Cu(1)—O(41)	1.941 (9)	Cu(3)—O(43)	2.598 (12)
Cu(1)—O(31)	2.822 (9)	Cu(3)—O(11)	2.686 (7)
Cu(1)—N(1)	2.057 (13)	Cu(3)—N(3)	2.044 (16)
Cu(2)—Cu(3)	3.154 (4)	Cu(4)—O(31)	1.924 (9)
Cu(2)—Cu(4)	3.794 (3)	Cu(4)—O(41)	1.914 (12)
Cu(2)—O(11)	1.947 (10)	Cu(4)—O(42)	1.954 (14)
Cu(2)—O(21)	1.930 (12)	Cu(4)—O(21)	2.692 (10)
Cu(2)—O(22)	1.948 (14)	Cu(4)—O(13)	2.877 (9)
Cu(2)—O(33)	2.443 (8)	Cu(4)—N(4)	2.011 (12)
O(11)—Cu(1)—O(23)	86.6 (4)	O(21)—Cu(3)—O(31)	91.5 (4)
O(12)—Cu(1)—O(23)	101.7 (5)	O(21)—Cu(3)—O(32)	98.2 (4)
O(11)—Cu(1)—O(41)	92.1 (3)	O(21)—Cu(3)—O(43)	80.7 (4)
O(12)—Cu(1)—O(41)	95.3 (4)	O(31)—Cu(3)—O(43)	85.6 (3)
O(23)—Cu(1)—O(41)	84.9 (5)	O(32)—Cu(3)—O(43)	110.3 (4)
O(11)—Cu(1)—N(1)	84.3 (4)	O(31)—Cu(3)—N(3)	84.3 (4)
O(12)—Cu(1)—N(1)	88.5 (4)	O(32)—Cu(3)—N(3)	89.1 (5)
O(23)—Cu(1)—N(1)	93.0 (6)	O(43)—Cu(3)—N(3)	87.0 (5)
O(11)—Cu(2)—O(21)	89.6 (4)	O(31)—Cu(4)—O(41)	91.7 (4)
O(11)—Cu(2)—O(22)	95.5 (5)	O(31)—Cu(4)—O(42)	94.6 (5)
O(11)—Cu(2)—O(33)	85.6 (3)	O(41)—Cu(4)—N(4)	85.2 (6)
O(21)—Cu(2)—O(33)	85.8 (4)	O(42)—Cu(4)—N(4)	89.7 (6)
O(22)—Cu(2)—O(33)	104.7 (4)	Cu(1)—O(11)—Cu(2)	108.8 (5)
O(21)—Cu(2)—N(2)	85.7 (5)	Cu(2)—O(21)—Cu(3)	109.1 (4)
O(22)—Cu(2)—N(2)	89.6 (6)	Cu(3)—O(31)—Cu(4)	108.2 (4)
O(33)—Cu(2)—N(2)	90.8 (4)	Cu(1)—O(41)—Cu(4)	113.4 (6)

One of the 3-bromobenzoate groups was shown to be disordered. Two positions were assigned to the Br atom of this group, with site occupancies of 0.75 for Br(3) and 0.25 for Br(30). Some ethanolato C atoms bonded to N atoms were also shown to be disordered (high displacement parameters and short C—C bonds). Geometric restraints were therefore used for these atoms during the refinement. The four phenyl rings were refined isotropically as rigid groups. The other non-H atoms were refined anisotropically. H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms.

Data collection: Nicolet *P*3 software. Cell refinement: Nicolet *P*3 software. Data reduction: Nicolet *P*3 software. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1020). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Ahlgrén, M., Turpeinen, U. & Hämäläinen, R. (1982). *Acta Cryst.* B**38**, 429–433.

North, A. C. T, Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1990). *SHELXTL/PC*. Realease 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Turpeinen, U., Ahlgrén, M. & Hämäläinen, R. (1979). *Acta Chem. Scand. Ser. A*, **33**, 593–596.

Turpeinen, U., Hämäläinen, R. & Ahlgrén, M. (1980). *Acta Cryst.* B**36**, 927–930.

Turpeinen, U., Hämäläinen, R. & Ahlgrén, M. (1985). *Acta Cryst.* C**41**, 1728–1730.

Turpeinen, U., Hämäläinen, R. & Reedijk, J. (1987). *Inorg. Chim. Acta*, **134**, 87–93.

Turpeinen, U., Hämäläinen, R. & Reedijk, J. (1988). *Inorg. Chim. Acta*, **154**, 201–207.

