O*(11)	*O*(21)	O(31$^{\mathrm{I}}$)	*O*(41$^{\mathrm{II}}$)	*O*(51$^{\mathrm{II}}$)	O(41$^{\mathrm{III}}$)
O(11)	2.707(3)	64.47(8)	78.34(8)	82.49(7)	89.44(9)	138.67(7)	150.82(7)	78.93(8)
O(51)	2.695(2)		71.34(7)	126.29(8)	141.21(6)	75.81(8)	129.07(8)	73.83(7)
O(11)	2.655(3)			60.88(9)	133.65(10)	100.05(10)	82.70(8)	144.05(7)
O(21)	2.855(3)				73.36(7)	133.24(6)	68.89(9)	141.70(9)
O(31$^{\mathrm{I}}$)	2.744(3)					117.24(8)	87.79(7)	73.27(8)
O(41$^{\mathrm{II}}$)	2.932(3)						66.42(8)	79.61(8)
O(51$^{\mathrm{II}}$)	2.760(2)							127.57(8)
O(41$^{\mathrm{III}}$)	2.731(2)							

Associated M–O–C angles
Ligand a: Ba–O(11,51)–C 133.8(2), 153.1(3); Ba–O(31,41)–C 160.0(2), 160.7(2)
Ligand b: Ba–O(11,21)–C 164.0(3), 137.5(3); Ba–O(41,51)–C 120.8(3), 121.4(2)
Transformations of the asymmetric unit: I $x, y, 1 + z$; II $1 - x, 1 - y, 1 - z$; III $\bar{x}, \bar{y}, \bar{z}$.

below 30° with O · · · O distances (*w* in Table 6) remaining at about the van der Waals sum of *ca.* 2.8 Å, irrespective of metal-atom size. We also find the metal atom lying relatively close to the C_5 ring plane, with the carboxyl dihedral angles pitched so that the two O(*n*1) atoms lie on either side of the C_5 plane. In the case of the bis(chelating) ligands found in the potassium and barium salts (ligand b) we find an ambiguous situation brought about by the apparent impossibility of the carboxyl substituents lying coplanar with the C_5 ring. In the barium salt (ligand b) we find one chelate to be well behaved in the above terms [O(11,21)], but the other necessarily contains a well out-of-plane carboxyl group and is not, while the ligand in the potassium salt has a pair of rather poorly behaved chelates.

In the salts of H, Li, Tl, and Ba (ligands a), a number of effects may be observed in the ligand geometries which diminish rapidly in both their effectiveness and/or precision of measurement as the metal size increases. C(*n*1)–O(*n*1) is longer than is the case in the non-chelated carboxyl CO groups, irrespective of whether the latter act in a unidentate manner or not, and this is particularly true of hydrogen (Table 6). C(*n*)–C(*n*1) is slightly shorter in chelated carboxyl groups, and C(*n*)–C(*n*′), *i.e.* the ring bond in the chelate, is very appreciably lengthened. Angular geometry appears to not be greatly affected; however, the O–C–O angle is diminished in the derivatives of H and Li relative to the remainder.

Within the C_5 ring, the C–C distances not involved in chelate rings lie around 1.40 Å; this is shorter than in [Ru{η-$C_5(CO_2Me)_5$}(η-C_5H_5)] (*ca.* 1.44 Å).[9] The latter value is in good agreement with the general run of C–C distances in [M(η^5-C_5H_5)$_2$] complexes, while the value of 1.40 Å compares more closely with the value of 1.38(1) Å found in [Na(C_5H_5)($Me_2NCH_2CH_2NMe_2$)]$_n$ to which is ascribed an ionic structure in spite of an η^5 confrontation with the sodium atom.[10] In all derivatives, C(*n*1) exhibit varying deviations from the C_5 plane, >0.1 Å being not unusual; these deviations do not correlate with carboxylate dihedral angles or mode of co-ordination.

