Pentakis(methoxycarbonyl)cyclopentadiene Chemistry. Part 1. Preparation and Properties of the Diene, and of Derivatives containing the Alkali Metals or Thallium(I): Crystal and Molecular Structures of $HC_5(CO_2Me)_5$, $Li[C_5(CO_2Me)_5]\cdot H_2O$, $K[C_5(CO_2Me)_5]\cdot MeOH$, and $Tl[C_5CO_2Me)_5]$ †

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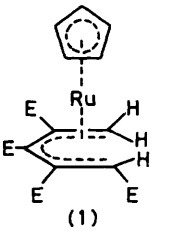
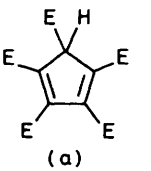
The alkali metal (Li, Na, K, Rb, and Cs) and thallium(I) derivatives of $HC_5(CO_2Me)_5$ have been prepared and characterised; their i.r., u.v., ^1H, and ^{13}C n.m.r. spectra are reported and discussed. Single-crystal *X*-ray structure determinations have been carried out on the diene and its Li, K, and Tl salts at 295 K. In the solid, as in non-polar solvents, the diene has the fulvenoid configuration, with the acidic proton bridging two adjacent carbonyl groups. This configuration is preserved in univalent metal cation salts. Lithium is four-co-ordinate (from two carbonyl oxygens, the water molecule, and a carbonyl oxygen from a second anion). In the potassium salt, the metal is co-ordinated by methanol, and five carbonyl oxygens from three different anions; all carbonyl oxygens of each anion are likewise involved in co-ordination to three different metal atoms. In the thallium salt the metal has irregular five-co-ordination, with two chelating carbonyl groups from one anion and three from separate anions; all carbonyl oxygens of each anion co-ordinate to four different metal atoms.

Since the fortuitous discovery of ferrocene, $[Fe(\eta\text{-}C_5H_5)_2]$, and the recognition of its remarkable properties, the cyclopentadienyl ligand has played an important role in the development of organometallic chemistry. The substitution chemistry of ferrocene has encompassed many attempts, but not many successes, to make penta- or deca-substituted derivatives. In recent years, however, the strong electron-donor characteristics of penta-alkylcyclopentadienyl ligands have resulted in syntheses of many unusual complexes,[1] not least being those of the early transition elements [2] and those containing multiple metal–metal bonds.[3]

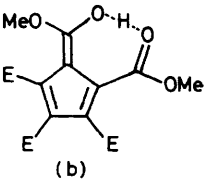
We have commenced a study of the chemistry of cyclopentadienyl ligands bearing four or five electron-withdrawing groups, exemplified in the first instance by the CO_2Me group. Our attention was drawn to this neglected area of chemistry by the isolation and characterisation of complex (1), which contains a η^5-tetrakis(methoxycarbonyl)pentadienyl ligand.[4] We also noted King's observation [3] that 'complete substitution of cyclopentadienyl hydrogens with electronegative groups such as cyano and alkoxycarbonyl should lead to removal of electron density from the filled ring *A* and E_1 orbitals to the extent that stable pentahapto metal–ring bonds are no longer possible,' which at that time appeared to be supported by the only available and relevant evidence that the iron(II) complex derived from pentakis(methoxycarbonyl)cyclopentadiene was soluble in water and appeared to have no covalent properties.[5] We also noted that other related compounds, derived from dicyanobis(ethoxycarbonyl)- and tetracyano-cyclopentadiene, were described as 'ferrous salts, which were not ferrocenes';[6] so-called decacyanoferrocene is a light green, non-volatile, and extremely air-sensitive solid, suggesting it to be an iron(II) derivative rather than a ferrocene.[7] On the other hand, poly-



(1)



(a)



(b)

(2)

E = CO_2Me

chloro-ferrocenes and -ruthenocenes had been described,[8] and the crystal structure of $[Ru(\eta^5\text{-}C_5Cl_5)_2]$ showed that this compound had the expected sandwich structure.[9]

Pentakis(methoxycarbonyl)cyclopentadiene, $HC_5(CO_2Me)_5$ or Hpmcp (2), has been known since 1942, when Diels [10] described its formation as one of the products from a reaction of potassium acetate with the dimethyl malonate–dimethyl acetylenedicarboxylate adduct. This reaction was further explored by Cookson *et al.* in 1961,[11] and by Le Goff and LaCount [12] 3 years later. The former reported that (2) is a strong acid, soluble in water to give solutions which have the same pH as aqueous solutions of HCl of similar concentrations. They further reported that such solutions dissolve iron with evolution of hydrogen, and formation of yellow $[Fe(pmcp)_2]$.[5] Further investigations of its inorganic derivatives appear to be limited to the synthesis of the silver derivative *in situ*, which has been used subsequently in alkylation studies, but not further characterised.[13]

This paper describes the syntheses and properties of several pmcp salts of univalent metal ions, including the *X*-ray crystal structures of the lithium, potassium, and thallium(I) derivatives, as well as of the parent diene. A preliminary account of some of this work has been published.[14]

† *Supplementary data available* (No. SUP 23352, 47 pp.): thermal parameters, methyl H-atom parameters and geometries, structure-factor amplitudes. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Infrared data (cm^{-1}) obtained from Nujol mulls

Compound	Significant bands	Other bands
(2) Hpmcp	ν(C=O) 1 748m, 1 731s, 1 713s ν(C=O + C=C) 1 610s ν(CO) 1 274m, 1 237s, 1 220s	1 493 (sh), 1 432m, 1 424w, 1 376w, 1 195m, 1 183m, 1 172w, 1 097m, 1 084m, 1 003m, 988m, 950w, 935m, 887m, 832w, 817w, 794m, 787w, 761m, 751w, 722w, 703w
(3) Li(pmcp)·H_2O	ν(OH) 3 570s, 3 509m ν(C=O) 1 725s, 1 715s ν(CO) 1 298s, 1 242s	1 488s, 1 455 (sh), 1 434m, 1 406w, 1 205s, 1 193s, 1 180s, 1 170 (sh), 1 082s, 1 009m, 988w, 965w, 943m, 887w, 861w, 839w, 816w, 789m, 767w, 751m, 721w, 699w
(4) Na(pmcp)	ν(C=O) 1 732w, 1 710s, 1 695s, 1 675s ν(CO) 1 291s, 1 240s	1 485 (sh), 1 445 (sh), 1 425w, 1 400w, 1 367w, 1 217w, 1 205w, 1 197m, 1 177m, 1 080m, 1 017m, 987w, 952w, 947w, 882w, 842w, 796w, 786w, 760w, 726w, 690w
(5) K(pmcp)	ν(C=O) 1 723s, 1 709s, 1 681s, 1 666s, 1 656 (sh) ν(CO) 1 295 (sh), 1 281s, 1 226s, 1 214s	1 512m, 1 490m, 1 432m, 1 424m, 1 398m, 1 370 (sh), 1 199s, 1 176s, 1 075 (sh), 1 069m, 1 010m, 999m, 988w, 955m, 937m, 882w, 872m, 857w, 845w, 804w, 789m, 781w, 765m, 755w, 722w, 700w, 693w, 644w, 611w
(6) Rb(pmcp)	ν(C=O) 1 715s, 1 700vs, 1 685s, 1 675 (sh), 1 668vs, 1 650 (sh) ν(CO) 1 292s, 1 272s, 1 220s	1 555w, 1 495s, 1 475 (sh), 1 429m, 1 393m, 1 366w, 1 195s, 1 175s, 1 085m, 1 070m, 1 010m, 995m, 986w, 963w, 940m, 874m, 859w, 844m, 805w, 795m, 791m, 781w, 765w, 755m, 722w, 695w, 673w, 655w
(7) Cs(pmcp)	ν(C=O) 1 730s, 1 720s, 1 695s, 1 675s ν(CO) 1 286m, 1 238s, 1 206s	1 554w, 1 489s, 1 480s, 1 439m, 1 424m, 1 395m, 1 385m, 1 367w, 1 195s, 1 173s, 1 160m, 1 155s, 1 073m, 1 004m, 990w, 964w, 940 (sh), 937m, 877w, 859w, 839m, 806w, 790m, 762w, 752m, 723w, 702m
(8) Tl(pmcp)	ν(C=O) 1 720 (sh), 1 715s, 1 695s, 1 670s ν(CO) 1 293m, 1 285m, 1 235s, 1 206m	1 552w, 1 488m, 1 475 (sh), 1 440m, 1 424m, 1 398w, 1 368 (sh), 1 200 (sh), 1 191m, 1 173m, 1 160m, 1 072m, 1 002m, 990m, 960w, 936w, 877w, 858w, 838m, 805w, 788m, 759w, 751w, 720w, 699w

Results and Discussion

Pentakis(methoxycarbonyl)cyclopentadiene.—Diene (2) was prepared in *ca.* 70% overall yield from dimethyl malonate and dimethyl acetylenedicarboxylate by a slight modification of the literature preparation.[12] This reaction has been discussed in detail previously. The compound forms white air-stable crystals, m.p. 146—148 °C, which turn red on heating. It is soluble in solvents with a wide range of polarity, such as benzene, chloroform, tetrahydrofuran, alcohols, acetone, and water, but insoluble in light petroleum or diethyl ether. The i.r. spectrum is detailed in Table 1, and is characterised by strong ν(CO) bands between 1 713 and 1 748 cm^{-1}; a broad strong absorption at 1 610 cm^{-1} is assigned to a stretching mode originating from the conjugated C=O and C=C system, and has been noted previously in carbonyl-substituted fulvenes with intramolecular hydrogen bonds. In addition, the ν_{asym}(CO) modes are found between 1 220 and 1 274 cm^{-1}. The electronic spectra are similar to those reported earlier: high ε values are indicative of extended conjugation in the molecule, while solvent shifts consistent with tautomeric changes were observed.[5]

Of interest are the ^1H and ^{13}C n.m.r. spectra, which have not been previously reported in detail. In non-polar solvents, such as benzene, the protons of the five Me groups resonated as a broad singlet at δ 3.5; in $CDCl_3$ this resonance occurred at δ 3.95, while the acidic proton is greatly deshielded and is found at δ 31.10. In contrast, solutions in polar solvents such as acetone and water allow complete ionisation, and in these solvents the CO_2Me resonance, now quite sharp, is found at δ 3.72 and 4.35, respectively. The ^{13}C n.m.r. spectrum contains three resonances assigned to the Me (δ 53.56), ring (118.18), and carbonyl carbons (170.47), respectively. In polar solvents, the equivalence of each type of ^1H or ^{13}C nucleus indicates that the compound is fully ionised; the broadening found in non-polar solvents may be the result of incomplete ionisation, or of rapid tautomerism. So far we have not been able to carry out any variable-temperature studies.