Acta Cryst. (1996). C**52**, 570–572

Sodium Tetraphenylcyclopentadienide Bis(dimethoxyethane)

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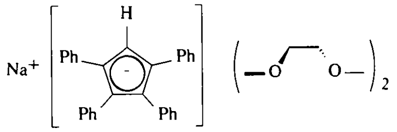
Abstract

The title compound, $Na^+.C_{29}H_{21}^-.2C_4H_{10}O_2$, has been prepared and its crystal structure determined at 200 K. The structure shows isolated contact pairs containing a nine-coordinate Na^+ ion, which is surrounded by two dimethoxyethane molecules and one η^5-coordinated cyclopentadienyl ring.

Comment

Alkali metal salts of cyclopentadiene and its derivatives are still of synthetic and theoretical interest. The use of cyclopentadienylsodium in tetrahydrofuran for the preparation of the transition metal η^5-cyclopentadienyl derivatives (Fischer & Jira, 1953) remains the most widely applicable route to this important class of organometallic compounds. Only a few alkali metal cyclopentadienyl derivatives, predominantly the corresponding lithium compounds, have been structurally characterized. We are interested in the coordination chemistry of the ionic cyclopentadienyl metal complexes such as those containing sodium. Their structural diversity needs to be explored in detail, especially their dependency on solvent effects, charge distribution and the structure of the anion. Here we report the crystal structure of a novel monomeric tetraphenylcyclopentadienyl sodium compound, (I).



(I)

The crystal structure contains monomeric units of the tetraphenylcyclopentadienyl anion (Fig. 1) fivefold coordinated to the Na^+ cation, which is surrounded, in addition, by two molecules of dimethoxyethane (Fig. 2), making the structure comparable to that of pentamethylcyclopentadienylsodium pyridine (Rabe, Roesky, Stalke, Pauer & Sheldrick, 1991), which is the first reported monomeric cyclopentadienyl derivative of sodium. In general, the sodium salts of cyclopentadienyl anions,

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especially those which are only partially substituted and less solvated, form polymeric structures such as that of cyclopentadienylsodium–tetramethylethylenediamine (Aoyagi, Shearer, Wade & Whitehead, 1979) or that of acetylcyclopentadienylsodium tetrahydrofuran (Rogers, Atwoord, Rausch, Macomber & Hart, 1982).

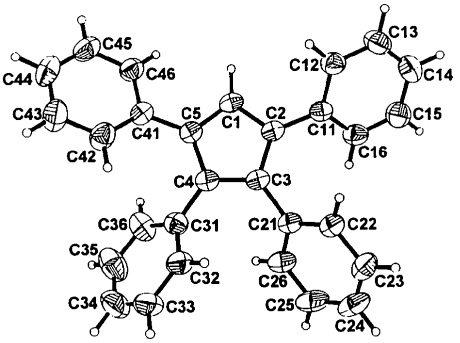

Fig. 1 View of the tetraphenylcyclopentadienide anion showing the labelling of the non-H atoms. Displacement ellipsoides are shown at the 50% probability level.

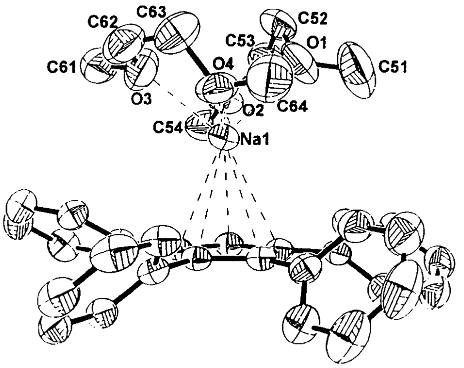

Fig. 2 View of the coordination sphere of the Na$^+$ cation. Displacement ellipsoids are shown at the 50% probability level. The Na$^+$ coordination is shown as dotted lines (for clarity the H atoms are omitted).

All bond distances for the tetraphenylcyclopentadienyl anion listed in Table 2 are within the range of standard values for metal cyclopentadienyl derivatives. The individual centres of the five-membered ring deviate by only 0.0024 Å from planarity and the four phenyl rings are arranged in a staggered conformation.

The Na$^+$ cation is almost symmetrically positioned above the cyclopentadienyl ring, with an Na$\cdots$Cp$_{\text{centroid}}$ distance of 2.58 Å. The five contact Na$\cdots$C distances range between 2.735 (2) and 2.908 (2) Å and, therefore, are significantly longer than those found in the pentamethylcyclopentadienylsodium pyridine complex. The coordination sphere of the Na$^+$ cation is a distorted pentagonal bipyramid with the Na$\cdots$O contact distances between 2.388 (2) and 2.513 (2) Å.

Summarizing, the monomeric structure of the title compound provides an additional example of the complex aggregation phenomenon of organometallic compounds, which depends on cation size, steric overcrowding of the anion, charge delocalization and the solvation enthalpy of the specific solvent (Bock, Näther, Havlas, John & Arad, 1994). Because of the complexity of this multiparameter problem, additional investigations are required.

