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Polymeric Caesium *o*-Phenylenedioxydiacetate Dihydrate

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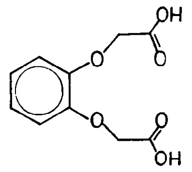
Abstract. $2Cs^+.C_{10}H_8O_6^{2-}.2H_2O$, $M_r = 526{\cdot}0$, orthorhombic, $Pbca$, $a = 28{\cdot}13\ (1)$, $b = 13{\cdot}908\ (4)$, $c = 7{\cdot}595\ (1)$ Å, $V = 2971\ (2)$ Å^3, $Z = 8$, $D_m = 2{\cdot}38$, $D_x = 2{\cdot}351$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 4{\cdot}90$ mm^{-1}, $F(000) = 1968$, $T = 293$ K. Final $R = 0{\cdot}037$ for 1779 observed reflections. The title compound, prepared by the reaction of *o*-phenylenedioxydiacetic acid with Cs_2CO_3 in aqueous ethanol, is polymeric with two different caesium centres, one six-coordinate [mean Cs—O, 3·161 (6) Å], the other eight-coordinate [mean Cs—O, 3·185 (6) Å]. Both caesium ions lie outside the ionophore cavity of the ligand but are bonded to the "inner" oxygens, while the waters and the carboxylate oxygens provide the polymer links.

Introduction. In most cases, metal complexes of *o*-phenylenedioxydiacetic acid (H_2bdda) have a stereochemistry based upon a pentagonal pyramid or bipyramid, with the metal ion within the ionophore cavity.



H_2bdda

Divalent metal ions Ca, Mn, Zn, Co (Smith, O'Reilly & Kennard, 1987) and Mg (Kennard, Smith, O'Reilly, Reynolds & Mak, 1988) are all pentagonal bipyramidal with both monomeric and polymeric forms. The Group I*a* metal ion complexes $[Li_2(bdda)(H_2O)_3]_2$ (Smith, O'Reilly & Kennard, 1986), $[K(Hbdda)(H_2bdda)]$ (Green, Duax, Smith & Wudl, 1975) and $[Na_4(bdda)_2(H_2O)_8]$ (Kennard *et al.*, 1988) show variations on a pentagonal pyramid or bipyramid with dimeric, monomeric and polymeric modes. However, with $(NH_4^+)_2(bdda)^{2-}$, the cations lie outside the ionophore cavity but are strongly hydrogen bonded to the carboxyl oxygens (Kennard *et al.*, 1988). In all complexes, the bdda cation is essentially planar. It was therefore of interest to observe the effect of a much larger cation (Cs^+) upon the mode of complexation with the bdda ligand.

Experimental. The title compound was prepared by the reaction of *o*-phenylendioxydiacetic acid (benzene-1,2-dioxydiacetic acid = H_2bdda) in 50% aqueous ethanol with excess caesium carbonate at 363 K. Hard colourless crystals grew from the filtrate after partial room-temperature evaporation. Density measured by flotation. A single prismatic crystal (0·32 × 0·22 × 0·12 mm) was used to collect data at room temperature on a Nicolet *R*3*m* four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ X-radiation ($\lambda = 0{\cdot}71069$ Å). Cell parameters were obtained using angle data from 21 reflections with $2\theta > 20°$. Data collection details: ω–2θ collection mode, 2·02–8·37° min^{-1}, variable scanning rate, $2\theta_{\max}$ 60°, collection range, h 0–35, k 0–17, l 0–9; total data (unique) 2716, unobserved data 937. Standards, variation: 002, 213, ±0·5%. 1779 reflections with $I > 2{\cdot}5\sigma(I)$ used in structure refinement. Data corrected for absorption (maximum and minimum transmission factors, 0·363, 0·227). The structure was solved by direct methods using *SHELX76* (Sheldrick, 1976). Blocked-matrix least squares (F's) with anisotropic thermal parameters for all non-hydrogens gave $R = 0{\cdot}037$ and $wR = 0{\cdot}038$ $\{w = 1{\cdot}6/[\sigma^2(F_o) + 4{\cdot}6 \times 10^{-4}(F_o)^2]\}$. Hydrogens were located by difference methods and their positional and thermal parameters refined. Maximum (Δ/σ) in the last cycle was 0·038