The structure of (2) has been written as the diene (2a) or as the tautomeric fulvene (2b); alkylation, either of (2) with diazomethane or of the silver derivative with iodomethane, results in attachment of the methyl group to a ring carbon. Infrared and ^1H n.m.r. studies of the related tetrasubstituted diene,[15] and of the di- and tri-carbaldehydes,[16] were interpreted in terms of the fulvenoid structure. The diffuse-reflectance spectrum of the solid is reported to resemble that of the anion in solution, although whether this was a result of lattice perturbations of absorptions expected for (2a) or (2b), or of a three-dimensional hydrogen-bonded structure in the solid, with an internally hydrogen-bonded hydroxyfulvene structure (2b) in solution, could not be determined.[5]

Solid-state structure of (2). We have determined the solid-state structure of (2) (Figures 1 and 2, Tables 2—5), and find that it corresponds to the hydroxyfulvene (2b); the acidic proton has been located, and bridges two of the carbonyl oxygens from adjacent CO_2Me groups. There is extensive delocalisation extending over eight bonds, from one of the hydrogen-bonded oxygens, around the five-membered ring, and out to the second of these oxygens. The single ring C–C bond which does not take part in this delocalisation is significantly longer than the other four ring C–C bonds.

The location of the acidic hydrogen atom is the chief feature of interest in this structure. Location and refinement of positional and thermal parameters for all hydrogen atoms, together with the evidence of the geometry of the cyclopentadienyl ring, shows that the acidic hydrogen is not associated with the central ring in any way at all, but is disposed or chelated slightly unsymmetrically between two of the carbonyl oxygen atoms of adjacent ring substituents, H · · · O(41,51) being 1.12(4), 1.32(4) Å with O · · · H · · · O 171(3)°. Carboxylate groups 2,4,5 lie almost parallel to the plane of the central ring, while carboxylates 1,3 lie almost normal (Table 7). Significant but trivial variations are observed in the internal angular geometry of the ring; significant and non-trivial variations are observed in the bonding distances within the ring. Four of these distances are essentially equal lying in the range 1.396(3)—1.410(5) Å; the fifth is quite different [C(4)–C(5) 1.453(5) Å] and, in fact, is the bond between the carbon atoms with those substituent carboxylate groups associated with the acidic hydrogen. About the ring, the exocyclic angles at the substituents are unsymmetrical at all carbon atoms except C(5); the asymmetry does not correlate with the deviation of the carboxylate from coplanarity with the central

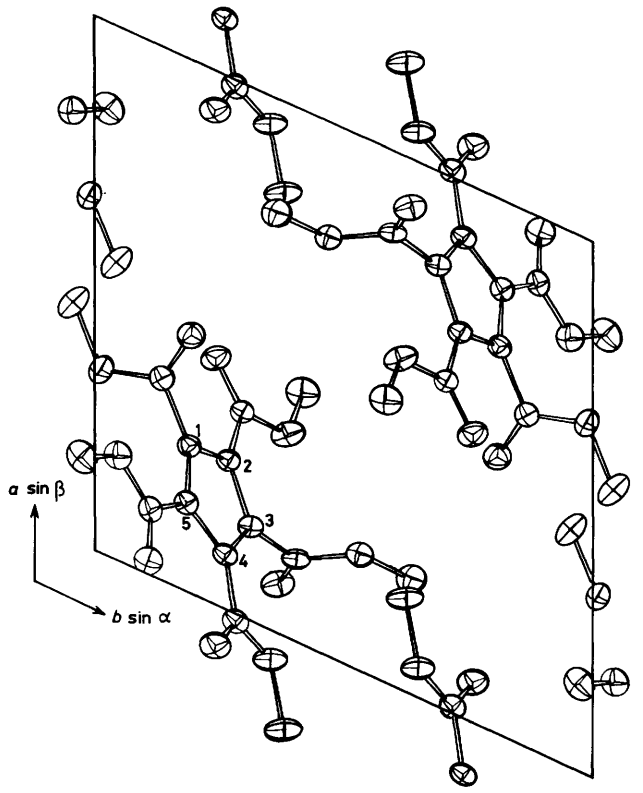
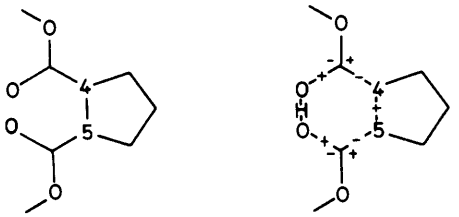


Figure 1. Unit-cell contents of (2) projected down *c*, showing non-hydrogen atoms with 20% thermal ellipsoids

ring, neither does it correlate with the '*cis*/*trans*' disposition of the substituent atoms at either end of the C(*n*)–C(*n*1) bond by which it is attached. Within the carboxylate groups, variation in the C–O–CH_3 distances and the angles C(*n*)–C(*n*1)–O(*n*1) is trivial; substantial variations are observed in the C(*n*)–C(*n*1) and C(*n*1)–O(*n*1) distances and the angles C(*n*)–C(*n*1)–O(*n*2) and O(*n*1)–C(*n*1)–O(*n*2) correlating with the presence or absence of interaction of the carboxylate group with the acidic hydrogen. In carboxylates 4 and 5 we find C(*n*1)–O(*n*1) and C(*n*)–C(*n*1)–O(*n*2) to be enlarged, while O(*n*1)–C(*n*1)–O(*n*2) is diminished relative to the non-interacting carboxylates. Changes in bond order associated with the protonation of carboxylates 4 and 5 may be summarised as below, a plus indicating an increase and a minus a decrease in the parameter indicated.



The overall effect thus appears to be strengthening of the C(*n*)–C(*n*1) bonds for $n = 4,5$ at the expense of the C(4)–C(5) bond and formation of O ··· H bond character at the expense of C(*n*1)–O(*n*1); variations in the angular geometry of the carboxylate are consistent with the electron-pair-repulsion prediction consequent upon such change in bond order. The change in the internal C(*n*)–C($n \pm 1$) distance of the ring relative to that of the symmetrical ring of potassium salt (5) (see below) is not significant. One final point worthy of note

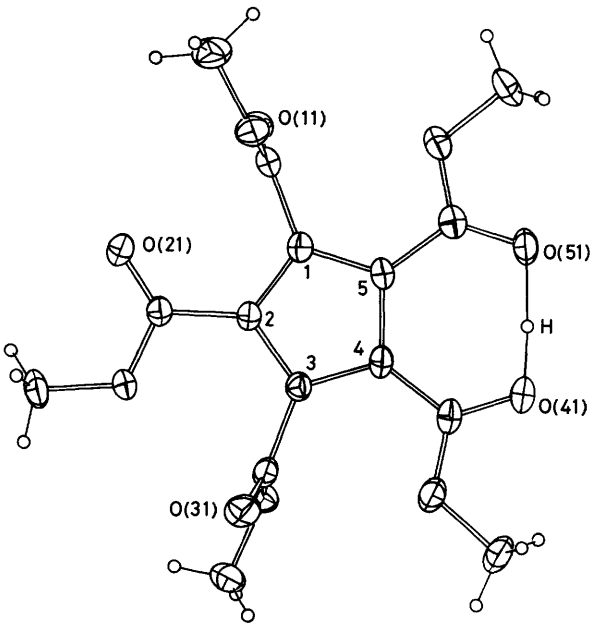


Figure 2. A ' molecule ' of (2). Hydrogen atoms are shown with an arbitrary radius of 0.1 Å. Projection is normal to the cyclopentadienide plane

is that the two adjacent carboxylate groups which lie parallel to the central ring plane chelate the hydrogen; the next two carboxylates adjacent to these are normal, while the last, opposite the hydrogen, is again parallel.

Salts of (2) *with Univalent Cations.*—We have prepared and characterised the lithium (3), sodium (4), potassium (5), rubidium (6), caesium (7), and thallium(I) (8) salts of diene (2). As reported earlier,[12] the potassium salt obtained by heating the octakis(methoxycarbonyl)cycloheptadiene isomers with potassium acetate is initially obtained as a yellow crystalline material, but on recrystallisation from water or methanol a pure white crystalline product is obtained. The diene (2) is a strong acid, and other alkali-metal salts are readily formed by treating the carbonates with (2) in aqueous solution. This reaction could also be applied to the synthesis of the thallium(I) derivative, which is a useful source of the $C_5(CO_2Me)_5$ group in exchange reactions with metal halides. Indeed, in the present work, the rubidium and caesium salts were also obtained in this way from the respective chlorides.

All six (Li, Na, K, Rb, Cs, and Tl) compounds form white air-stable crystals, soluble in water and alcohols. In solution, all are completely ionised to give the $[C_5(CO_2Me)_5]^-$ ion and appropriate cation, as indicated by virtually identical electronic spectra [$\lambda_{max.}$ 261 (log ε 4.69) and 295 nm (4.21) in MeOH] and n.m.r. spectra [^{1}H, δ 3.87 (s); ^{13}C, δ 53.38 (s, Me), 118.12 (s, ring C), and 170.35 (s, CO)].

