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Sodium Salts of the Bis-μ-peroxo-hexacarbonatodicerate(IV) Anion. Crystal Structure of $Na_8[Ce(O_2)(CO_3)_3]_2 \cdot 18H_2O$

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A recent determination of the crystal structure of the orange–red complex $K_8[Ce(O_2)(CO_3)_3]_2 \cdot 12H_2O$ [1] showed that the dimeric anion contains two symmetrically bridging and doubly bidentate peroxide groups linking the cerium atoms which are 3.523 Å apart. Each cerium atom is 10-coordinate, with three bidentate carbonate ligands. The corresponding sodium salt $Na_8[Ce(O_2)(CO_3)_3]_2 \cdot 30H_2O$ is well known as unstable red–black needles [2].

The carbonate ligands can be replaced by acetate and benzoate ions in solution but no crystals have been obtained [2]. Ehtylene diamine tetraacetate reacts with the potassium salt to give microscopic brown crystals [3]. An attempt to prepare a nitrilotriacetate analogue gave crystals which have been shown to be $Na_8[Ce(O_2)(CO_3)_3]_2 \cdot 18H_2O$. This hydrate, which has not been reported previously, contains the same dimeric anions as the potassium salt.

Experimental

Crystallographic Data

$Na_8[Ce(O_2)(CO_3)_3]_2 \cdot 18H_2O$, $M_r = 1212.51$, monoclinic, $P2_1/c$, $a = 7.53(3)$, $b = 11.38(4)$, $c = 22.17(4)$ Å, $\beta = 115.16(8)°$, $V = 1719.5$ Å^3, $Z = 4$, $D_x = 4.68$ Mg m^{-3}, λ(Cu Kα) = 1.5418 Å, $\mu = 218.5$ cm^{-1}, $F(000) = 1152$, $T = 293$ K, $R = 0.096$ for 1549 reflexions.

Final refinement (minimizing $\Sigma w||F_o|-|F_c||^2$) 263 refined parameters, $R = 0.096$, $R_w = 0.117$, $w = 1000/\sigma^2(F) + 0.021576(F^2)$, mean shift/e.s.d = 0.016 (excl. U_{ij} O(282)), max.shift/e.s.d = 0.94 (U_{ij} for O(282)), max. negative peak = 5.3 e Å^{-3}, residual diff. peaks discussed below.

The addition of sodium nitrilotriacetate to a solution of $[Ce(O_2)(CO_3)_3]^{8-}$ in saturated aqueous Na_2CO_3 prepared by the method of Melloche [2] slowly precipitated a mixture of orange–red needles and yellow plates. These were separated under the microscope. A needle 0.39 × 0.28 × 0.17 mm was mounted in a Lindemann glass capillary. Initial oscillation and Weissenberg photographs showed the needle axis to be the *b*-axis of a monoclinic cell in space group $P2_1/c$ with $a = 15.06$, $b = 11.38$, $c = 22.17$ Å, $\beta = 115.16°$. These photographs showed that the festoons for odd values of h contained relatively few reflexions above background.

Data were collected by equi-inclination Weissenberg photography for layers ($h0$–$9l$), after which the crystal was remounted on the ac diagonal and varnished for protection. Layers 0 and 1 of this setting were collected before the crystal deteriorated. Intensities were measured by the S.E.R.C. Microdensitometer Service, Daresbury Laboratory. The unit cell was refined as part of the measurement routine. 1737 unique reflexions were recorded above background with an internal consistency index of 0.071; only 188 of these had h odd. The ranges covered were $-16 \leqslant h \leqslant 16$, $0 \leqslant k \leqslant 11$, $0 \leqslant l \leqslant 26$. Data were corrected for the Lorentz and polarisation factors and for absorption.

All calculations were performed on the University of Dundee DEC 10 computer using SHELX76 [4], XANADU [5] and PLUTO [6]. Atomic scattering parameters were taken from International Tables for X-ray Crystallography [7].