Table 4. Ligand non-hydrogen geometries: distances (Å), angles (°)

	Ligand	
	a	b
C(1)–C(2)	1.395(5)	1.437(4)
C(2)–C(3)	1.407(5)	1.400(4)
C(3)–C(4)	1.395(5)	1.416(4)
C(4)–C(5)	1.407(4)	1.404(4)
C(5)–C(1)	1.435(5)	1.398(4)
C(1)–C(11)	1.461(4)	1.460(4)
C(2)–C(21)	1.462(7)	1.470(4)
C(3)–C(31)	1.461(4)	1.487(5)
C(4)–C(41)	1.482(5)	1.457(4)
C(5)–C(51)	1.449(5)	1.492(4)
C(11)–O(11)	1.222(4)	1.203(4)
C(21)–O(21)	1.195(6)	1.214(3)
C(31)–O(31)	1.207(5)	1.204(4)
C(5)–C(1)–C(2)	107.7(3)	107.3(2)
C(1)–C(2)–C(3)	108.4(4)	107.6(3)
C(2)–C(3)–C(4)	108.2(3)	108.4(3)
C(3)–C(4)–C(5)	108.8(3)	107.6(2)
C(4)–C(5)–C(1)	106.9(3)	109.0(3)
C(5)–C(1)–C(11)	128.7(3)	124.4(3)
C(2)–C(1)–C(11)	123.4(4)	128.1(3)
C(1)–C(2)–C(21)	128.3(3)	127.2(3)
C(3)–C(2)–C(21)	123.0(3)	125.1(3)
C(2)–C(3)–C(31)	126.6(4)	128.0(3)
C(4)–C(3)–C(31)	125.1(3)	123.5(3)
C(3)–C(4)–C(41)	123.4(2)	129.4(3)
C(5)–C(4)–C(41)	127.4(3)	122.9(3)
C(4)–C(5)–C(51)	125.8(3)	124.7(3)
C(1)–C(5)–C(51)	127.2(2)	126.2(3)
C(1)–C(11)–O(11)	126.8(3)	128.0(3)
C(2)–C(21)–O(21)	126.6(5)	127.4(3)
C(3)–C(31)–O(31)	125.5(4)	124.3(4)
C(41)–O(41)	1.206(3)	1.221(4)
C(51)–O(51)	1.210(3)	1.202(5)
C(11)–O(12)	1.331(5)	1.337(4)
C(21)–O(22)	1.312(6)	1.346(4)
C(31)–O(32)	1.338(7)	1.328(6)
C(41)–O(42)	1.327(4)	1.332(5)
C(51)–O(52)	1.343(4)	1.321(4)
O(12)–C(12)	1.456(6)	1.437(5)
O(22)–C(22)	1.548(11)	1.441(5)
O(32)–C(32)	1.437(7)	1.435(8)
O(42)–C(42)	1.431(7)	1.445(5)
O(52)–C(52)	1.445(6)	1.457(6)
C(4)–C(41)–O(41)	123.0(3)	123.3(3)
C(5)–C(51)–O(51)	126.8(3)	125.0(3)
C(1)–C(11)–O(12)	111.6(3)	111.5(3)
C(2)–C(21)–O(22)	109.3(4)	111.2(2)
C(3)–C(31)–O(32)	112.0(3)	112.3(2)
C(4)–C(41)–O(42)	114.3(2)	113.9(3)
C(5)–C(51)–O(52)	111.6(2)	112.2(3)
O(11)–C(11)–O(12)	121.5(3)	120.6(3)
O(21)–C(21)–O(22)	124.0(6)	121.3(3)
O(31)–C(31)–O(32)	122.6(3)	123.3(4)
O(41)–C(41)–O(42)	122.7(3)	122.7(3)
O(51)–C(51)–O(52)	121.5(3)	122.8(3)
C(11)–O(12)–C(12)	117.3(3)	117.1(3)
C(21)–O(22)–C(22)	107.7(4)	116.2(2)
C(31)–O(32)–C(32)	118.0(5)	114.4(3)
C(41)–O(42)–C(42)	115.3(3)	117.8(4)
C(51)–O(52)–C(52)	115.6(2)	116.2(4)