In the solid state, the i.r. spectra contain few common features. For example, those of the derivatives of Li, Na, and K contain respectively two, three, and four strong ν(CO) bands in the 1 600—1 750 cm^{-1} region; ν(OH) bands are found only for (3). Analytical samples were dried *in vacuo* for several hours, and, except for the lithium salt, gave values consistent with the non-solvated M(pmcp) salt. *X*-Ray studies of the lithium and potassium salts (below) revealed that in the crystals examined the metal atom is also co-ordinated by water and methanol, respectively. In order to resolve the origins of differences in the i.r. spectra, the single-crystal *X*-ray structures of the lithium, potassium, and thallium derivatives have been determined.

Table 2. Metal-atom environments in (3), (5), and (8). The first column in each matrix is the metal–oxygen distance (Å); the other entries are the angles (°) subtended at the metal by the two relevant oxygen atoms

(3) Li

Primed atoms are generated by the transformation $(x, \frac{1}{2} - y, z - \frac{1}{2})$

	r(Li–O)	O (water)	O(11′)	O(51′)
O(41)	1.904(9)	112.1(4)	111.2(4)	111.5(4)
O (water)	1.881(8)		118.1(4)	107.6(4)
O(11′)	1.914(7)			95.1(3)
O(51′)	1.900(7)			

(5) K

Symmetry transformations are I $(x, y - \frac{1}{2}, \frac{1}{2} - z)$, II $(\frac{1}{2} - x, y - \frac{1}{2}, 1 - z)$, and III $(\frac{1}{2} + x, \frac{1}{2} - y, z)$

	r(K–O)	O(11[I])	O(21[I])	O(31[II])	O(41[II])	O (solvent[III])
O(51)	2.645(3)	109.8(1)	76.8(1)	98.9(1)	158.8(1)	96.1(1)
O(11[I])	2.657(3)		66.7(1)	151.0(1)	86.1(1)	75.4(1)
O(21[I])	2.862(3)			126.0(1)	97.9(1)	135.7(1)
O(31[II])	2.762(3)				67.3(1)	98.2(1)
O(41[II])	2.726(3)					101.6(1)
O (solvent[III])	2.884(5)					

(8) Tl

Symmetry transformations are I $(x - 1, y, z)$, II $(1 - x, 1 - y, 1 - z)$, and III $(1 - x, 1 - y, \bar{z})$

	r(Tl–O)	O(31)	O(51[I])	O(11[II])	O(41[III])
O(21)	2.822(5)	61.6(1)	100.8(1)	130.4(1)	117.2(1)
O(31)	2.682(5)		126.6(1)	93.7(1)	67.8(1)
O(51[I])	2.992(5)			127.0(1)	81.0(1)
O(11[II])	3.244(5)				85.8(1)
O(41[III])	3.087(5)				

Angles subtended at the chelating oxygen atoms

(2) H–O(41,51)–C	109.8(16), 109.8(13)
(3) Li–O(11,51)–C	138.1(3), 138.3(3)
(5) K–O(11,21)–C	134.6(3), 132.1(3)
K–O(31,41)–C	123.1(3), 136.7(3)
(8) Tl–O(21,31)–C	148.2(4), 137.3(4)

Crystal structures of M(pmcp) (M = Li, K *or* Tl). The unit-cell contents in each case comprise anionic $C_5(CO_2Me)_5$ units interacting in various ways with the accompanying counter ion; in each case, one of each species, together with an associated solvent molecule in the cases of (3) and (5), comprise the asymmetric unit. In all cases the integrity of the cyclopentadienide ring is preserved; the disposition of the planes of the carboxylate moiety relative to the cyclopentadienide plane varies from coplanar to normal; their bulk is such that it is not possible for all five groups to be simultaneously coplanar with each other and the central ring.

(*a*) *Lithium pentakis(methoxycarbonyl)cyclopentadienide monohydrate*, $Li[C_5(CO_2Me)_5]\cdot H_2O$ (3). As in (2), the disposition of the carboxylate moieties about the central ring is such that three of the substituent groups lie quasi-parallel to the central ring and the other two are normal or nearly so (Figures 3 and 4; Tables 2—4, 6). Of the coplanar groups, two are disposed with their carbonyl oxygen atoms directed towards each other [O(11,51)] and effectively chelate in two of the four co-ordination positions of the nearby lithium atom. We find a rather similar distortion pattern throughout the ligand to that already observed for the acid, *viz.*: (*i*) the cyclopentadienyl ring has four equivalent bond lengths, with the fifth appreciably longer and corresponding to the bond between the two chelating substituent groups [C(1)–C(5) 1.447(5) Å], while there are no substantial distortions in the internal angular geometry of the ring; (*ii*) substantial asymmetries are found in the exocyclic angular geometry, and again there are no observable correlations of the type suggested above. In this case we note, however, that the asymmetries at the junctions of the two chelated carboxylate groups are similarly disposed, so that the larger angle is nearest the lithium atom. However, the pattern of planarity/non-coplanarity of the carboxylate groups relative to the central ring is as described for that of (2).

As opposed to these observations, however, although irregularities are observed in the C(*n*)–C(*n*1) distances, these do not correlate with co-ordinated *versus* unco-ordinated carboxylate groups. There is no marked variation in C(*n*1)–O(*n*1) nor in C(*n*1)–O(*n*2) distance, or for that matter O(*n*2)–C(*n*2). Angles C(*n*)–C(*n*1)–O(*n*1,2) exhibit no non-trivial variations, and while variations in O(*n*1)–C(*n*1)–O(*n*2) are non-trivial, they are not non-random.

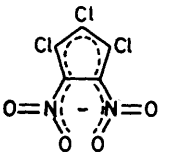
The metal-atom environment in (3) is four-co-ordinate, comprising the two chelating oxygen atoms mentioned above, together with O(41) from a second nearby anion and the water of crystallisation. The Li–O distances are almost identical [range 1.881(8)—1.914(7) Å], and are significantly shorter than those found in other derivatives, such as 1.923(6)—1.967(6) Å (average 1.944 Å) in $[L(acac)]_n$ (acac = acetylacetonate),[17] 1.931(4)—2.071(4) Å (average 2.007 Å) in $Li_2C_2O_4$,[18] 2.035(2)—2.057(3) Å (average 2.052 Å) in aqua-(2-hydroxy-3,4-dioxocyclobut-1-en-1-olato)lithium,[19] or an average value of 1.94 Å reported for $[K(C_{14}H_{28}N_2O_4)]$-$[Li_2(Et\ acetoacetate)]$ ($C_{14}H_{28}N_2O_4$ = 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]icosane).[20] The Li atom in all of these derivatives has approximately tetrahedral co-ordination. In $[Li(C_{14}H_{28}N_2O_4)]I$, where the Li has a distorted octahedral co-ordination, the Li–O distances are 2.081(6) and 2.173(24) Å.[21] In (3), the angular geometry lies well removed from the tetrahedral limit, being perturbed by the rather small 'bite' angle of the 'chelating' ligand [95.1(3)°], and the correspondingly enlarged angle between the other two ligand

