

**Polymeric [Tetrahydrofuran-tetracarboxylato(1–)]caesium (I), [Cs(C<sub>8</sub>H<sub>7</sub>O<sub>9</sub>)], and Hexaaqua[tetrahydrofuran-tetracarboxylato(4–)]dicalcium Dihydrate (II), [Ca<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>O<sub>9</sub>)(H<sub>2</sub>O)<sub>6</sub>].2H<sub>2</sub>O**

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**Abstract.** (I),  $M_r = 380.04$ , monoclinic,  $P2_1/c$ ,  $a = 8.8423$  (9),  $b = 11.3895$  (8),  $c = 11.3589$  (9) Å,  $\beta = 100.82$  (10)°,  $U = 1123.6$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.22$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 3.1$  mm<sup>-1</sup>,  $F(000) = 724$ ,  $T = 293$  K;  $R = 0.079$  for 3114 observed reflexions. (II),  $M_r = 468.38$ , triclinic,  $P\bar{1}$ ,  $a = 9.150$  (10),  $b = 10.512$  (8),  $c = 9.138$  (10) Å,  $\alpha = 95.17$  (11),  $\beta = 91.48$  (7),  $\gamma = 77.67$  (8)°,  $U = 855.2$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.82$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 6.48$  mm<sup>-1</sup>,  $F(000) = 480$ ,  $T = 293$  K;  $R = 0.086$  for 1409 observed reflexions. The anions in both these polymeric structures are of the *trans-cis,trans* isomer. In (I) the eight-coordinate Cs atoms are linked into pairs by a square of O atoms. In (II) eight-coordinate Ca atoms are linked into sheets by  $\mu$ -carboxylato and cross-ligand bridging. The furan O atom is coordinated in (II) but not in (I).

**Introduction.** The structure of the  $\text{Co}(\text{en})_3^{3+}$  salt (III) showed the *trans,cis,trans* isomer of tetrahydrofuran-tetracarboxylic acid H<sub>4</sub>TTA (Barnes & Paton, 1982). Two further structures have now been determined to see whether other cations would isolate different isomers from the commercially available mixture. The caesium and calcium salts were among the very few salts of H<sub>4</sub>TTA to give suitable crystals.

**Experimental.** (I) was prepared as colourless crystals,  $0.50 \times 0.25 \times 0.60$  mm, by slow evaporation of an equimolar aqueous solution of CsNO<sub>3</sub> and H<sub>4</sub>TTA (Aldrich). (II) was obtained as colourless laths,  $0.6 \times 0.4 \times 0.2$  mm, from H<sub>4</sub>TTA neutralized with Ca(OH)<sub>2</sub>. Both compounds were stable in air.

All calculations performed on the Dundee University DEC 10 computer using *SHELX76* (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978). Atomic scattering parameters from *International Tables for X-ray Crystallography* (1974).

Compound (I). After initial oscillation and Weissenberg photographs, data collected on a Stoe STADI II

diffractometer. Cell dimensions refined during alignments of the crystals. Levels collected  $0-9kl$  and  $h0l$ ,  $2\theta_{\text{max}} = 52.0^\circ$ , giving 3462 unique reflexions, 3114 with  $F_o > 3\sigma(F_o)$  used in refinement after absorption correction. No significant variation observed in standards measured every 100 reflexions. Direct-methods routine *TANG* (Ashida, 1973) showed the Cs atom and the C<sub>4</sub>O ring. Structure extended by least-squares refinement and difference syntheses. Anisotropic thermal parameters introduced for all non-H atoms. H atoms did not appear in final difference map and were not included. Two peaks of  $ca\ 5\ e\ \text{\AA}^{-3}$  remained. These appear to be artifacts; they do not refine satisfactorily as water molecules and are probably series-termination ripples about the Cs atom, as are the remaining features above  $1\ e\ \text{\AA}^{-3}$ . Final refinement (minimizing  $\sum w|F_o - |F_c||^2$ ): 164 refined parameters,  $R = 0.079$ ,  $wR = 0.106$ ,  $w = 3.2037/|\sigma(F) + 0.001495F^2|$ , mean shift/e.s.d. = 0.008, max. shift/e.s.d. = 0.040.