A density calculation suggested that there would be two independent Ce atoms in the unit cell. These were revealed by the direct methods routine EEES. The structure was extended by conventional least squares refinement and difference synthesis during which it became clear that the anion was $[Ce(O_2)(CO_3)_3]_2{}^{8-}$ and that no nitrilotriacetate had been incorporated. At R 0.21 no further improvements could be obtained on a model which contained many unsatisfactory bond lengths and angles. It appeared that the anion was centrosymmetric about (0.75,0,0) which is not a crystallographic centre of inversion in $P2_1/c$. This local symmetry was added to the model and the bond lengths constrained to be similar to those found in the potassium salt. With these constrains $R = 0.18$ and inspection of the data showed that 78 of the 80 reflexions for which $(|F_o| - |F_c|)/F_o$ was greatest had h odd. This suggested a model in which the main structure had $a = 7.53$ Å and the axial doubling arose from a degree of disorder. All the data for h odd were excluded, the data set reindexed for the smaller cell for which the space group is again $P2_1/c$ and the atomic coordinates recalculated to place half the anion (now the unique fragment) close to the centre of inversion at (0.5,0,0). No constraints on bond lengths were applied. The model refined to convergence at $R = 0.096$ with four sodium ions and eight water molecules included. One sodium ion, Na(41)/Na(42), is disordered almost equally over two sites. This leads to disorder for five

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of the water molecules coordinated to Na(41)/Na(42). No hydrogen atoms were included in the refinements reported, anisotropic thermal parameters were used for all atoms except the disordered oxygen atoms O(241)–O(282).

Final atomic parameters and equivalent isotropic thermal parameters are given in Table I while bond lengths and angles in the anion are listed in Table II. Lists of anisotropic thermal parameters together with observed and calculated structure factors along with other bond lengths and angles are available from the authors.

The disorder described above is within the smaller unit cell and does not explain the observed cell doubling. Examination of the final difference map shows several features close to the cerium atom position, with five peaks above 2 e Å^{-3}. Some of these are probably Fourier series-termination ripple arising from the limited data set but two peaks could be interpreted as alternative positions for Ce atoms

TABLE Ia. Coordinates $\times 10^{-4}$ for Non-hydrogen Atoms with e.s.d.s in Parentheses, $U_{eq}/U \times 10^{-3}$

	x/a	y/b	z/c	U_{eq} (Å^2) [a]
Ce1	4725(2)	1152(1)	9424(1)	23(1)
O1	7100(24)	446(16)	10434(10)	44(6)
O2	6821(25)	−423(19)	9926(8)	49(6)
C3	6777(36)	3167(25)	10203(13)	40(8)
O4	4990(23)	2742(14)	10147(8)	31(4)
O5	7209(23)	2702(14)	9756(8)	35(5)
O6	7699(27)	3901(18)	10590(8)	55(6)
C7	5688(30)	348(18)	8372(9)	21(6)
O8	6729(22)	1074(14)	8811(7)	29(4)
O9	6077(24)	−4(14)	7926(8)	35(5)
O10	4083(20)	−42(12)	8423(7)	24(4)
C11	1366(34)	2387(24)	8456(12)	36(7)
O12	1251(21)	1627(13)	8855(7)	30(4)
O13	3185(24)	2582(17)	8523(8)	44(6)
O14	−54(25)	2914(15)	8055(8)	41(5)
Na1	7155(15)	3560(9)	2374(5)	41(3)
Na2	8518(16)	3002(10)	8963(5)	47(3)
Na3	362(17)	172(10)	1215(7)	65(4)
Na41	8856(27)	−3215(18)	8521(9)	44(6)
Na42	11203(36)	3356(19)	10915(12)	50(8)
O21	3751(25)	−6(13)	3582(9)	40(6)
O22	896(31)	1606(23)	543(13)	74(8)
O23	1414(27)	1087(17)	4830(12)	61(7)
O241	559(63)	541(37)	7269(20)	47(13)
O242	−3(53)	56(31)	7652(18)	49(11)
O251	5007(66)	2419(34)	1391(22)	81(15)
O252	−3423(49)	2661(28)	6506(15)	12(10)
O261	4288(49)	2428(28)	2439(16)	54(11)
O262	5557(54)	3046(31)	7828(17)	23(12)
O271	−490(49)	3431(32)	6769(16)	34(11)
O272	10506(57)	2394(33)	11700(19)	52(12)
O281	7535(52)	−4893(31)	8890(21)	97(13)
O282	7356(82)	138(54)	3484(27)	0(21)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