Table 5. Ligand least-squares planes 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 and Z in the ac plane. σ (defining atoms) and atom deviations δ are given in Å. Defining atoms are C(1)—C(5). $\theta(n)/°$ is the dihedral angle to the plane defined by $C(n,n1)$–$O(n1,2)$

	Ligand	
	a	*b*
10^4p	4 194	−6 030
10^4q	8 988	7 348
10^4r	−1 280	3 106
s	1.705	1.225
σ	0.003	0.006
δC(1)	0.003	−0.005
δC(2)	−0.001	0.008
δC(3)	−0.002	−0.007
δC(4)	0.003	0.004
δC(5)	−0.004	0.001
δC(11)	−0.093	0.066
δC(21)	0.116	0.106
δC(31)	0.080	−0.011
δC(41)	−0.127	−0.014
δC(51)	0.044	0.010
δO(11)	−0.633	0.286
δO(21)	1.082	−0.297
δO(31)	0.519	0.866
δO(41)	−1.128	0.541
δO(51)	0.358	0.998
δO(12)	0.447	−0.131
δO(22)	−1.045	0.740
δO(32)	−0.405	−1.119
δO(42)	0.960	−0.714
δO(52)	−0.271	−1.209
δC(12)	0.310	−0.048
δC(22)	−0.928	0.873
δC(32)	−0.205	−1.209
δC(42)	0.821	−0.812
δC(52)	−0.095	−1.300
θ(1)	27.1	10.5
θ(2)	74.1	28.7
θ(3)	24.5	63.3
θ(4)	69.9	34.2
θ(5)	16.4	88.0

Experimental

General experimental conditions have been described previously.[1]

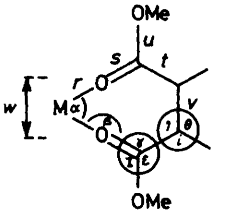
Preparation of $M[C_5(CO_2Me)_5]_2$.—(*a*) *From the metal acetate.* Magnesium acetate (122 mg, 0.85 mmol) was added to a solution of $HC_5(CO_2Me)_5$ (500 mg, 1.4 mmol) in methanol (10 cm³). After 2 h, the filtered reaction mixture was evaporated to dryness. Recrystallisation (MeOH) of the residue afforded white $Mg[C_5(CO_2Me)_5]_2{\cdot}H_2O$ (1) (191 mg, 53%), m.p. >300 °C (Found: C, 48.1; H, 3.90. $C_{30}H_{32}MgO_{21}$ requires C, 47.85; H, 4.25%).

(*b*) *From the metal carbonate.* Calcium carbonate (74 mg, 0.74 mmol) was added to an aqueous solution of $HC_5(CO_2Me)_5$ (500 mg, 1.4 mmol). Rapid evolution of CO_2 occurred, after which the solution was filtered. The filtrate was then reduced in volume until crystals formed on cooling. These were collected and recrystallised (MeOH) to give white $Ca[C_5(CO_2Me)_5]_2$ (2) (322 mg, 58%), m.p. 295—298 °C (Found: C, 47.9; H, 3.90. $C_{30}H_{30}CaO_{20}$ requires C, 48.0; H, 4.00%). Conductivity (H_2O): Λ 130 ohm^{-1} cm^2 mol^{-1}.

The following compounds were similarly prepared: white $Ba[C_5(CO_2Me)_5]_2$ (4) (78%), m.p. >300 °C (Found: C, 42.45; H, 3.50. $C_{30}H_{30}BaO_{20}$ requires C, 42.5; H, 3.55%); this compound was dried by azeotropic distillation of water with a benzene–ethanol mixture; white $Zn[C_5(CO_2Me)_5]_2{\cdot}3H_2O$ (5) (57%), m.p. 185 °C (decomp.) (Found: C, 43.55; H, 4.10. $C_{30}H_{36}O_{23}Zn$ requires C, 43.4; H, 4.35%); co-ordinated water was not removed after heating for 8 h at 100 °C *in vacuo*; white $Cd[C_5(CO_2Me)_5]_2$ (6) (44%), m.p. >300 °C (Found: C, 43.75; H, 3.55. $C_{30}H_{30}CdO_{20}$ requires C, 43.75; H, 3.65%).