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

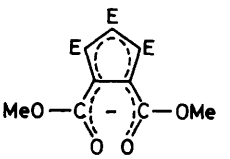
	Compound					Compound			
	(2)	(3)	(5)	(8)		(2)	(3)	(5)	(8)
C(1)–C(2)	1.408(4)	1.400(5)	1.416(6)	1.386(8)	C(5)–C(1)–C(11)	128.3(2)	128.2(3)	125.2(4)	126.5(5)
C(2)–C(3)	1.410(5)	1.415(5)	1.417(5)	1.448(7)	C(2)–C(1)–C(11)	122.9(2)	124.5(3)	126.7(3)	123.6(5)
C(3)–C(4)	1.396(3)	1.406(5)	1.394(5)	1.390(8)	C(1)–C(2)–C(21)	123.5(3)	128.1(3)	126.3(3)	124.2(5)
C(4)–C(5)	1.453(5)	1.393(5)	1.426(5)	1.424(7)	C(3)–C(2)–C(21)	128.4(3)	123.3(3)	126.2(4)	128.1(5)
C(5)–C(1)	1.403(4)	1.447(5)	1.404(5)	1.398(8)	C(2)–C(3)–C(31)	123.6(2)	124.0(3)	126.0(4)	125.4(5)
C(1)–C(11)	1.488(5)	1.453(5)	1.478(5)	1.487(8)	C(4)–C(3)–C(31)	127.6(3)	128.3(3)	125.3(3)	127.3(5)
C(2)–C(21)	1.460(3)	1.499(5)	1.446(5)	1.474(8)	C(3)–C(4)–C(41)	125.1(3)	124.0(3)	124.0(3)	125.6(5)
C(3)–C(31)	1.498(5)	1.461(6)	1.484(6)	1.451(7)	C(5)–C(4)–C(41)	127.6(2)	126.9(3)	127.8(4)	125.9(5)
C(4)–C(41)	1.428(5)	1.495(5)	1.464(5)	1.487(8)	C(4)–C(5)–C(51)	126.9(3)	123.9(3)	126.2(3)	124.5(5)
C(5)–C(51)	1.426(4)	1.450(5)	1.457(6)	1.458(8)	C(1)–C(5)–C(51)	126.0(3)	128.5(3)	125.8(3)	127.7(5)
C(11)–O(11)	1.205(4)	1.210(5)	1.199(5)	1.193(7)	C(1)–C(11)–O(11)	124.0(3)	127.2(3)	125.7(4)	123.3(5)
C(21)–O(21)	1.198(4)	1.191(6)	1.229(5)	1.204(7)	C(2)–C(21)–O(21)	124.9(3)	126.0(4)	126.2(4)	127.9(5)
C(31)–O(31)	1.194(4)	1.198(5)	1.208(5)	1.207(7)	C(3)–C(31)–O(31)	125.5(3)	125.4(3)	125.9(4)	125.6(5)
C(41)–O(41)	1.256(3)	1.198(5)	1.217(5)	1.179(8)	C(4)–C(41)–O(41)	125.2(3)	125.3(4)	125.4(4)	124.2(5)
C(51)–O(51)	1.259(4)	1.212(5)	1.203(5)	1.212(8)	C(5)–C(51)–O(51)	125.5(3)	128.1(3)	126.6(4)	125.0(5)
C(11)–O(12)	1.328(4)	1.338(4)	1.335(5)	1.340(6)	C(1)–C(11)–O(12)	111.6(2)	112.2(3)	110.5(3)	112.6(5)
C(21)–O(22)	1.331(4)	1.334(6)	1.331(5)	1.334(7)	C(2)–C(21)–O(22)	112.0(3)	110.3(4)	112.0(3)	109.1(4)
C(31)–O(32)	1.342(4)	1.333(4)	1.329(5)	1.343(7)	C(3)–C(31)–O(32)	109.5(2)	112.0(3)	110.7(3)	113.2(5)
C(41)–O(42)	1.316(4)	1.323(5)	1.338(5)	1.340(7)	C(4)–C(41)–O(42)	116.1(2)	111.5(4)	112.1(3)	111.6(5)
C(51)–O(52)	1.320(5)	1.345(4)	1.340(5)	1.327(7)	C(5)–C(51)–O(52)	115.4(3)	111.7(3)	111.5(3)	111.5(5)
O(12)–C(12)	1.452(8)	1.430(6)	1.443(8)	1.438(8)	O(11)–C(11)–O(12)	124.4(3)	120.5(3)	123.8(4)	124.1(5)
O(22)–C(22)	1.443(4)	1.441(6)	1.453(7)	1.446(8)	O(21)–C(21)–O(22)	123.1(2)	123.7(4)	121.8(4)	123.0(5)
O(32)–C(32)	1.455(6)	1.452(6)	1.445(8)	1.441(8)	O(31)–C(31)–O(32)	125.0(3)	122.6(4)	123.4(4)	121.2(5)
O(42)–C(42)	1.460(6)	1.459(6)	1.442(7)	1.438(9)	O(41)–C(41)–O(42)	118.7(3)	123.2(3)	122.5(4)	124.2(6)
O(52)–C(52)	1.472(5)	1.442(6)	1.454(10)	1.448(8)	O(51)–C(51)–O(52)	119.1(3)	120.3(3)	121.9(4)	123.5(5)
					C(11)–O(12)–C(12)	115.6(3)	117.5(3)	115.8(4)	114.7(5)
C(5)–C(1)–C(2)	108.6(3)	107.2(3)	108.2(3)	109.0(5)	C(21)–O(22)–C(22)	117.5(4)	117.4(4)	118.5(4)	117.7(4)
C(1)–C(2)–C(3)	108.1(2)	108.6(3)	107.5(3)	107.6(5)	C(31)–O(32)–C(32)	116.9(3)	117.5(3)	116.8(4)	115.0(5)
C(2)–C(3)–C(4)	108.8(3)	107.7(3)	108.7(3)	107.3(4)	C(41)–O(42)–C(42)	119.8(3)	115.5(4)	117.5(4)	115.6(5)
C(3)–C(4)–C(5)	107.3(3)	109.2(3)	107.8(3)	108.3(5)	C(51)–O(52)–C(52)	118.2(3)	116.8(3)	116.4(5)	116.9(5)
C(4)–C(5)–C(1)	107.2(2)	107.3(3)	107.9(3)	107.8(5)					

atoms [118.1(4)°]. About the co-ordinated H_2O, H(A,B) are found at distances 0.76(6), 0.83(5) Å, subtending an angle 108(6)°, and angles of 124(4), 116(4)° with Li. Hydrogen bonds found are H(A) · · · O(21) ($x,y,z-1$), H(B) · · · O(31) ($2-x$, $1-y$, $1-z$) 2.09(6), 2.04(5) Å respectively with angles subtended at the hydrogen atoms of 167(5), 167(5)°.

(*b*) *Potassium pentakis(methoxycarbonyl)cyclopentadienide–methanol* (1/1), $K[C_5(CO_2Me)_5]\cdot MeOH$ (5). In this compound, all O(*n*1) atoms of all five substituent carboxylate groups are involved in ' co-ordination ' to the potassium, the environment of the latter being comprised of two pairs of ' chelating ' carboxylate groups O(11,21) and O(31,41) from different ligands and O(51) from yet another ligand (Figures 5 and 6; Tables 2—4, 7). The sixth co-ordination site of the potassium is occupied by the methanol solvent oxygen. The environment of the potassium is well distorted from the octahedral ideal, and this and the non-systematic nature of the disposition of the anions suggests that the ligand–cation interactions are weaker than in (2) or (3). Bond lengths and angles among ' equivalent ' parameters of the anion exhibit no non-trivial deviations, while carboxylate-substituent dispositions relative to the central ring plane are not ' parallel ' or ' normal ' but at a variety of pitches in between. The K–O distances range from 2.645(3) to 2.884(5) Å, which may be compared with values of 2.75—2.94(2) Å in dipotassium tetrafluorophthalate[22] and 2.76—3.01(1) Å in $K(acac)\cdot 0.5H_2O$.[23] In the latter, K is co-ordinated by six oxygens from four different acac ligands, and a seventh from the water molecule [at 2.83(1) Å]. The K–O distances in the diglymepotassium cation are 2.385(14) Å (average) in the ion pair with 1,3,5,7-tetramethylcyclo-octatetraenedi-ide,[24] but are 2.741(4) and 2.792(5) Å in the aggregate with $[Ce(C_8H_8)_2]^-$.[25] The K in $K[C_5Cl_3(NO_2)_2]$ has distorted octahedral co-ordination, interacting with six oxygens from four cyclopentadienide anions at distances ranging from one at 2.580(12) Å to five between 2.817(12) and 2.942(11) Å. In this compound the interaction is considered to be ionic, and a long ring C–C distance of 1.457(23) Å [compared to the other four between 1.383(23) and 1.410(23) Å] was attributed to ' over-crowding ' of the two NO_2 groups bonded to these carbons.[26] Our results suggest that an alternative interpretation may be a fulvenoid structure (9) for this anion, analogous to that found in the pmcp anion (10).



(9)



(10)

E = CO_2Me

In the methanol solvent molecule O–H is 0.96(6) Å, the hydrogen being also hydrogen bonded to O(21) (x, $y-\frac{1}{2}$, $\frac{1}{2}-z$), 2.04(6) Å, with the angle subtended being 159(6)°. Angles H–O–C,K respectively at the methanol oxygen are 105(4), 120(4)°, the angle subtended by the carbon and potassium being 109.5(5)°.

(*c*) *Thallium(I) pentakis(methoxycarbonyl)cyclopentadienide*, $Tl[C_5(CO_2Me)_5]$ (8). Again, although there is a good spread in the interplanar dihedral angles, two of the carboxylate

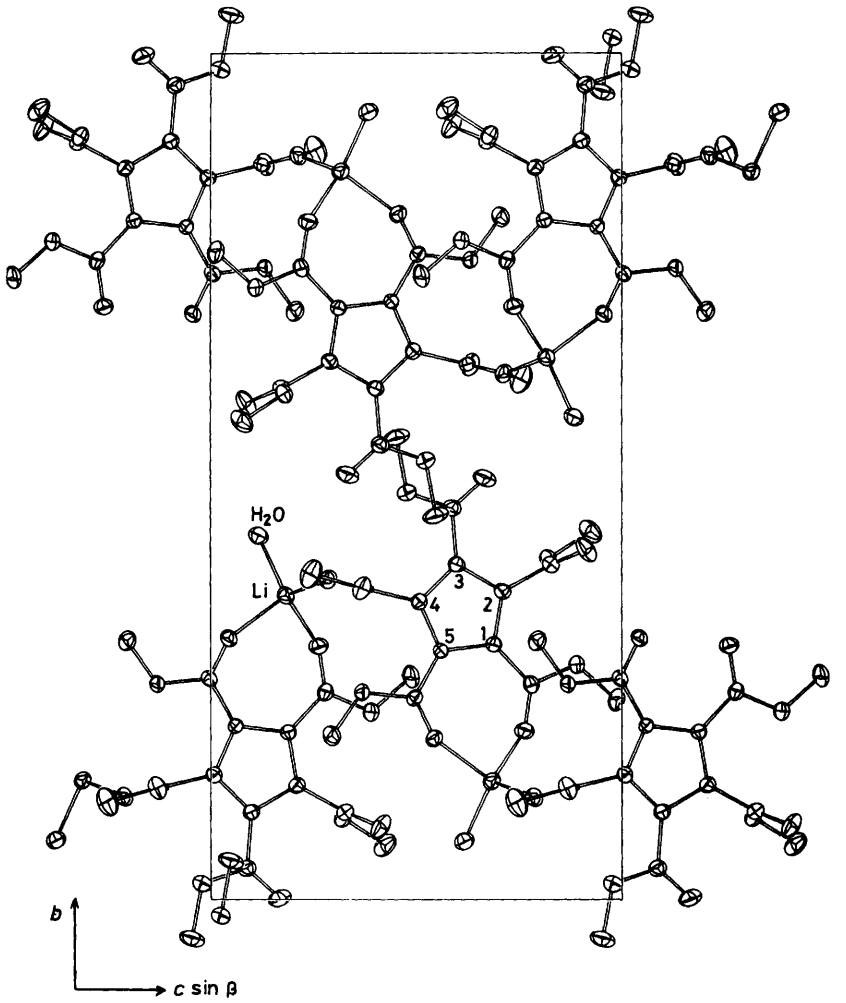


Figure 3. Unit-cell contents of (3) projected down *a*

groups (1 and 4) lie reasonably ' normal ' to the ring plane, while the other three are ' quasi-parallel '; of the latter, two are adjacent ring substituents (2,3) and, as in (2), lie with their carbonyl oxygen atoms [O(21,31)] directed toward each other ' chelating ' the thallium atom in two of its five co-ordination sites (Figures 7 and 8, Tables 2—4, 8). Again, we find that the longest bond of the ring skeleton lies between the two chelating carboxylate groups [C(2)–C(3) 1.448(7) Å], with the two shortest bonds on either side [C(1)–C(2) 1.386(8); C(3)–C(4) 1.390(8) Å]. There is no correlation between variation in C(*n*)–C(*n*1) and chelation. Variations within the values of each C–O distance are trivial.