Compound (II). Initial cell dimensions derived from zero-level Weissenberg photographs on each axis of a cell in space group  $B\bar{1}$  ( $a = 12.896$ ,  $b = 10.555$ ,  $c = 13.188$  Å,  $\alpha = 78.9$ ,  $\beta = 88.5$ ,  $\gamma = 84.2^\circ$ ). Intensities measured from equi-inclination Weissenberg photographs scanned by the SERC Microdensitometer Service, Daresbury Laboratory. Data collected for levels  $0-10kl$  and  $h0-2l$  of the centred cell and transformed to the primitive cell after absorption correction. 1682 weak reflexions below threshold included with  $F = 0.5 F(\text{min})$  to improve the statistics for the direct-methods routine *TANG*, which then revealed the Ca atoms with part of the anion and some water molecules. Structure expanded by least-squares refinement and difference syntheses on the 1409 measured reflexions only. Anisotropic thermal parameters introduced for all non-H atoms. H atoms not included. At convergence C(23), C(24), C(26), O(27) and C(29) gave non-positive definite thermal parameters. The water molecule represented by O(10) refined to a very large value of  $U_{22}$  although the ellipsoid is positive definite. This molecule is not coordinated and is held on a lattice site by hydrogen

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bonding alone. It may well be disordered over several closely adjacent sites. This point is of no chemical interest and was not investigated further because of the low quality of the data set. The internal consistency indices for the individual crystals were 0.090 and 0.078 and for the combined data 0.084. These rather high values for a compound of this type suggest that the crystals were not entirely satisfactory although the diffraction patterns showed no obvious defects. Also, slight deterioration of the crystals, by for example loss of lattice water, would not be noticeable in the collection of photographic data. The solution and refinement of this structure were unusually protracted, again suggesting that the data were not of high quality. For these reasons it was decided not to apply a cosmetic correction for secondary extinction. Final refinement (minimizing  $\sum w|F_o - F_c|^2$ ): 245 refined parameters,  $R = 0.086$ ,  $wR = 0.089$ ,  $w = 1.0000/[\sigma(F) + 0.017126F^2]$ , mean shift/e.s.d. = 0.008, max. shift/e.s.d. = 0.033, max. difference peak = 0.8 e Å<sup>-3</sup>.

**Discussion.** Atomic coordinates and equivalent isotropic thermal parameters are given in Tables 1 and 2.\* Table 3 gives the bond lengths and bond angles in the two anions and the stereochemistry is compared in Table 4. In (I) the bond lengths in the carboxylate show clearly that O(10), O(14) and O(16) are protonated but that there is a COO<sup>-</sup> group at C(6). In (II) all of the carboxylate groups are deprotonated. Comparison with (III) suggests that the carboxylate groups on C(2) and C(5) are more acidic than the remainder.

Fig. 1 shows that the anions in (I) and (II) adopt the *trans,cis,trans* configuration found for both the anions in (III). The stereochemistry of the carbon framework is very similar in each case. Using (I) as an example, O(1), C(2), C(3) and C(5) are within 0.025 Å of their mean plane, but C(4) is 0.569 Å out of this plane. In consequence, the torsion angles between the carboxylate C atoms are C(6)–C(2)–C(3)–C(9) 94.4 (6), C(9)–C(3)–C(4)–C(12) –50.4 (6) and C(12)–C(4)–C(5)–C(15) 153.8 (6)°. This is a stable configuration for an unsubstituted tetrahydrofuran ring which in the present context maximizes the distance C(9)···C(12), 2.908 Å. In a model with an imposed mirror plane and a torsion angle of zero for C(9)–C(3)–C(4)–C(12) the distance C(9)···C(12) would be 2.58 Å.