TABLE Ib. Anisotropic Temperature Factors $\times 10^{-3}$ with e.s.d.s in Parentheses

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ce1	23(1)	29(1)	23(1)	−2(1)	17(1)	−6(1)
O1	24(9)	38(12)	67(12)	43(10)	17(8)	17(7)
O2	34(9)	86(14)	27(7)	17(9)	15(7)	15(10)
C3	30(12)	49(19)	50(13)	−23(12)	27(11)	7(11)
O4	34(9)	37(10)	36(7)	−20(7)	30(7)	−20(7)
O5	27(8)	50(11)	35(8)	−8(8)	20(7)	−3(8)
O6	48(10)	73(14)	46(9)	−40(11)	22(8)	−12(11)
C7	25(11)	21(13)	24(10)	4(7)	17(8)	9(8)
O8	27(8)	32(9)	32(7)	−2(7)	16(6)	−4(7)
O9	40(9)	28(9)	41(9)	16(7)	22(7)	1(7)
O10	26(7)	21(9)	35(7)	13(6)	24(6)	−3(6)
C11	26(12)	54(17)	40(12)	−2(11)	26(10)	−3(11)
O12	27(8)	25(9)	46(8)	11(7)	22(6)	−5(6)
O13	30(9)	77(15)	33(8)	10(8)	21(7)	−13(9)
O14	40(10)	36(10)	44(9)	5(8)	14(8)	28(8)
Na1	48(6)	42(6)	36(4)	−4(4)	22(4)	6(4)
Na2	44(6)	58(7)	55(6)	−11(5)	36(5)	−13(5)
Na3	40(7)	47(8)	103(10)	20(7)	25(6)	−3(6)
Na41	42(11)	40(13)	47(11)	3(8)	16(8)	−25(9)
Na42	67(16)	36(13)	69(15)	−1(11)	51(13)	−2(12)
O21	47(11)	8(9)	73(12)	−4(8)	33(9)	1(7)
O22	42(12)	84(16)	106(18)	22(14)	40(12)	10(12)
O23	27(9)	46(12)	105(17)	−7(12)	24(10)	9(9)

TABLE IIa. Bond Lengths (Å) and Bond Angles (°) in the $[Ce(O_2)(CO_3)_3]_2^{8-}$ Anion

	Present determination	Potassium salt[a]
(a) To cerium		
Ce(1)···Ce(1)′	3.558(2)	3.523(1)
Ce(1)–O(1)	2.335(16)	2.332(4)
Ce(1)–O(1)′	2.378(15)	2.345(4)
Ce(1)–O(2)	2.334(19)	2.367(3)
Ce(1)–O(2)′	2.355(17)	2.373(3)
Ce(1)–O(4)	2.369(17)	2.412(4)
Ce(1)–O(5)	2.446(16)	2.458(4)
Ce(1)–O(8)	2.425(20)	2.447(3)
Ce(1)–O(10)	2.469(15)	2.402(3)
Ce(1)–O(12)	2.433(14)	2.426(3)
Ce(1)–O(13)	2.454(17)	2.390(4)
O(1)–Ce(1)–O(2)	36.1(6)	36.4(1)
O(1)′–Ce(1)–O(2)′	35.6(6)	36.2(1)
O(4)–Ce(1)–O(5)	54.0(7)	53.9(1)
O(8)–Ce(1)–O(10)	54.0(7)	53.9(1)
O(12)–Ce(1)–O(13)	53.0(6)	56.3(1)
O(1)–Ce(1)–O(4)	78.7(6)	75.3(1)
O(2)–Ce(1)–O(10)	80.8(5)	75.5(1)
O(1)–Ce(1)–O(5)	122.5(6)	122.5(1)
O(2)–Ce(1)–O(8)	123.0(5)	123.0(1)
(b) Within ligands		
O(1)–O(2)	1.45(3)	
C(3)–O(4)	1.39(3)	

(continued)

TABLE IIa. *(continued)*

	Present determination
C(3)–O(5)	1.28(4)
C(3)–O(6)	1.19(3)
C(7)–O(8)	1.26(2)
C(7)–O(9)	1.21(3)
C(7)–O(10)	1.34(3)
C(11)–O(12)	1.27(3)
C(11)–O(13)	1.33(3)
C(11)–O(14)	1.22(3)
O(4)–C(3)–O(5)	110(2)
O(5)–C(3)–O(6)	126(3)
O(6)–C(3)–O(4)	124(3)
O(8)–C(7)–O(9)	124(2)
O(9)–C(7)–O(10)	119(2)
O(10)–C(7)–O(8)	116(2)
O(12)–C(11)–O(13)	114(2)
O(13)–C(11)–O(14)	123(3)
O(14)–C(11)–O(12)	123(3)

[a]See ref. 1.