Experimental

Sodium tetraphenylcyclopentadienide bis(dimethoxyethane) was prepared from a sodium metal mirror generated by vacuum distillation of 100 mg (4.3 mmol) of Na into a carefully dried Schlenk trap. 20 ml of absolute 1,2-dimethoxyethane and 370 mg (1 mmol) of tetraphenylcyclopentadiene (Aldrich) were added under argon. After 3 days all the sodium had vanished. A layer of 5 ml of absolute *n*-hexane was added to the resulting colourless solution. Colourless air- and moisture-sensitive crystals grew within 4 days.

Crystal data

$Na^+.C_{29}H_{21}^-.2C_4H_{10}O_2$
$M_r = 572.69$
Triclinic
$P\overline{1}$
$a = 8.5870\,(10)$ Å
$b = 10.3900\,(10)$ Å
$c = 19.707\,(3)$ Å
$\alpha = 81.000\,(10)^\circ$
$\beta = 86.960\,(10)^\circ$
$\gamma = 69.110\,(10)^\circ$
$V = 1622.4\,(3)$ Å^3
$Z = 2$
$D_x = 1.172$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 112 reflections
$\theta = 13.5–19.0^\circ$
$\mu = 0.086$ mm^{-1}
$T = 200\,(2)$ K
Prism
0.4 × 0.3 × 0.3 mm
Colourless

Data collection

Stoe Siemens four-circle diffractometer
ω–θ scans
Absorption correction: none
6268 measured reflections
5838 independent reflections
3916 observed reflections [$I > 2\sigma(I)$]

$R_{\text{int}} = 0.016$
$\theta_{\text{max}} = 25.51^\circ$
$h = 0 \rightarrow 10$
$k = -11 \rightarrow 12$
$l = -23 \rightarrow 23$
4 standard reflections
frequency: 120 min
intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$

$\Delta\rho_{\text{max}} = 0.450$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.443$ e Å^{-3}

$wR(F^2) = 0.130$
$S = 1.068$
5837 reflections
384 parameters
H atoms refined using a riding model
$w = 1/[\sigma^2(F_o^2) + (0.0608P)^2 + 1.1263P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0253 (21)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.6741 (3)	0.2056 (2)	−0.26565 (12)	0.0381 (5)
C2	0.6882 (3)	0.1184 (2)	−0.31548 (12)	0.0356 (5)
C3	0.7124 (3)	−0.0177 (2)	−0.27883 (12)	0.0358 (5)
C4	0.7111 (3)	−0.0101 (2)	−0.20731 (12)	0.0368 (5)
C5	0.6872 (3)	0.1302 (2)	−0.19950 (12)	0.0374 (5)
C11	0.6676 (3)	0.1686 (2)	−0.38970 (12)	0.0370 (5)
C12	0.7104 (3)	0.2837 (3)	−0.41840 (13)	0.0472 (6)
C13	0.6844 (4)	0.3387 (3)	−0.48727 (15)	0.0581 (7)
C14	0.6160 (4)	0.2800 (3)	−0.53013 (14)	0.0597 (7)
C15	0.5724 (4)	0.1666 (3)	−0.50309 (14)	0.0569 (7)
C16	0.5978 (3)	0.1124 (3)	−0.43431 (13)	0.0465 (6)
C21	0.7450 (3)	−0.1458 (2)	−0.31013 (12)	0.0378 (5)
C22	0.8554 (3)	−0.1750 (2)	−0.36522 (12)	0.0430 (6)
C23	0.8832 (3)	−0.2918 (3)	−0.39644 (14)	0.0535 (7)
C24	0.8041 (4)	−0.3838 (3)	−0.3735 (2)	0.0640 (8)
C25	0.6976 (4)	−0.3592 (3)	−0.3180 (2)	0.0632 (8)
C26	0.6667 (3)	−0.2418 (2)	−0.28685 (15)	0.0491 (6)
C31	0.7334 (3)	−0.1253 (2)	−0.14993 (13)	0.0429 (6)
C32	0.8689 (4)	−0.2500 (3)	−0.14678 (15)	0.0558 (7)
C33	0.8888 (5)	−0.3549 (3)	−0.0918 (2)	0.0784 (10)
C34	0.7740 (6)	−0.3383 (4)	−0.0390 (2)	0.0864 (12)
C35	0.6402 (5)	−0.2153 (4)	−0.0408 (2)	0.0783 (10)
C36	0.6206 (3)	−0.1108 (3)	−0.09555 (15)	0.0594 (7)
C41	0.6931 (3)	0.1889 (2)	−0.13656 (12)	0.0399 (5)
C42	0.7916 (3)	0.1121 (3)	−0.07979 (14)	0.0556 (7)
C43	0.8026 (4)	0.1724 (3)	−0.0232 (2)	0.0659 (8)
C44	0.7186 (4)	0.3113 (3)	−0.0216 (2)	0.0628 (8)
C45	0.6208 (4)	0.3906 (3)	−0.0769 (2)	0.0583 (7)
C46	0.6067 (3)	0.3304 (3)	−0.13320 (13)	0.0477 (6)
Na1	0.37666 (11)	0.14289 (10)	−0.25735 (5)	0.0481 (3)
O1	0.1655 (3)	0.2218 (3)	−0.17387 (12)	0.0883 (8)
O2	0.2449 (2)	0.3972 (2)	−0.28087 (11)	0.0654 (6)
C51	0.1844 (7)	0.2146 (5)	−0.1090 (2)	0.140 (2)
C52	0.0431 (4)	0.3457 (4)	−0.2072 (2)	0.0759 (9)
C53	0.1172 (4)	0.4534 (3)	−0.2340 (2)	0.0691 (9)
C54	0.3086 (4)	0.4984 (4)	−0.3156 (2)	0.0851 (11)
O3	0.1960 (3)	0.1586 (3)	−0.34878 (12)	0.0909 (8)
O4	0.2722 (2)	−0.0571 (2)	−0.24009 (12)	0.0690 (6)
C61	0.1715 (5)	0.2521 (5)	−0.4104 (2)	0.0998 (13)
C62	0.1500 (5)	0.0431 (4)	−0.3496 (2)	0.0908 (12)
C63	0.1349 (5)	−0.0286 (4)	−0.2824 (2)	0.0916 (12)
C64	0.2594 (5)	−0.1356 (5)	−0.1769 (2)	0.1000 (13)