Table 4 shows that only certain rotational positions of the carboxylate groups about their C–C vectors are found. (I) and (IIIa) are particularly similar because of the internal hydrogen bond O(16)···O(7). In (II) and (IIIb) there is no proton available for this hydrogen

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\times 10^3$ ) for non-H atoms of (I) with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{eq}(\text{Å}^2)$
Cs(1)	–3355 (1)	10736 (1)	6313 (1)	32 (1)
O(1)	8836 (6)	–784 (3)	489 (5)	26 (1)
C(2)	8440 (7)	319 (5)	962 (5)	21 (1)
C(3)	7255 (6)	21 (5)	1751 (5)	19 (1)
C(4)	7626 (7)	–1274 (5)	2121 (5)	22 (1)
C(5)	8111 (7)	–1743 (5)	969 (5)	24 (1)
C(6)	7785 (7)	1089 (5)	–101 (5)	23 (1)
O(7)	6864 (8)	642 (5)	9051 (5)	41 (1)
O(8)	8179 (6)	2161 (4)	–69 (4)	29 (1)
C(9)	7180 (8)	777 (5)	2838 (6)	24 (1)
O(10)	7828 (7)	1814 (4)	2829 (4)	34 (1)
O(11)	6532 (7)	439 (5)	3606 (5)	42 (1)
C(12)	9024 (7)	–1355 (5)	3132 (5)	24 (1)
O(13)	9914 (7)	–544 (5)	3433 (6)	42 (1)
O(14)	9183 (6)	–2418 (4)	3590 (5)	35 (1)
C(15)	6710 (8)	–2221 (6)	101 (6)	31 (1)
O(16)	6064 (6)	–1551 (5)	–796 (5)	36 (1)
O(17)	6247 (7)	–3174 (5)	258 (6)	46 (1)

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\times 10^3$ ) for non-H atoms of (II) with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{eq}(\text{Å}^2)$
Ca(1)	3762 (2)	2925 (2)	2978 (2)	10 (1)
Ca(2)	–242 (2)	–1633 (2)	811 (2)	13 (1)
O(3)	9082 (8)	6281 (8)	10685 (9)	32 (2)
O(4)	4679 (10)	5461 (9)	6542 (10)	36 (2)
O(5)	11603 (8)	7418 (8)	8865 (9)	31 (2)
O(6)	9189 (9)	8430 (10)	13504 (9)	42 (3)
O(7)	3626 (7)	3958 (7)	636 (8)	19 (2)
O(8)	8174 (9)	15064 (8)	6691 (10)	39 (2)
O(10)	8594 (12)	1719 (19)	4270 (12)	102 (6)
O(11)	–1231 (13)	4790 (13)	3252 (16)	79 (5)
O(21)	5878 (7)	9456 (6)	6608 (8)	12 (2)
C(22)	6972 (10)	10187 (10)	7188 (11)	7 (2)
C(23)	6097 (10)	11399 (9)	8036 (10)	7 (2)
C(24)	4526 (9)	11568 (9)	7343 (10)	6 (2)
C(25)	4371 (10)	10164 (10)	6890 (10)	12 (2)
C(26)	8156 (11)	9316 (10)	8101 (11)	9 (2)
O(27)	9175 (7)	9797 (7)	8671 (8)	12 (2)
O(28)	8016 (8)	8158 (7)	8241 (9)	22 (2)
C(29)	6691 (10)	12623 (9)	8117 (10)	7 (2)
O(30)	8040 (7)	12609 (7)	7838 (9)	20 (2)
O(31)	5789 (8)	13670 (7)	8553 (9)	18 (2)
C(32)	4389 (10)	12303 (10)	5952 (11)	16 (3)
O(33)	5497 (8)	12360 (8)	5219 (8)	21 (2)
O(34)	3047 (7)	12793 (7)	5527 (8)	18 (2)
C(35)	3704 (11)	9576 (10)	8120 (12)	15 (3)
O(36)	4202 (8)	8389 (7)	8282 (8)	19 (2)
O(37)	2599 (8)	10281 (8)	8790 (9)	32 (2)

bond and the C(6) carboxylate group is rotated by ca 30° from its position in (I) and (IIIa).