The thallium environment is irregular ' five co-ordinate ' with five Tl–O distances varying between 2.682(5) and 3.244(5) Å, correlating inversely with the angular crowding of the site. The five oxygen atoms are comprised of two chelating from the same ligand, while the other three are drawn from different ligands, the net result being that with each ligand all five of the O(*n*1) atoms are involved in ' co-ordination ' to *four different thallium atoms*. Comparisons with other reported structures of molecules containing Tl–O bonds shows that in thallium(I) hexafluoroacetylacetonate, where each thallium is also co-ordinated by five oxygens, the range is 2.62(3)—3.04(3) Å (average 2.89 Å);[27] in thallium(I) picrate the metal is co-ordinated by nine oxygens between 2.83 and 3.22 Å,[28] and in $[Tl(C_{14}H_{28}N_2O_4)^+$ (studied as the formate) the thallium is eight-co-ordinate, with Tl–O distances of 2.898—2.913(6) Å [average 2.904(4) Å].[29]

Conclusions

Pentakis(methoxycarbonyl)cyclopentadiene is a strong organic acid. In the solid state, and also in non-polar solvents, the acidic hydrogen bridges two carbonyl groups of adjacent CO_2Me groups; the molecule adopts a fulvenoid configuration, which is preserved in the monovalent metal cation salts. In these, the metal ion is co-ordinated by, or interacts electrostatically with, the carbonyl oxygens rather than the ring carbons. This contrasts with the situation found in derivatives of the parent hydrocarbon, such as $[Na(Me_2NCH_2CH_2NMe_2)(C_5H_5)]_n$[30] or $[Tl(C_5H_5)]_n$,[31] in which the metal ions form $-M(C_5H_5)M(C_5H_5)M(C_5H_5)-$ chains, puckered in the former case. The C_5 rings are each η^5-bonded to two metal ions. Nevertheless, the metal–ring interaction is predominantly ionic, as indicated by the ring C–C distances of 1.38(1) Å, considerably shorter than those usually found for covalent metal cyclopentadienyls (*ca.* 1.42 Å). These differences are readily accounted for by the presence of the highly electronegative CO_2Me groups, and the expected concentration of charge on the carbonyl oxygens. It is also entirely to be expected that the relatively small and non-polarisable (hard) metal ions prefer to co-ordinate to the hard oxygen donors,

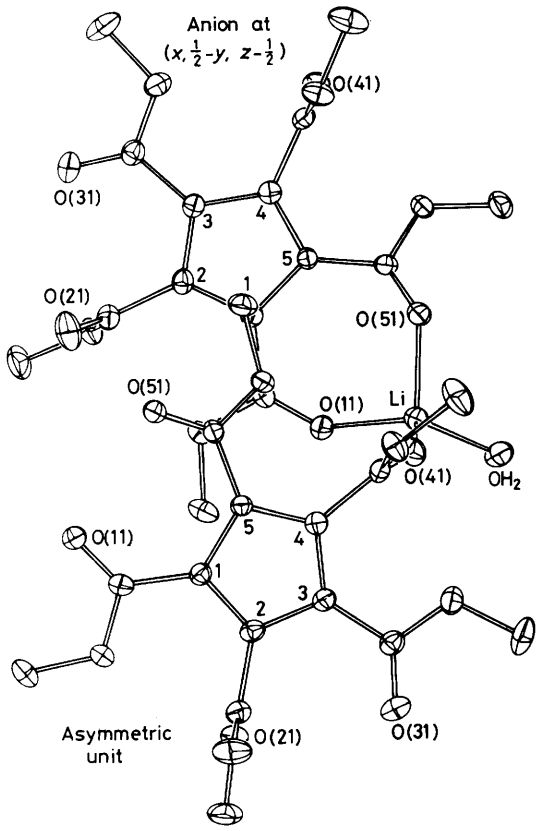


Figure 4. A pair of anions of (3), showing their mode of co-ordination about the lithium. Projection is normal to the plane of the nearest anion

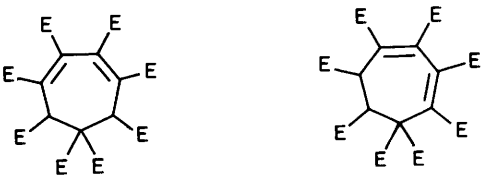
rather than the relatively soft carbon centres. Later papers will describe the variation of bonding encountered with the transition elements and particularly with the Group 1B metals.

Experimental

General.—Spectra were recorded with Perkin-Elmer 683 (i.r.), Varian Techtron 635 (electronic), Varian T60 (^{1}H n.m.r. at 60 MHz), Bruker WP80 (^{1}H n.m.r. at 80 MHz, or ^{13}C n.m.r. at 20.1 MHz), and AEI–GEC MS3074 [mass, ionising energy 70 eV (*ca.* 1.12×10^{-17} J)] instruments; ^{13}C n.m.r. spectra of compounds in D_2O solution were referenced to internal Bu^{t}OH (δ 30.79), and chemical shifts are given relative to $SiMe_4$. Melting points were taken with samples in sealed capillary tubes, and are not corrected. Magnetic measurements were obtained by the Gouy method, osmometric molecular weights with a Knauer osmometer, in chloroform, and conductivity measurements at 25 °C under nitrogen using a Phillips PR9500 AC conductance bridge. Microanalyses were by the Canadian Microanalytical Service, Vancouver.

AR grade solvents were used where possible; other materials were commercial products used as received. In general, all reactions were carried out under nitrogen, but no special precautions were used to exclude oxygen during work-up, unless otherwise noted.

Synthesis of Potassium Pentakis(methoxycarbonyl)cyclopentadienide.—(*a*) *Preparation of* 1,1,2,3,4,5,6,7-*octa(methoxycarbonyl)cycloheptadiene isomers.* A mixture of pyridine and acetic acid (1 : 1, 2.5 cm^3) was added to a stirred solution of



(11) (12)

E = CO_2Me

dimethyl acetylenedicarboxylate (38 g, 0.27 mol; Fluka) and dimethyl malonate (11.7 g, 0.9 mol; BDH) in diethyl ether (60 cm^3). A dark red colouration developed, and a vigorous reaction occurred; after this had subsided, the mixture was heated at reflux point for 2 h, with periodic scraping to break up the product which separated. After cooling, the solid was collected, washed with ether, and dried *in vacuo* to give a light brown powder. Most of this material dissolved on heating with methanol (*ca.* 500 cm^3); filtration of the hot solution at this stage left the less soluble ' 4,6 '-diene (11) on the sinter. Recrystallisation from a large volume of methanol gave a pure sample (4.5 g, 9%) m.p. 185—187 °C (lit.,[12] 182—183 °C). The filtrate was cooled to give the white crystalline ' 3,5 '-diene (12) (34.1 g, 69%), m.p. 225—226 °C (lit.,[12] 226 °C).

(*b*) *Conversion of* (12) *into* $K[C_5(CO_2Me)_5]$. A stirred mixture of the ' 3,5 '-diene (12) (34 g, 62 mmol), potassium acetate (56 g, 0.57 mol), and water (170 cm^3) was heated at reflux point for 2 h to give a clear yellow solution, which was filtered while hot. The filtrate was cooled, and the resulting yellow crystals were collected, washed with a small amount of cold methanol, and dried *in vacuo* to give $K[C_5(CO_2Me)_5]$ (5) (21 g, 86%), which was pure enough for most purposes. A small sample was recrystallised (methanol) to give white solvated prismatic crystals, m.p. 217—218 °C (lit.,[12] m.p. 217—218 °C), which lost solvent on heating *in vacuo* (100 °C, 6 h) (Found: C, 45.8; H, 3.80. $C_{15}H_{15}KO_{10}$ requires C, 45.7; H, 3.80%). N.m.r.: ^{1}H, δ (D_2O, external $SiMe_4$ reference) 4.27 (s); δ [$(CD_3)_2CO$] 3.61 (s); ^{13}C, δ (D_2O, internal Bu^{t}OH reference) 53.38 (s, OMe), 118.12 (s, ring C), and 170.12 (s, CO_2Me). $\lambda_{max.}$(MeOH) 261 (log ε 4.69) and 295 nm (4.21). Conductivity (acetone) 89 ohm^{-1} cm^2 mol^{-1}.

(*c*) *Conversion of* (11) *into* $K[C_5(CO_2Me)_5]$. A similar procedure to (*b*) above, using the ' 4,6 '-diene (11) (4.5 g, 8.2 mmol) and potassium acetate (7.5 g, 77 mmol) in water (25 cm^3), afforded $K[C_5(CO_2Me)_5]$ (2.8 g, 87%), identical with the product obtained in (*b*).