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

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

	x	y	z	U_{eq}
Cs(1)	0·33271	−0·12452 (4)	−1·1366 (7)	0·0522 (3)
Cs(2)	0·31607 (2)	0·12922 (3)	−0·87068 (6)	0·0408 (3)
O*w*(1)	0·2377 (2)	−0·0088 (4)	−1·0188 (8)	0·060 (4)
O*w*(2)	0·2551 (2)	−0·2881 (4)	−1·2347 (12)	0·100 (5)
C(1)	0·4520 (3)	0·0572 (4)	−0·8540 (9)	0·035 (4)
C(2)	0·4503 (2)	0·1120 (5)	−1·0069 (9)	0·030 (4)
C(3)	0·4871 (3)	0·1711 (5)	−1·0512 (10)	0·037 (4)
C(4)	0·5273 (3)	0·1772 (5)	−0·9405 (11)	0·040 (4)
C(5)	0·5290 (3)	0·1246 (5)	−0·7886 (11)	0·041 (4)
C(6)	0·4914 (3)	0·0635 (5)	−0·7475 (11)	0·041 (4)
O(71)	0·4129 (2)	0·0006 (3)	−0·8194 (6)	0·034 (3)
C(81)	0·4144 (3)	−0·0560 (5)	−0·6640 (10)	0·037 (4)
C(91)	0·3675 (3)	−0·1110 (5)	−0·6370 (9)	0·032 (4)
O(101)	0·3333 (2)	−0·0906 (4)	−0·7372 (7)	0·044 (3)
O(111)	0·3687 (2)	−0·1697 (4)	−0·5125 (7)	0·044 (3)
O(72)	0·4097 (2)	0·0981 (3)	−1·1074 (6)	0·037 (3)
C(82)	0·4077 (3)	0·1527 (5)	−1·2669 (9)	0·035 (4)
C(92)	0·3606 (2)	0·1344 (5)	−1·3620 (9)	0·033 (4)
O(102)	0·3289 (2)	0·0858 (4)	−1·2859 (8)	0·055 (4)
O(112)	0·3569 (2)	0·1731 (4)	−1·5082 (7)	0·056 (4)

(non-hydrogen) and 0·061 (hydrogen). Maximum and minimum difference peaks, 0·95 and −0·93 e Å^{-3} (adjacent to Cs). Scattering factors and f', f'' terms for anomalous dispersion are from *International Tables for X-ray Crystallography* (Ibers & Hamilton, 1974). Atomic positional and thermal parameters are listed in Table 1* while bond distances and angles are given in Table 2.

Discussion. The structure of the title compound comprises two independent caesium centres, one irregular six-coordinate [Cs(1)—O, 3·090–3·246 (6): mean, 3·161 (6) Å], the other eight-coordinate [Cs(2)—O, 3·045–3·282 (6): mean 3·185 (6) Å] (Fig. 1). Unlike the other Group I*a* complexes of *o*-phenylenedioxydiacetic acid, [$Li_4(bdda)_2(H_2O)_6$] (Smith *et al.*, 1986), [$Na_4(bdda)_2(H_2O)_8$] (Kennard *et al.*, 1988) and [K(Hbdda)(H_2bdda)] (Green *et al.*, 1975), the metal ion lies outside the ionophore cavity. However, Cs(2) is symmetrically located relative to the 'inner' oxygens [O(71), O(72), O(101) and O(102)] of the bdda ligand system but 2·081 (1) Å away from the ligand plane. In addition, Cs(2) is linked to symmetry-generated bdda ligands O(112) as well as both waters [O*w*(1) and O*w*(2)]. These waters are alternately bridged to the second caesium [Cs(1)], giving zigzag chains which extend through the structure in the direction of the *b* axis, at $a = \frac{1}{4}, \frac{3}{4}$. With