TABLE IIb. Bond Lengths and Angles to Sodium Atoms

	Both	Na(41) present	Na(42) present
Na(1)–O(9)	2.39(4)		
Na(1)–O(14)	2.61(3)		
Na(1)–O(21)	2.53(4)		
Na(1)–O(242)			2.54(4)
Na(1)–O(251)		2.46(4)	
Na(1)–O(252)			2.26(4)
Na(1)–O(261)		2.54(4)	
Na(1)–O(262)			2.61(3)
Na(2)–O(5)	2.38(2)		
Na(2)–O(8)	2.52(2)		
Na(2)–O(12)	2.68(3)		
Na(2)–O(14)	2.66(3)		
Na(2)–O(23)	2.44(4)		
Na(2)–O(262)			2.56(4)
Na(2)–O(281)		2.49(4)	
Na(2)–O(282)			2.36(4)
Na(3)–O(1)	2.35(2)		
Na(3)–O(8)	2.63(3)		
Na(3)–O(9)	2.55(2)		
Na(3)–O(12)	2.35(3)		
Na(3)–O(242)			2.65(4)
Na(3)–O(22)	2.36(3)		
Na(3)–O(271)		2.26(4)	
Na(3)–O(272)			2.73(3)
Na(41)–O(6)		2.62(4)	
Na(41)–O(22)		2.71(4)	
Na(41)–O(241)		2.43(4)	
Na(41)–O(261)		2.58(5)	
Na(41)–O(271)		2.26(4)	
Na(41)–O(281)		2.45(5)	
Na(42)–O(6)			2.50(3)
Na(42)–O(22)			2.13(3)
Na(42)–O(23)			2.56(4)
Na(42)–O(272)			2.30(5)
Na(42)–O(282)			2.42(5)

giving a Ce···Ce distance of 3.559(5) Å compound with 3.558(2) Å in the main anion. This second position for the anion is displaced from the centre of inversion at (0.5,0,0) and can therefore contribute to the *h* odd reflexions of the larger cell.

When this cerium disorder was introduced into the data for the larger cell, *R* fell to 0.15 with the secondary Ce position occupied to 8%. With the limited data set available no attempt was made to introduce the rest of the anion, many atoms of which would be adjacent to atoms of the majority component. The minority component will also contribute to the *h* even reflextions for the larger cell and hence to all reflexions of the smaller cell, leading to the high final *R* of 0.096.

$Na_8[Ce(O_2)(CO_3)_3]_2 \cdot 30H_2O$

This compound was prepared by the method of Melloche [2]. Storage of the final solution at 276 K gave an excellent yield of red-black needles up to 10 × 2 × 2 mm embedded in Na_2CO_3. These crystals lose water and decompose in minutes on the open bench. Even when mounted in Lindemann glass capillaries small crystals deteriorated within 48 h at 293 K in the X-ray beam.

The needle axis was found to be a for a monoclinic cell with $a = 8.15(5)$, $b = 11.02(2)$, $d_{001} = 13.45(3)$ Å. The β angle was not determined. This suggests a cell volume in the region 1100–1200 Å^3 for one formula unit, in excellent agreement with the addition of $12H_2O$ to the volume of 860 Å^3 for $Na_8[Ce(O_2)(CO_3)_3]_2 \cdot 18H_2O$ reported above.

Close examination of the photographs of the 30-hydrate showed that two very weak lines of spots lie between each row on the 8.15 Å axis. These weak lines are commensurate with the main pattern indicating an axial length of 24.45 Å. Photographs at 233, 178 and 138 K showed no changes in the spot pattern or in the relative intensities of strong and weak rows, indicating that no phase change was occurring over this temperature range. It seems likely that the explanation for the weak layers in the 30-hydrate is a similar static anionic disorder to that found in the 18-hydrate.