Preparation of 1,2,3,4,5-*Pentakis(methoxycarbonyl)cyclopentadiene.*—Concentrated hydrochloric acid (*ca.* 10 cm^3) was added slowly to a solution of the crude potassium salt (5) (5.0 g, 0.013 mol) in water (20 cm^3), until precipitation of the white solid was complete. This material was collected by filtration and dried *in vacuo* to give the diene (2) (4.0 g, 90%). A portion was recrystallised (methanol–diethyl ether) to give white prismatic crystals, m.p. 146—148 °C (lit.,[12] m.p. 147—148 °C) (Found: C, 50.45; H, 4.50. $C_{15}H_{16}O_{10}$ requires C, 50.55; H, 4.50%). N.m.r.: ^{1}H, δ (D_2O, external $SiMe_4$ reference) 4.35 (s); δ [$(CD_3)_2CO$] 3.72 (s); δ (C_6D_6) 3.55 (s, br); δ ($CDCl_3$) 3.95 (s, br), 31.10 (acidic H); ^{13}C, δ (D_2O, internal Bu^{t}OH reference) 53.56 (s, OMe), 118.18 (s, ring C), and 170.47 (s, CO_2Me). $\lambda_{max.}$(MeOH) 261 nm (log ε 4.69), 295 nm (4.16).

Preparation of Other Alkali-metal Salts.—(*a*) *From diene* (2) *and the carbonates.* A solution of the diene in water was treated with a slight deficiency of the solid alkali-metal carbonate; carbon dioxide was evolved rapidly. After stirring

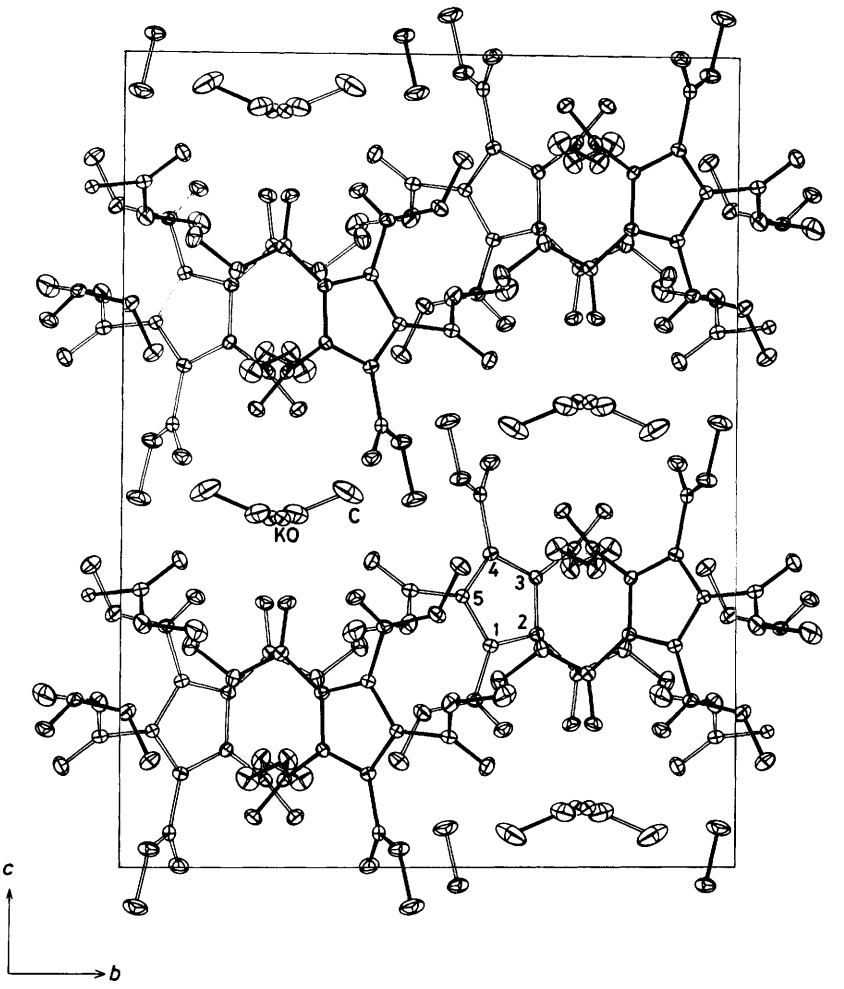


Figure 5. Unit-cell contents of (5) projected down *a*

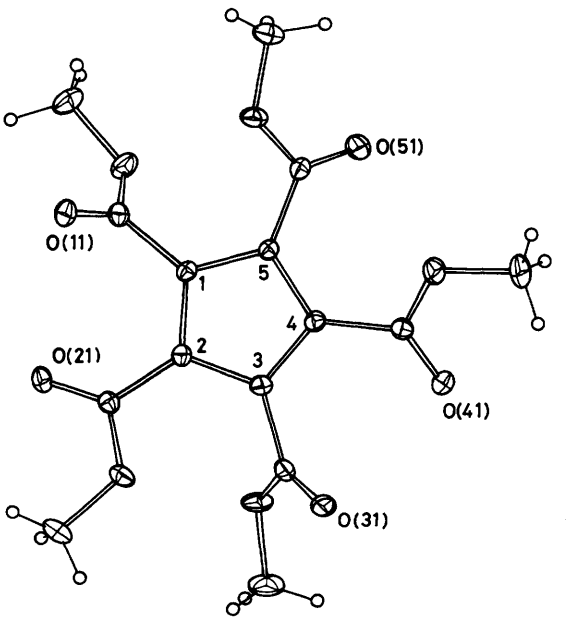


Figure 6. The anion of (5) projected normal to the cyclopentadienide plane

for 30 min, the filtered solution was evaporated to small volume and cooled, whereupon the alkali-metal derivative crystallised. In this way were made $Li[C_5(CO_2Me)_5]\cdot H_2O$ (3), white rod-shaped crystals, m.p. 275—278 °C (Found: C, 47.65; H, 4.10. $C_{15}H_{17}LiO_{11}$ requires C, 47.35; H, 4.45%), ^1H n.m.r. δ (D_2O) 4.26 (s), δ [$(CD_3)_2CO$] 3.70 (s), and $Na[C_5(CO_2Me)_5]$ (4), white crystals, m.p. 295—300 °C (decomp.) (Found: C, 47.0. H, 3.90. $C_{15}H_{15}NaO_{10}$ requires C, 47.6; H, 3.95%), ^1H n.m.r. δ (D_2O) 4.23 (s), δ [$(CD_3)_2CO$] 3.63 (s).

(*b*) *From* $Tl[C_5(CO_2Me)_5]$ *and the chlorides.* Solutions of $Tl[C_5(CO_2Me)_5]$ (see below) and the alkali-metal chloride in methanol were mixed, resulting in an immediate precipitate of thallium chloride. After stirring for 2 h, the solution was filtered and the residue washed once with methanol. Evaporation of the combined filtrates and recrystallisation (methanol–diethyl ether) afforded the pure alkali-metal derivative. In this way were prepared $Rb[C_5(CO_2Me)_5]$, (6) a white solid, m.p. 196—198 °C (Found: C, 40.95; H, 3.70. $C_{15}H_{15}O_{10}Rb$ requires C, 40.85; H, 3.40%), ^1H n.m.r. δ (D_2O) 4.40 (s), δ [$(CD_3)_2CO$] 3.60 (s), and $Cs[C_5(CO_2Me)_5]$ (7), white crystals, m.p. 179—180 °C (Found: C, 36.7; H, 2.85. $C_{15}H_{15}CsO_{10}$ requires C, 36.9; H, 3.05%), ^1H n.m.r. δ (D_2O) 4.40 (s), δ [$(CD_3)_2CO$] 3.63 (s), conductivity (acetone) 90 ohm^{-1} cm^2 mol^{-1}.

*Preparation of Thallium(*I*) Pentakis(methoxycarbonyl)-cyclopentadienide.*—Thallium carbonate (1.7 g, 3.6 mmol) was added to a solution of the diene (2.5 g, 7.0 mmol) in water (20 cm^3); evolution of CO_2 occurred, and the mixture was stirred