Table 2. *Selected geometric parameters* (Å, °)

Na1···C1	2.843 (2)	C1—C5	1.400 (3)
Na1···C2	2.795 (2)	C1—C2	1.410 (3)
Na1···C3	2.817 (2)	C2—C3	1.432 (3)
Na1···C4	2.881 (2)	C2—C11	1.472 (3)
Na1···C5	2.908 (2)	C3—C4	1.423 (3)
Na1···O3	2.388 (2)	C3—C21	1.484 (3)
Na1···O1	2.390 (2)	C4—C5	1.430 (3)
Na1···O2	2.453 (2)	C4—C31	1.478 (3)
Na1···O4	2.513 (2)	C5—C41	1.476 (3)
C5—C1—C2	110.4 (2)	C3—C4—C5	108.1 (2)
C1—C2—C3	106.6 (2)	C3—C4—C31	127.2 (2)
C1—C2—C11	123.6 (2)	C5—C4—C31	124.7 (2)
C3—C2—C11	129.6 (2)	C1—C5—C4	106.9 (2)
C4—C3—C2	107.9 (2)	C1—C5—C41	123.4 (2)
C4—C3—C21	126.1 (2)	C4—C5—C41	129.3 (2)
C2—C3—C21	125.8 (2)		

All C, O and Na atoms were refined with anisotropic displacement parameters; all H atoms were located from a difference map and refined with fixed individual isotropic displacement parameters [$U_{\rm iso} = 1.2U_{\rm eq}$(C) if C belongs to an aromatic or methylene group, $U_{\rm iso} = 1.5U_{\rm eq}$(C) otherwise] using a riding model with C—H(aromatic) 0.95, C—H(methylene) 0.99 and C—H(methyl) 0.98 Å.

Data collection: *DIF*4 (Stoe & Cie, 1991*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1991*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1987). Software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1228). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Aoyagi, T., Shearer, M. M. H., Wade, K. & Whitehead, G. (1979). *J. Organomet. Chem.* **175**, 21–31.

Bock, H., Näther, C., Havlas, Z., John, A. & Arad, C. (1994). *Angew. Chem.* **106**, 931; *Angew. Chem. Int. Ed. Engl.* **33**, 875–878.

Fischer, E. O. & Jira, R.(1953). *Z. Naturforsch.* **8**, 217–219.

Rabe, G., Roesky, H. W., Stalke, D., Pauer, F. & Sheldrick, G. M. (1991). *J. Organomet. Chem.* **403**, 11–19.

Rogers, R. D., Atwoord, J. L., Rausch, M. D., Macomber, D. W. & Hart, W. P. (1982). *J. Organomet. Chem.* **238**, 79–85.

Sheldrick, G. M. (1987). *SHELXTL-Plus*. PC version. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Stoe & Cie (1991*a*). *DIF*4. *Diffractometer Control Program*. Version 7.08. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1991*b*). *REDU*4. *Data Reduction Program*. Version 7.08. Stoe & Cie, Darmstadt, Germany.