(*c*) *From the metal chloride.* A solution of $Tl[C_5(CO_2Me)_5]$ (281 mg, 0.5 mmol) in methanol (15 cm³) was added to a solution of $SrCl_2{\cdot}6H_2O$ (69 mg, 0.26 mmol) in methanol (10

Table 6. ' Ionic ' ligand parameters: a tabulation of a number of significant ligand parameters for the compounds of ref. 1 and the present complex about the vicinity of the pairs of chelating ligand substituents CO-OMe at ring carbon atoms *l*, *m* where $l < m$. Also given are ranges R_x for the same parameters about the non-chelating ligand substituents (square brackets denote a single value only). Angles χ are the dihedral angles between the carboxyl plane defined by $C-CO_2(1)$ and the ring plane and δ is the deviation of the metal atom from the carboxyl plane and Δ the deviation from the ring plane. All distances are in Å and all angles in degrees. In each entry the upper value corresponds to the first of the two oxygen atoms and the lower to the second. In relevant cases, parameters of the η^5-$C_5(CO_2Me)_5$ group in $[Ru\{C_5(CO_2Me)_5\}(C_5H_5)]$ are included for comparison



Compound/ ligand	H	Li	K	K	Tl	Ba/a	Ba/b	Ba/b	Ru
Chelate	O(41)	O(11)	O(11)	O(31)	O(21)	O(11)	O(11)	O(41)	
system	O(51)	O(51)	O(21)	O(41)	O(31)	O(51)	O(21)	O(51)	
Distances/Å									
r	1.12(7)	1.914(7)	2.657(3)	2.762(3)	2.822(5)	2.707(3)	2.655(3)	2.932(3)	
	1.32(7)	1.900(7)	2.862(3)	2.726(3)	2.682(5)	2.695(2)	2.855(3)	2.760(2)	
s	1.256(3)	1.210(5)	1.199(5)	1.208(5)	1.204(7)	1.222(4)	1.203(4)	1.221(4)	
	1.259(4)	1.212(5)	1.229(5)	1.217(5)	1.207(7)	1.210(3)	1.214(3)	1.202(5)	
R_s	1.194(4)—	1.191(6)—	[1.203(5)]	[1.203(5)]	1.179(8)—	1.195(6)—	[1.204(4)]	[1.204(4)]	1.192(2)—
	1.205(4)	1.198(5)			1.212(8)	1.207(5)			1.200(2)
t	1.428(5)	1.453(5)	1.478(5)	1.484(6)	1.474(8)	1.461(4)	1.460(4)	1.457(4)	
	1.426(4)	1.450(5)	1.446(5)	1.464(5)	1.451(7)	1.449(5)	1.470(4)	1.492(4)	
R_t	1.460(3)—	1.461(6)—	[1.457(6)]	[1.457(6)]	1.458(8)—	1.461(4)—	[1.487(5)]	[1.487(5)]	1.485(2)—
	1.498(5)	1.499(5)			1.487(8)	1.482(5)			1.502(2)
u	1.316(4)	1.338(4)	1.335(5)	1.329(5)	1.334(7)	1.331(5)	1.337(4)	1.332(5)	
	1.320(5)	1.345(4)	1.331(5)	1.338(5)	1.343(7)	1.343(4)	1.346(4)	1.321(4)	
R_u	1.328(4)—	1.323(5)—	[1.340(5)]	[1.340(5)]	1.327(7)—	1.312(6)—	[1.328(6)]	[1.328(6)]	1.331(2)—
	1.342(4)	1.334(5)			1.340(5)	1.338(7)			1.335(3)
v	1.453(5)	1.447(5)	1.416(6)	1.394(5)	1.448(7)	1.435(5)	1.437(4)	1.404(4)	
R_v	1.396(3)—	1.393(5)—	1.404(5)—	1.404(5)—	1.386(8)—	1.395(6)—	1.398(4)—	1.398(4)—	1.430(2)—