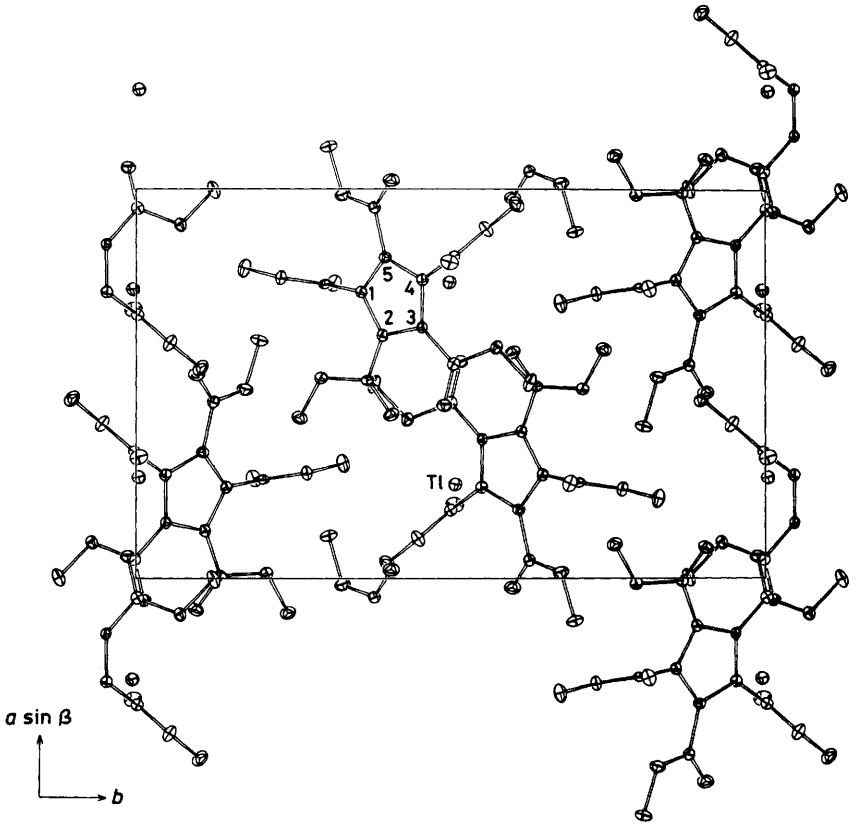


Figure 7. Unit-cell contents of (8) projected down *c*

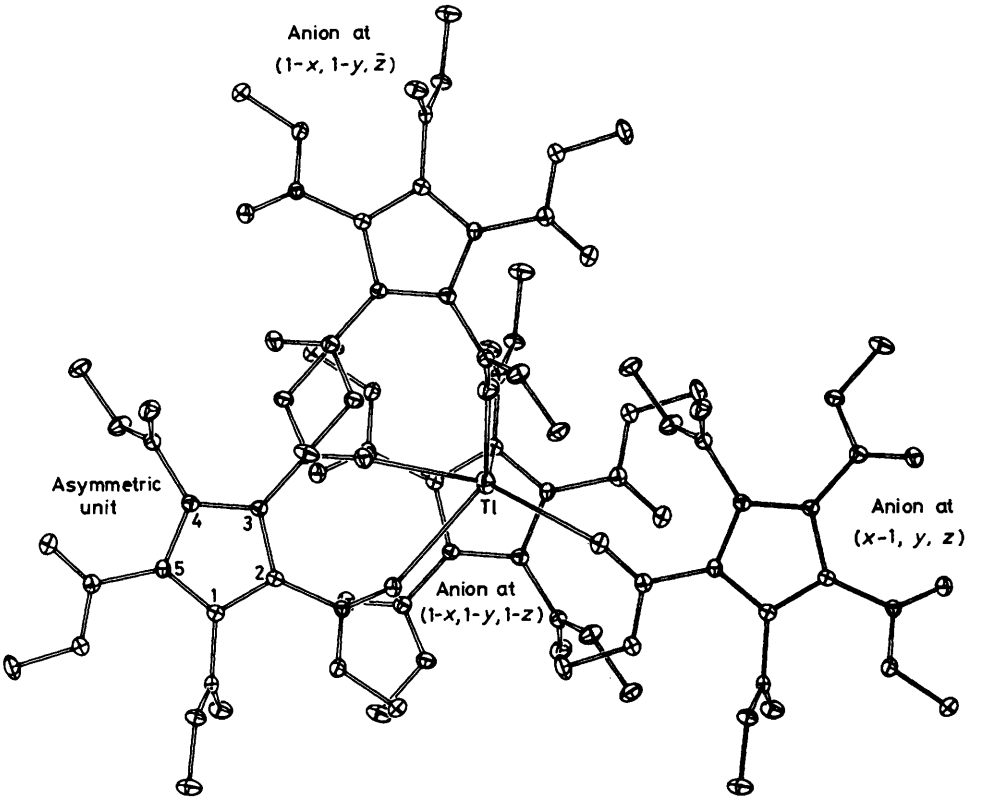


Figure 8. The thallium environment in (8); projection is normal to the plane of the ' chelating ' ligand

Table 4. 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 in Å. Defining atoms are C(1)—C(5). θ(n)/° is the dihedral angle to the plane defined by $C(n,n1)$–$O(n1,2)$

	Compound			
	(2)	(3)	(5)	(8)
10^4p	3 914	9 416	8 048	0 678
10^4q	8 187	−0 474	5 656	6 171
10^4r	−4 202	−3 334	1 801	7 839
s	−0.091	1.767	9.319	7.369
σ	0.002	0.002	0.005	0.008
δC(1)	0.001	−0.001	−0.002	0.000
δC(2)	−0.002	0.003	0.005	−0.006
δC(3)	0.002	−0.003	−0.007	0.010
δC(4)	−0.001	0.002	0.005	−0.010
δC(5)	0.000	−0.001	−0.002	0.006
δC(11)	0.100	0.068	−0.018	0.219
δC(21)	−0.001	0.033	0.029	0.015
δC(31)	0.055	−0.057	−0.097	0.002
δC(41)	−0.029	0.008	0.151	−0.158
δC(51)	−0.017	−0.108	−0.089	0.000
δO(11)	1.141	0.174	0.780	1.280
δO(21)	−0.158	−0.916	−0.317	0.466
δO(31)	−0.885	−0.012	0.723	−0.429
δO(41)	0.028	0.980	−0.300	−1.151
δO(51)	−0.013	−0.560	−0.710	−0.204
δO(12)	−1.098	0.046	−1.060	−0.899
δO(22)	0.183	1.293	0.460	−0.556
δO(32)	1.328	−0.195	−1.228	0.541
δO(42)	−0.095	−1.210	0.902	0.968
δO(52)	−0.030	0.338	0.589	0.214
δC(12)	−1.099	0.135	−1.082	−0.727
δC(22)	0.116	1.501	0.363	−0.577
δC(32)	1.576	−0.224	−1.373	0.622
δC(42)	−0.132	−1.312	1.113	0.904
δC(52)	0.003	0.202	0.342	0.212
θ(1)	88.1	4.4	56.0	77.7
θ(2)	8.8	90.0	20.5	27.4
θ(3)	83.7	5.6	62.5	25.9
θ(4)	3.3	82.3	34.1	72.2
θ(5)	0.7	24.0	35.7	10.8

Table 5. Non-hydrogen atom co-ordinates for $HC_5(CO_2Me)_5$ (2)

Atom	x	y	z
Ligand anion			
C(1)	0.275 6(3)	0.188 4(3)	0.676 6(3)
C(11)	0.378 3(3)	0.133 0(3)	0.666 8(3)
O(11)	0.482 9(2)	0.192 8(2)	0.618 2(3)
O(12)	0.342 6(2)	0.011 9(2)	0.723 7(3)
C(12)	0.444 3(6)	−0.043 2(5)	0.739 3(6)
C(2)	0.282 1(3)	0.267 3(3)	0.827 7(3)
C(21)	0.384 3(3)	0.295 0(3)	0.993 1(3)
O(21)	0.461 5(2)	0.241 8(2)	1.025 8(3)
O(22)	0.381 3(2)	0.386 6(2)	1.107 0(2)
C(22)	0.471 2(5)	0.416 5(6)	1.280 5(5)
C(3)	0.176 4(3)	0.311 7(3)	0.787 4(3)
C(31)	0.154 5(3)	0.402 9(3)	0.913 8(3)
O(31)	0.092 4(2)	0.367 4(2)	1.027 7(3)
O(32)	0.218 1(2)	0.531 6(2)	0.882 2(2)
C(32)	0.216 0(5)	0.635 3(5)	1.001 9(6)
C(4)	0.103 3(3)	0.260 8(3)	0.613 3(3)
C(41)	−0.013 4(3)	0.281 8(3)	0.526 6(4)
O(41)	−0.075 7(2)	0.241 3(2)	0.367 6(3)
O(42)	−0.055 2(2)	0.351 6(2)	0.622 9(2)
C(42)	−0.174 0(4)	0.377 5(6)	0.545 3(6)
C(5)	0.166 1(3)	0.182 3(3)	0.542 2(3)
C(51)	0.124 2(3)	0.110 6(3)	0.369 3(4)
O(51)	0.026 1(2)	0.106 2(2)	0.249 4(2)
O(52)	0.197 2(2)	0.045 1(2)	0.337 0(3)
C(52)	0.162 8(6)	−0.026 9(5)	0.159 0(5)
'Cation'			
H	−0.038(3)	0.172(3)	0.310(4)

Table 6. Non-hydrogen atom co-ordinates for $Li[C_5(CO_2Me)_5]\cdot H_2O$ (3)

Atom	x	y	z
Ligand anion			
C(1)	0.925 7(5)	0.301 8(2)	0.688 6(3)
C(11)	1.014 3(5)	0.254 6(2)	0.779 7(3)
O(11)	1.004 9(4)	0.199 9(1)	0.762 8(3)
O(12)	1.119 3(4)	0.277 9(1)	0.890 7(2)
C(12)	1.216 6(7)	0.235 9(3)	0.987 5(5)
C(2)	0.954 8(5)	0.364 6(2)	0.709 8(3)
C(21)	1.074 0(6)	0.396 0(2)	0.827 3(4)
O(21)	1.031 9(4)	0.413 5(2)	0.913 9(3)
O(22)	1.236 9(3)	0.402 7(1)	0.821 5(2)
C(22)	1.366 0(7)	0.435 1(3)	0.924 3(6)
C(3)	0.853 2(5)	0.396 2(2)	0.598 2(3)
C(31)	0.844 8(5)	0.462 7(2)	0.587 1(4)
O(31)	0.930 6(5)	0.497 9(1)	0.666 6(3)
O(32)	0.725 2(4)	0.481 0(1)	0.477 2(3)
C(32)	7.707 3(10)	0.546 2(2)	0.452 7(6)
C(4)	0.762 0(5)	0.352 4(2)	0.507 1(3)
C(41)	0.640 9(5)	0.367 8(2)	0.375 6(3)
O(41)	0.687 7(4)	0.378 7(1)	0.286 7(2)
O(42)	0.472 1(3)	0.368 2(1)	0.368 3(3)
C(42)	0.344 0(8)	0.385 1(4)	0.244 4(6)
C(5)	0.803 2(5)	0.294 3(2)	0.559 7(3)
C(51)	0.721 0(5)	0.238 7(2)	0.495 8(3)
O(51)	0.699 3(4)	0.190 9(1)	0.543 5(2)
O(52)	0.661 0(4)	0.245 2(1)	0.368 4(2)
C(52)	0.566 2(7)	0.194 1(2)	0.294 5(5)
Cation			
Li	0.826 6(9)	0.359 7(3)	0.183 0(6)
Solvent molecule (water)			
O	0.896 3(5)	0.430 3(2)	0.116 3(3)
H(A)	0.924(7)	0.430(2)	0.057(5)
H(B)	0.964(7)	0.454(2)	0.169(5)