In (I) each anion is coordinated to seven Cs atoms, each of which is eight-coordinate, with Cs–O distances in the range 3.009–3.342 Å (Table 5\*). The pair of Cs atoms related by the centre of symmetry at 0.5, 0, 0.5 is bridged by four O atoms O(11), O(11)', O(17)'' and

\* Lists of structure factors, anisotropic thermal parameters and Tables 5 and 6 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39599 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

\* Table 5 has been deposited.

Table 3. *Interatomic distances (Å) and angles (°) in the anions*

	(I)	(II)*		(I)	(II)		(I)	(II)
O(1)—C(2)	1.435 (7)	1.450 (12)	C(6)—O(7)	1.248 (8)	1.235 (13)	C(12)—O(13)	1.220 (8)	1.244 (13)
C(2)—C(3)	1.539 (8)	1.511 (12)	C(6)—O(8)	1.269 (7)	1.269 (13)	C(12)—O(14)	1.315 (7)	1.290 (11)
C(3)—C(4)	1.552 (8)	1.538 (12)	C(3)—C(9)	1.517 (8)	1.495 (15)	C(5)—C(15)	1.531 (9)	1.530 (15)
C(4)—C(5)	1.547 (8)	1.532 (14)	C(9)—O(10)	1.314 (7)	1.264 (12)	C(15)—O(16)	1.315 (9)	1.255 (12)
C(5)—O(1)	1.424 (7)	1.437 (10)	C(9)—O(11)	1.193 (8)	1.265 (11)	C(15)—O(17)	1.185 (8)	1.255 (12)
C(2)—C(6)	1.516 (8)	1.541 (13)	C(4)—C(12)	1.524 (8)	1.535 (15)			
O(1)—C(2)—C(3)	105.4 (4)	103.5 (7)	O(1)—C(2)—C(6)	107.0 (5)	109.7 (8)	O(7)—C(6)—O(8)	123.4 (6)	124.0 (9)
C(2)—C(3)—C(4)	103.6 (4)	103.5 (7)	C(2)—C(3)—C(9)	119.2 (5)	118.6 (8)	O(10)—C(9)—O(11)	124.4 (6)	121.6 (9)
C(3)—C(4)—C(5)	100.2 (4)	103.7 (7)	C(3)—C(4)—C(12)	111.2 (5)	112.3 (8)	O(13)—C(12)—O(14)	124.8 (6)	121.4 (10)
C(4)—C(5)—O(1)	106.0 (4)	104.5 (7)	C(4)—C(5)—C(15)	110.4 (5)	111.7 (8)	O(16)—C(15)—O(17)	122.4 (7)	124.7 (11)
C(5)—O(1)—C(2)	111.7 (5)	112.0 (7)						

\* Atoms numbered C(20 + *n*) etc.Table 4. *Stereochemistry of the tetrahydrofuran-tetra-carboxylate anions*

Line	(I)	(II)*	(IIIa)†	(IIIb)†
Angle between line and normal to plane of tetrahydrofuran ring (°)				
C(2)—C(6)	132.4 (4)	129.3 (4)	131.0 (8)	131.3 (9)
C(3)—C(9)	65.6 (3)	64.7 (6)	68.4 (8)	68.9 (9)
C(4)—C(12)	7.1 (4)	11.9 (5)	8.6 (9)	7.4 (9)
C(5)—C(15)	160.6 (3)	160.5 (6)	164.6 (8)	166.0 (9)
Angle between the normals to the plane of the carboxylate group and the tetrahydrofuran ring (°)				
Group				
C(6)	70.8 (4)	44.3 (6)	70.7 (11)	40.1 (12)
C(9)	26.8 (5)	27.5 (5)	17.5 (11)	30.6 (11)
C(12)	87.3 (4)	85.3 (6)	86.6 (12)	85.2 (11)
C(15)	82.3 (3)	69.5 (5)	86.4 (11)	82.9 (11)

\* In (II) the anion has atoms C(20 + *n*).

† From Barnes &amp; Paton (1982) with atoms renumbered for consistency.