Table 2. *Bond distances* (Å) *and angles* (°) *associated with* Cs

Cs(1)—O*w*(1)	3·246 (6)	Cs(2)—O*w*(1)	3·132 (6)
Cs(1)—O*w*(2)	3·240 (6)	Cs(2)—O*w*(2)	3·156 (7)
Cs(1)—O(101)	3·070 (6)	Cs(2)—O(71)	3·282 (6)
Cs(1)—O(111^{i})	3·093 (6)	Cs(2)—O(101)	3.257 (6)
Cs(1)—O(111^{ii})	3·179 (6)	Cs(2)—O(72)	3·219 (5)
Cs(1)—O(102)	3·139 (6)	Cs(2)—O(102)	3·231 (5)
		Cs(2)—O(112^{iii})	3·045 (5)
		Cs(2)—O(112^{iv})	3·157 (5)
O*w*(1)—Cs(1)—O*w*(2)	81·8 (2)	O*w*(2)—Cs(2)—O(71)	150·4 (2)
O*w*(1)—Cs(1)—O(101)	69·9 (2)	O*w*(2)—Cs(2)—O(101)	130·5 (2)
O*w*(1)—Cs(1)—O(111^{i})	128·7 (2)	O*w*(2)—Cs(2)—O(72)	142·8 (2)
O*w*(1)—Cs(1)—O(111^{ii})	128·8 (2)	O*w*(2)—Cs(2)—O(102)	121·4 (2)
O*w*(1)—Cs(1)—O(102)	67·0 (2)	O*w*(2)—Cs(2)—O(112^{iii})	78·6 (2)
O*w*(2)—Cs(1)—O(101)	109·8 (2)	O*w*(2)—Cs(2)—O(112^{iv})	74·3 (2)
O*w*(2)—Cs(1)—O(111^{i})	82·3 (2)	O(71)—Cs(2)—O(101)	47·8 (2)
O*w*(2)—Cs(1)—O(111^{ii})	69·6 (2)	O(71)—Cs(2)—O(72)	46·7 (2)
O*w*(2)—Cs(1)—O(102)	123·3 (2)	O(71)—Cs(2)—O(102)	85·5 (2)
O(101)—Cs(1)—O(111^{i})	160·3 (2)	O(71)—Cs(2)—O(112^{iii})	71·9 (2)
O(101)—Cs(1)—O(111^{iii})	81·0 (2)	O(71)—Cs(2)—O(112^{iv})	102·2 (2)
O(101)—Cs(1)—O(102)	102·4 (2)	O(101)—Cs(2)—O(72)	85·8 (2)
O(111^{i})—Cs(1)—O(111^{ii})	89·2 (2)	O(101)—Cs(2)—O(102)	96·4 (2)
O(111^{i})—Cs(1)—O(102)	82·4 (2)	O(101)—Cs(2)—O(112^{iii})	81·4 (2)
O(111^{ii})—Cs(1)—O(102)	163·1 (2)	O(101)—Cs(2)—O(112^{iv})	150·0 (2)
O*w*(1)—Cs(2)—O*w*(2)	95·8 (2)	O(72)—Cs(2)—O(102)	48·6 (2)
O*w*(1)—Cs(2)—O(71)	107·0 (2)	O(72)—Cs(2)—O(112^{iii})	102·9 (2)
O*w*(1)—Cs(2)—O(101)	69·0 (2)	O(72)—Cs(2)—O(112^{iv})	68·6 (2)
O*w*(1)—Cs(2)—O(72)	107·0 (2)	O(102)—Cs(2)—O(112^{iii})	151·4 (2)
O*w*(1)—Cs(2)—O(102)	67·3 (2)	O(102)—Cs(2)—O(112^{iv})	78·4 (2)
O*w*(1)—Cs(2)—O(112^{iii})	135·5 (2)	O(112^{iii})—Cs(2)—O(112^{iv})	89·3 (2)
O*w*(1)—Cs(2)—O(112^{iv})	132·1 (2)		

Symmetry code: (i) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, 1+z$; (iii) $x, y, 2+z$; (iv) $x, \frac{1}{2}-y, 1\frac{1}{2}+z$.

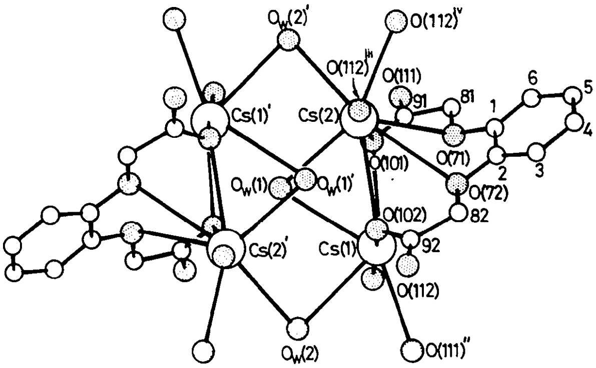


Fig. 1. Molecular configuration and atom-naming scheme for [$Cs_2(bdda)(H_2O)_2$]$_n$.