Discussion

Figure 1 shows that compound **I** contains the dimeric anion already described in $K_8[Ce(O_2)(CO_3)_3]_2 \cdot 12H_2O$ [1]. The structure are compared in Tables II and III. The extensive disorder in **I** combines

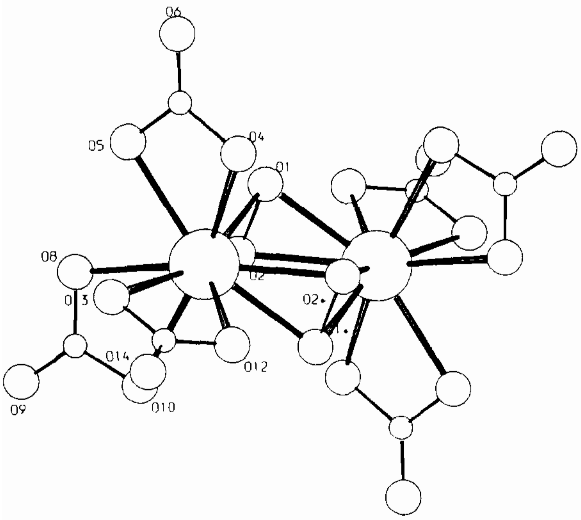

Fig. 1. The $[Ce(O_2)(CO_3)_3]^{8-}$ anion in **I**.

TABLE III. Angles between the Normals to the Plane O(1), O(2), O(1)', O(2)' and Planes Containing the Cerium Atom in the Sodium and Potassium Salts

Plane	Present structure	Potassium salt[a]
Ce(1), O(4), O(5)	150.3(4)	152.7(2)
Ce(1), O(8), O(10)	151.5(4)	152.6(2)
Ce(1), O(12), O(13)	92.5(4)	90.1(3)
Ce(1), O(1), O(2)	126.7(5)	127.8(2)

[a] See ref. 1.

with the limited photographic data set to give a structure of far lower precision than that for the ordered potassium salt which was determined from high quality data collected on a diffractometer. There are few significant differences except for the increase of 0.035 Å (17σ) in the Ce···Ce distance in **I**. The average Ce–peroxide (2.350 Å) and Ce–carbonate (2.433 Å) distances agree closely with those found previously (2.354 and 2.423 Å). The carbonate ligands are again distorted from 3-fold symmetry with the C–O bonds which are not coordinated to Ce shorter (1.21 Å) than those which are coordinated (1.31 Å) and the angles at carbon in Ce–O–C–O rings smaller (113°) than the other O–C–O angles (123°). Na–O distances range from 2.13 to 2.73 Å but the average distances about six of the eight Na^+ ions are in the range 2.49–253 Å. The remaining two average distances are 2.38 and 2.42 Å.

Table IV shows that four of the sodium environments can be described as distorted octahedra, two have seven oxygen neighbours giving approximations to D_{5h} pyramidal coordination and two are best described as square based pyramids. The last may well be six-coordinate sites with one disordered water molecule undiscovered among the many weak features of the final difference map. For this reason the molecule is described as the 18-hydrate although positions for only 16 (8 unique) water molecules are reported.

TABLE IV. Coordination Environments of the Sodium Atoms

	CN	Approximate shape
(a) Na(41) present		
Na(1)	5	square based pyramid
Na(2)	6	distorted octahedron
Na(3)	6	distorted octahedron
Na(41)	6	octahedron
(b) Na(42) present		
Na(1)	6	distorted octahedron
Na(2)	7	D_{5h} pyramid Σ(equatorial angles) = 390°
Na(3)	7	D_{5h} pyramid Σ(equatorial angles) = 393°
Na(42)	5	square based pyramid

The existence of two hydrates containing as many as 18- and 30-H_2O per formula weight, both showing disorder must imply that hydrated sodium ion is not bulky enough to give efficient packing with the large $[Ce(O_2)(CO_3)_3]_2^{8-}$ anion. K^+ is larger and adopts higher coordination numbers than Na^+ and gives a lattice which is highly ordered and somewhat more thermally stable.

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