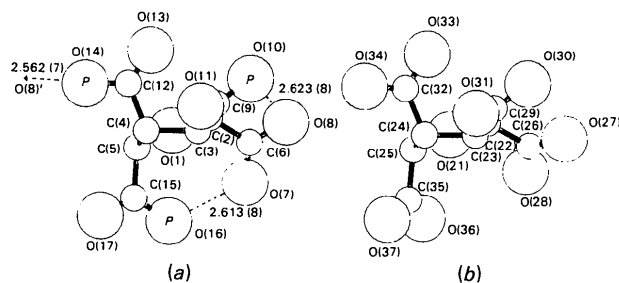


Fig. 1. (a) Anion of (I) and (b) anion of (II) viewed down the bisector of the angle C(3)...O(1)...C(4) or C(23)...O(21)...C(24). The protonated O atoms are denoted by P. Hydrogen bonds (Å) are shown by dashed lines, putative hydrogen bonds to water molecules in (II) are not included.

O(17)''' forming an approximate square of side 3.23 Å perpendicular to the Cs—Cs axis. The appropriate O(7), O(10) and O(13) atoms form a triangle on the other side of each Cs atom, tilted relative to the Cs...Cs axis with O(10) further from the O(11), O(11)', O(17)'', O(17)''' plane to create space for O(8) (Fig. 2). The coordination geometry is thus 4 + 1 + 3, and could be described as approximately face-sharing cubic coordination with two unshared ligand atoms O(8) and

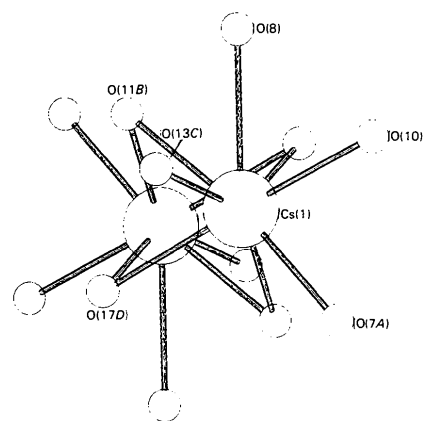


Fig. 2. Coordination of the centrosymmetric Cs dimer in (I). O(8) and O(10) belong to the same anion but each of the other O atoms comes from a separate anion. Thus each anion is attached to seven different Cs atoms.

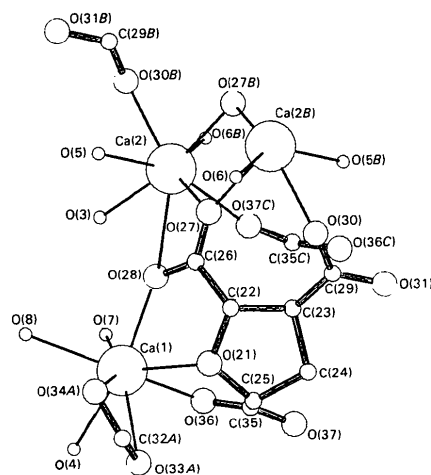


Fig. 3. Coordination of Ca atoms in (II). View perpendicular to the tetrahydrofuran ring showing the eightfold coordination of Ca(1) and Ca(2) and the bridging between Ca(1)...Ca(2) and Ca(2)...O(8). Ligands are shown incomplete for clarity. Atoms O(3) to O(8) belong to water molecules.

O(13) very much displaced from the ideal positions. O(1), the furan oxygen, takes no part in coordination.

In (II), Fig. 3, each anion links four Ca atoms to give chains Ca(2)'...Ca(2)...Ca(1)...Ca(2)'', cross-linked by Ca(1)...Ca(1)', where the mid-point of Ca(2)...Ca(2)' [3.965 (1) Å] is the origin and the mid-point of Ca(1)...Ca(1)' is 0.5,0,0.5. O(27) and O(27)'' link Ca(2) and Ca(2)' and O(28) links Ca(1) and Ca(2) but Ca(1) and Ca(1)' are only connected across the anion from O(21), the furan oxygen, to O(33). Each Ca atom is eight-coordinate and of irregular geometry including three water molecules. Bond lengths and angles are given in Table 6.\* The water molecules O(10) and

O(11) take part in the extensive network of hydrogen bonds.