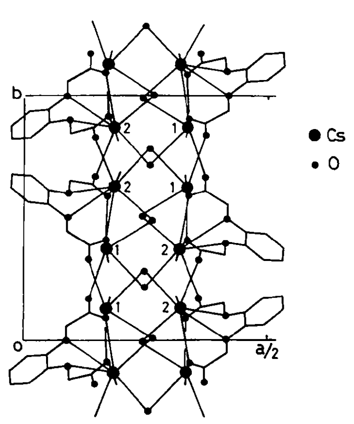


Fig. 2. Packing in the unit cell viewed perpendicular to *ab*.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and intraligand bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52068 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Cs(1), the six-coordination comprises the two waters, both 'inner' carboxylate oxygens [O(101) and O(102)] and the oxygens of two bridging carboxylate groups [O(111) and O(111)']. The two caesium ions are separated by 4·093 (2) Å. This system of bonds accounts for the stability of the crystal structure, despite the inability of the metal ion to fit the ionophore cavity. The structure is also stabilized by interpolymer hydrogen-bonding interactions involving the water molecules and carboxylate oxygens, O*w*(1)···O(101), 2·94 Å ($\frac{1}{2}-x$, $-y$, $-\frac{1}{2}+z$); O*w*(1)···O(102), 2·79 Å ($\frac{1}{2}-x$, $-y$, $-1\frac{1}{2}+z$); O*w*(2)···O(111), 2·77 Å (x, $-\frac{1}{2}-y$, $-\frac{1}{2}+z$), O*w*(2)···O(102), 2·97 Å ($\frac{1}{2}-x$, $\frac{1}{2}+y$, $-2+z$). The bdda ligand itself is essentially planar [torsion angles C(1)—C(2)—O(72)—C(82), C(2)—O(72)—C(82)—C(92), C(72)—C(82)—C(92)—O(102), −179, −178, +8 (1)°; C(2)—C(1)—O(72)—C(81), C(1)—O(71)—C(81)—C(91), O(71)—C(81)—C(91)—O(101), −180, +177, −9 (1)°, respectively], consistent with observed conformations in both univalent and divalent bdda complexes (coordinated) and in ionic $(NH_4^+)_2(bdda)^{2-}$ (Kennard *et al.*, 1988). Fig. 2 is a view of the packing in the unit cell.

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Structure of $[N(C_4H_9)_4]_2[Fe(C_3H_7NO)_6][Fe_4Br_4S_4]_2$

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Abstract. Bis(tetrabutylammonium) hexa(dimethylaminoformaldehyde)iron(2+) bis[tetrabromotetrakis-μ_3-thio-tetraferrate(2−)], $[N(C_4H_9)_4]_2$-$[Fe(C_3H_7NO)_6][Fe_4Br_4S_4]_2$, $M_r = 2321·8$, monoclinic, $P2_1/n$, $a = 10·840$ (6), $b = 19·860$ (10), $c = 21·180$ (7) Å, $\beta = 104·24$ (4)°, $V = 4420$ (7) Å^3, $Z = 2$, $D_x = 1·745$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 52·4$ cm^{-1}, $F(000) = 2320$, $T = 203$ K, final $R = 0·050$ for 5119 unique observed reflections with $I_o > 2\sigma(I_o)$. The $[Fe(C_3H_7NO)_6]^{2+}$ cation has crystallographically imposed $\bar{1}$ symmetry and the three unique Fe^{II}—O(DMF) distances are 2·092 (6), 2·142 (7) and 2·150 (8) Å. The Fe—S distances in $[Fe_4S_4Br_4]^{2-}$ range from 2·266 (2) to 2·284 (3) Å with the average being 2·275 Å. Similar values for Fe—Br are 2·326 (2), 2·346 (2) and 2·339 Å.

Introduction. The iron–sulfur cubane-like core $[Fe_4S_4(SR)_4]^{2-}$ has been the subject of numerous studies concerned with the active sites of ferredoxins, nitrogenase and hydrogenase (Berg & Holm, 1982). We, and others, have recently shown that the complex $[Fe_4S_4Br_4]^{2-}$ can form from $FeBr_3$ and Na_2S in DMF solution *via* a self-assembly process that involves a sequence of dimerization and redox reactions (Rutchik, Kim & Walters, 1988; Müller & Schladerbeck, 1985; Müller, Schladerbeck & Bögge, 1985). We have attempted to utilize this type of reaction to synthesize heterobimetallic complexes. The compound reported here is an unanticipated product from that work.

Experimental. The title compound resulted from an attempt to synthesize a heteronuclear bimetallic compound containing Fe, Cl, Mn, S, CO and Bu_4N^+ in DMF. When the reaction solution was concentrated to minimum volume and left standing under a nitrogen atmosphere for several days a black crystalline product was obtained. This has been determined by X-ray crystallographic analysis to be an Fe–S

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