Table 7. Non-hydrogen atom co-ordinates for $K[C_5(CO_2Me)_5]\cdot MeOH$ (5)

Atom	x	y	z
Ligand anion			
C(1)	0.306 5(3)	0.599 3(3)	0.271 9(2)
C(11)	0.346 9(3)	0.573 4(3)	0.205 1(2)
O(11)	0.395 6(2)	0.620 7(2)	0.168 9(1)
O(12)	0.321 3(2)	0.488 6(2)	0.189 8(1)
C(12)	0.367 7(7)	0.450 9(5)	0.130 4(3)
C(2)	0.244 9(3)	0.674 4(3)	0.286 0(2)
C(21)	0.211 3(3)	0.741 3(3)	0.237 9(2)
O(21)	0.207 0(2)	0.731 9(2)	0.176 1(1)
O(22)	0.182 6(2)	0.817 3(2)	0.268 2(1)
C(22)	0.133 9(5)	0.886 3(4)	0.227 7(4)
C(3)	0.222 5(3)	0.672 2(3)	0.356 1(2)
C(31)	0.154 6(3)	0.734 5(3)	0.392 2(2)
O(31)	0.176 7(2)	0.784 0(2)	0.438 4(1)
O(32)	0.063 5(2)	0.728 3(2)	0.367 3(2)
C(32)	−0.007 9(5)	0.793 5(5)	0.391 3(4)
C(4)	0.270 8(3)	0.598 5(3)	0.385 1(2)
C(41)	0.274 0(3)	0.580 7(3)	0.458 0(2)
O(41)	0.207 5(2)	0.596 4(2)	0.497 8(1)
O(42)	0.361 7(2)	0.548 1(2)	0.477 6(1)
C(42)	0.374 2(6)	0.526 9(6)	0.548 3(3)
C(5)	0.322 8(3)	0.552 4(3)	0.332 7(2)
C(51)	0.377 4(3)	0.468 0(3)	0.339 7(2)
O(51)	0.356 5(2)	0.405 5(2)	0.375 9(1)
O(52)	0.455 4(2)	0.465 3(2)	0.297 8(2)
C(52)	0.502 8(8)	0.377 8(6)	0.289 4(4)
Cation			
K	0.354 77(9)	0.240 40(6)	0.427 36(5)
Solvent molecule (methanol)			
C	0.089 9(8)	0.365 4(6)	0.460 6(4)
O	0.066 7(3)	0.280 8(3)	0.432 8(2)
H	0.105(5)	0.277(4)	0.392(3)

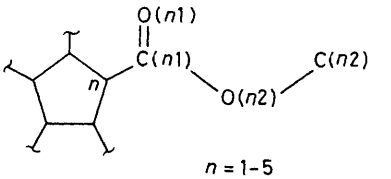
Table 8. Non-hydrogen atom co-ordinates for $Tl[C_5(CO_2Me)_5]$ (8)

Atom	x	y	z
Ligand anion			
C(1)	0.733 9(5)	0.356 2(3)	0.438 1(6)
C(11)	0.754 0(5)	0.298 5(3)	0.563 3(7)
O(11)	0.756 2(4)	0.313 0(2)	0.698 3(5)
O(12)	0.770 4(4)	0.229 2(2)	0.507 5(5)
C(12)	0.795 1(7)	0.171 9(3)	0.624 5(9)
C(2)	0.622 6(5)	0.390 0(3)	0.394 2(6)
C(21)	0.507 8(5)	0.366 0(3)	0.449 7(7)
O(21)	0.419 9(4)	0.404 1(2)	0.464 8(5)
O(22)	0.514 1(3)	0.292 6(2)	0.483 7(5)
C(22)	0.411 9(6)	0.258 8(4)	0.547 6(8)
C(3)	0.642 9(5)	0.452 4(3)	0.292 0(7)
C(31)	0.549 8(5)	0.502 4(3)	0.219 4(7)
O(31)	0.443 5(4)	0.487 2(2)	0.191 6(6)
O(32)	0.592 7(4)	0.570 3(2)	0.183 9(5)
C(32)	0.502 2(7)	0.623 6(3)	0.119 3(8)
C(4)	0.765 8(5)	0.453 1(3)	0.274 0(7)
C(41)	0.824 5(5)	0.502 1(3)	0.164 7(7)
O(41)	0.810 9(5)	0.495 5(2)	0.028 1(5)
O(42)	0.896 8(4)	0.553 8(2)	0.240 7(5)
C(42)	0.960 7(7)	0.602 3(4)	0.144 4(9)
C(5)	0.823 3(5)	0.394 1(3)	0.366 6(7)
C(51)	0.952 6(5)	0.377 3(3)	0.378 8(7)
O(51)	1.023 2(4)	0.404 0(2)	0.296 5(6)
O(52)	0.984 0(3)	0.327 0(3)	0.489 8(5)
C(52)	1.110 3(6)	0.304 7(4)	0.511 9(10)
Cation			
Tl	0.240 90(2)	0.504 62(1)	0.330 26(3)

at room temperature for 90 min. Filtration and evaporation gave a white solid which was washed with cold methanol and diethyl ether. Recrystallisation (methanol) gave white crystals of pure $Tl[C_5(CO_2Me)_5]$ (8) (3.5 g, 90%), m.p. 197—198 °C (Found: C, 32.3; H, 2.45. $C_{15}H_{15}O_{10}Tl$ requires C, 32.2; H, 2.70%). ^1H N.m.r.: δ (D_2O) 4.37 (s). Conductivity (H_2O) 89 ohm^{-1} cm^2 mol^{-1}.

Crystallography.—General. For each compound a unique data set was measured at 295(1) K within a preset $2\theta_{max.}$ limit determined by the scope of the data, using a Syntex $P2_1$ four-circle diffractometer, equipped with Mo-K_α radiation (λ = 0.7106$_9$ Å), in conventional 2θ—θ scan mode. N independent reflections were obtained and of these N_o with $I > 3\sigma(I)$ were considered 'observed' and used in the refinement of the structure without absorption correction after solution of the structure by direct methods. [Exception: compound (8) was solved by the heavy-atom method.] Refinement was basically by 9 × 9 block diagonal least-squares methods (C,O,Li,K thermal motion anisotropic; form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$ but with $(x,y,z,U)_H$, where refined, included in the block of the parent atom. Where U_H could not be refined meaningfully it was set at 1.25 $\bar{U}_{il}$(parent atom). Final residuals quoted (on F) are R,R',S, reflection weights being $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral atom scattering factors were used (Li^+, K^+ excepted), those for the non-hydrogen atoms being corrected for anomalous dispersion (f',f'').[32] Computation used the GENTAN and *X*-RAY 76 program systems[33] implemented on a Perkin-Elmer 8/32 computer.

Ligand-atom numbering is as below, hydrogen-atom numbering following that of the parent carbon, suffixed A,B,C for distinguishing purposes.



Crystal data. $HC_5(CO_2Me)_5$ (2), $C_{15}H_{16}O_{10}$, M = 356.3, Triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 10.944(4), b = 10.891(4), c = 7.743(3) Å, α = 91.32(3), β = 101.28(3), γ = 113.91(3)°, U = 821.9(5) Å^3, D_m = 1.44(1), Z = 2, D_c = 1.44 g cm^{-3}, $F(000)$ = 372, μ_{Mo} = 1.3 cm^{-1}, $2\theta_{max.}$ = 50°, N = 2 167, N_o = 1 484, R,R',S = 0.037, 0.045, 1.4, specimen size 0.20 × 0.35 × 0.40 mm.

$Li[C_5(CO_2Me)_5]\cdot H_2O$ (3), $C_{15}H_{17}LiO_{11}$, M = 380.2, Monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), a = 7.990(2), b = 21.890(3), c = 11.170(3) Å, β = 109.99(2)°, U = 1 835.8(7) Å^3, D_m = 1.37(1), Z = 4, D_c = 1.38 g cm^{-3}, $F(000)$ = 792, μ_{Mo} = 1.3 cm^{-1}, $2\theta_{max.}$ = 50°, N = 3 260, N_o =

1 469, R,R',S = 0.044, 0.051, 1.3, specimen size 0.18 × 0.13 × 0.46 mm.

$K[C_5(CO_2Me)_5]\cdot MeOH$ (5), $C_{16}H_{19}KO_{11}$, M = 426.4, Orthorhombic, space group *Pcab* (variant of *Pbca*, D_{2h}^{25}, no. 61), a = 13.52(1), b = 14.793(5), c = 19.751(9) Å, U = 3 951(4) Å^3, D_m = 1.44(1), Z = 8, D_c = 1.43 g cm^{-3}, $F(000)$ = 1 776, μ_{Mo} = 3.2 cm^{-1}, $2\theta_{max.}$ = 50°, N = 3 504, N_o = 1 695, R,R',S = 0.042, 0.048, 1.2, specimen size 0.20 × 0.40 × 0.25 mm.

$Tl[C_5(CO_2Me)_5]$ (8), $C_{15}H_{15}O_{10}Tl$, M = 559.7, Monoclinic, space group $P2_1/n$ (variant of $P2_1/c$, no. 14), a = 11.098(11), b = 17.726(7), c = 8.644(7) Å, β = 96.42(7)°, U = 1 690(3) Å^3, D_m = 2.18(1), Z = 4, D_c = 2.20 g cm^{-3}, $F(000)$ = 1 064, μ_{Mo} = 93 cm^{-1}, $2\theta_{max.}$ = 60°, N = 4 970, N_o = 3 159, R,R',S = 0.038, 0.047, 1.3, specimen size 0.42 × 0.35 × 0.20 mm.

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