#### References

- ASHIDA, T. (1973). *The Universal Crystallographic Computing System, Osaka*. The Computation Center, Osaka Univ., Japan.  
 BARNES, J. C. & PATON, J. D. (1982). *Acta Cryst.* **B38**, 1588–1591.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 MOTHERWELL, S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.  
 ROBERTS, P. & SHELDRIK, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

\* Table 6 has been deposited.

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## Tris(1,2-dimethoxyethane)lithium $\mu$ -Chloro- $\mu$ -oxo-bis[chloro(pentamethylcyclopentadienyl)(1-pyrrolyl)zirconate(IV)] Dimethoxyethane Solvate, [Li(C<sub>4</sub>H<sub>10</sub>O<sub>2</sub>)<sub>3</sub>][Zr<sub>2</sub>Cl<sub>3</sub>O(C<sub>4</sub>H<sub>4</sub>N)<sub>2</sub>(C<sub>10</sub>H<sub>15</sub>)<sub>2</sub>].C<sub>4</sub>H<sub>10</sub>O<sub>2</sub>

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**Abstract.**  $M_r = 1074.9$ , monoclinic,  $C2/c$ ,  $a = 12.203$  (3),  $b = 30.853$  (9),  $c = 15.194$  (4) Å,  $\beta = 106.82$  (4)°,  $V = 5475$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.30$  g cm<sup>-3</sup>, Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 5.67$  cm<sup>-1</sup>,  $T = 293$  K,  $F(000) = 2248$ ;  $R = 0.082$  for the 1850 reflections with  $F_o^2 > 3\sigma(F_o^2)$ . The Zr–O length is short, 1.910 (6) Å, while the Zr–Cl(bridge) distance is long, 2.665 (4) Å, especially compared to the Zr–Cl(terminal) distance of 2.472 (4) Å. The angles at the bridge are Zr–O–Zr = 132.5 (8)° and Zr–Cl–Zr = 82.0 (2)°. Both the cation and the anion reside on crystallographic twofold axes. An uncoordinated dimethoxyethane (dme) lies highly disordered about a twofold axis.

**Introduction.** The pyrrolyl anion,  $\bar{N}C_4H_4$ , is isoelectronic with the cyclopentadienyl anion, but the chemistry of the former is not nearly so well developed as that of the latter. In the course of our investigations of pyrrolyl complexes of the early transition metals, we have noted an interesting competitive effect:  $\bar{N}C_4H_4$  is able

reversibly to displace  $\bar{C}_5H_5$  in some instances. For example, the reaction of  $(\eta^5-C_5H_5)_2ZrCl_2$  with  $NaNc_4H_4$  in  $H_4$ furan‡ leads to the formation of the expected  $(\eta^5-C_5H_5)_2Zr(Nc_4H_4)_2$  upon extraction with toluene. However, it has been demonstrated that  $[Na(H_4furan)_6]_2[Zr(Nc_4H_4)_6]$  is formed as an intermediate (Bynum, Hunter, Rogers & Atwood, 1980). This allows the inference of an unexpected lability of the cyclopentadienyl rings. In order to learn of the range of this behavior, the reaction of  $(C_5Me_5)_2ZrCl_2$  with  $NaNc_4H_4$  was undertaken in dme.

**Experimental.** Straw-colored crystal, air-sensitive. Specimen, 0.20 × 0.25 × 0.30 mm sealed under N<sub>2</sub> in a glass capillary. CAD-4 diffractometer; unit-cell parameters refined from Bragg angles of 24 reflections,  $2\theta$  25–30°, space group  $C2/c$  or  $Cc$  from systematic absences, shown to be  $C2/c$  by successful refinement; 4474 reflections measured in the quadrant  $h = -14$  to 14,  $k = 0$  to 34,  $l = 0$  to 17,  $\theta - 2\theta$  scan (0.80° + 0.20° tan  $\theta$ ), net count of 4000 obtained if scan time of less than 240 s required, 2° < 2 $\theta$  < 50°; three standard reflections every 200 reflections, only

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‡ Tetrahydrofuran.