	1.410(5)	1.415(5)	1.426(5)	1.426(5)	1.424(7)	1.407(4)	1.416(4)	1.416(4)	1.442(2)
w	2.431(4)	2.813(3)	3.039(4)	3.041(4)	2.820(7)	2.881(4)	2.796(4)	3.120(4)	
δ	0.15	0.807	1.894	2.298	1.197	1.858	0.207	1.520	
	0.07	0.780	2.092	1.906	1.816	0.920	1.909	1.537	
R_δ		[0.675]	[1.926]	[1.926]					
Δ	0.07	0.540	0.995	0.493	0.534	0.173	0.561	3.141	1.796
Angles/°									
α	171(3)	95.1(3)	66.7(1)	67.3(1)	61.6(1)	64.47(8)	60.88(9)	66.42(8)	
β	109.8(16)	138.1(3)	134.6(3)	123.1(3)	148.2(4)	133.8(2)	164.0(3)	120.8(3)	
	109.8(13)	138.3(3)	132.1(3)	136.7(3)	137.3(4)	153.1(3)	137.5(3)	121.4(2)	
γ	125.2(7)	127.2(3)	125.7(4)	125.9(4)	127.9(5)	126.8(3)	128.0(3)	123.3(3)	
	125.5(3)	128.1(3)	126.2(4)	125.4(4)	125.6(5)	126.8(3)	127.4(3)	125.0(3)	
R_γ	124.0(3)—	125.3(4)—	[126.6(4)]	[126.6(4)]	123.3(5)—	123.0(3)—	[124.3(4)]	[124.3(4)]	121.3(2)—
	125.5(3)	126.0(4)			125.0(5)	126.6(5)			125.9(2)
ε	116.1(2)	112.2(3)	110.5(3)	110.7(3)	109.1(4)	111.6(3)	111.5(3)	113.9(3)	
	115.4(3)	111.7(3)	112.0(3)	112.1(3)	113.2(5)	111.6(2)	111.2(2)	112.2(3)	
R_ε	109.5(2)—	110.3(4)—	[111.5(3)]	[111.5(3)]	111.5(5)—	109.3(4)	[112.3(2)]	[112.3(2)]	108.8(1)
	112.0(3)	112.0(3)			112.6(5)	−114.3(2)			−113.7(1)
ς	118.7(3)	120.5(3)	123.8(4)	123.4(4)	123.0(5)	121.5(3)	120.6(3)	122.7(3)	
	119.1(3)	120.3(3)	121.8(4)	122.5(4)	121.2(5)	121.5(3)	121.3(3)	122.8(3)	
R_ζ	123.1(2)—	122.6(4)—	[121.9(4)]	[121.9(4)]	123.0(5)—	122.6(3)—	[123.3(4)]	[123.3(4)]	124.8(2)—
	125.0(3)	123.7(4)			124.1(5)	124.0(6)			125.3(2)
η	127.6(2)	128.2(3)	126.7(3)	125.3(3)	128.1(5)	128.7(3)	128.1(3)	122.9(3)	
	126.9(3)	128.5(3)	126.3(3)	124.0(3)	125.4(5)	127.2(2)	127.2(3)	124.7(3)	
$R_{\eta,i}$	122.9(2)—	123.3(3)—	125.8(4)—	125.8(4)—	123.6(5)—	123.0(3)—	123.5(3)—	123.5(3)—	122.4(1)—
	128.4(3)	128.3(3)	126.2(4)	126.2(4)	128.1(5)	128.3(3)	128.0(3)	128.0(3)	128.7(1)
θ	107.3(2)	107.2(3)	108.2(3)	108.7(3)	107.6(5)	107.7(2)	107.3(2)	107.6(2)	
	107.2(2)	107.3(3)	107.5(3)	107.8(3)	107.3(4)	106.9(3)	107.6(3)	109.0(3)	
R_θ	108.1(2)—	107.7(3)—	[107.9(3)]	[107.9(3)]	107.8(5)—	108.2(3)—	[108.4(3)]	[108.4(3)]	107.8(1)—
	108.8(3)	109.2(3)			109.0(5)	108.8(3)			108.4(1)
i	125.1(3)	124.5(3)	125.2(4)	126.0(4)	124.2(5)	123.4(4)	124.4(3)	129.4(3)	
	126.0(3)	123.9(3)	126.2(4)	127.8(4)	127.3(5)	125.8(3)	125.1(3)	126.2(3)	
χ	3.3	4.4	56.0	62.5	27.4	27.1	10.5	34.2	
	0.7	24.0	20.5	34.1	25.9	16.4	28.7	88.0	
R_χ	8.8	5.6	[35.7]	[35.7]	10.8	24.5	[63.3]	[63.3]	5.2
	−88.1	−90.0			−77.7	−74.1			−89.2

cm^3). Immediate precipitation of TlCl occurred, and after 2 h the mixture was filtered. Evaporation and recrystallisation (MeOH) afforded white $Sr[C_5(CO_2Me)_5]_2\cdot 3H_2O$ (3) (51%), m.p. 218 °C (decomp.) (Found: C, 42.45; H, 4.20. $C_{30}H_{36}O_{23}Sr$ requires C, 42.3; H, 4.25%). Conductivity (H_2O): Λ 155.6 ohm^{-1} cm^2 mol^{-1}.

Crystallography.—The general procedure was outlined in the previous paper.[1]

Crystal data. $C_{30}H_{30}BaO_{20}$, $M = 847.9$, Triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 14.499(4)$, $b = 12.940(4)$, $c = 10.745(2)$ Å, $\alpha = 100.54(2)$, $\beta = 100.02(2)$, $\gamma = 114.23(2)°$, $U = 1\,736.1(7)$ Å^3, $D_m = 1.62(1)$, $Z = 2$, $D_c = 1.62$ g cm^{-3}, $F(000) = 852$, specimen size 0.24 × 0.12 × 0.06 mm (plate mounted in capillary), $\mu_{Mo} = 11.8$ cm^{-1}, $N = 10\,549$, $N_o = 8\,173$, R,R', $S = 0.036, 0.047, 1.43$.

Data acquisition was terminated at $h = 14$ due to instrument malfunction, in consequence the intensities of a small number of very strong reflections were not determined and these are omitted from the structure-factor listing.

Conclusions

The Group 2A metals all form hydrocarbon analogues of the compounds reported above, which are unstable in air, and rapidly hydrolyse in contact with water.[11-13] In the vapour phase,[14] both $Mg(C_5H_5)_2$ and $Ca(C_5H_5)_2$ have structures in which the C_5 rings are symmetrically attached to the metal ion. In the crystal, the structure of the magnesium compound is the same,[15] but the calcium derivative adopts a polymeric structure in which each calcium is co-ordinated by one σ, one η^3, and two η^5 rings.[16] In both cases, the interaction is described as ionic (' electrostatic '), *i.e.* the compounds are $M^{2+}(C_5H_5^-)_2$. The zinc analogue has covalent ring–metal bonds, but is also air- and water-sensitive.[17] No cadmium derivative has been reported. The pmcp compounds described above all showed the marked stability now expected of derivatives containing the new ligand. On the basis of their i.r. spectra, and the *X*-ray structure determination, all are considered to have the pmcp group attached *via* metal–oxygen bonds; in the zinc case, and perhaps also the magnesium and strontium compounds, one or more co-ordination sites are probably occupied by water molecules.

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