normal, the bonds Cu(1)—N(2) (2·18) and Cu(2)—N(4) (2·15 Å) are somewhat elongated. The strongest distortion due to the Jahn–Teller effect leads to axial bond lengths Cu(1)—O(1) of 2·30 and Cu(2)—O(5) of 2·28 Å, respectively. This fact is in contrast to the structure of an analogous C-substituted Cu^{2+} complex (Moi, Yanuck, Deshpande, Hope, Denardo & Meares, 1987), in which the metal ion is situated in the N_2O_2 plane and the two amino nitrogens with the non-coordinated COOH groups are in axial positions with bond lengths of 2·37, 2·43 Å. Interesting also is the comparison with the structure of a Ni^{2+} complex with the related ligand 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N,N'*-diacetic acid (Xu Ji-De, Ni Shi-Sheng & Lin Yu-Juan, 1986) for which a *cis*-octahedral structure was found. Finally the Cu^{2+} complex of the analogous 12-membered macrocycle dota also gives a *cis*-octahedral structure with two elongated Cu—N bonds (Riesen *et al.*, 1986). All these results show that these macrocyclic amino carboxylic acids, having so many donor atoms, can coordinate metal ions in so many different ways that a prediction is practically impossible.

In our compound the Ba^{2+} cation is surrounded by eight O atoms, of which five are carboxylates and three water molecules. A total of six crystal water molecules could be localized in the crystal.

It is interesting to note that another form of the same compound also exists. The blue-green crystals have been partially studied by X-ray diffraction and the unit-cell parameters were $a = 8{\cdot}619\ (1)$, $b = 10{\cdot}578\ (1)$, $c = 16{\cdot}787\ (2)$ Å, $\alpha = 99{\cdot}89\ (2)$, $\beta = 97{\cdot}73\ (2)$, $\gamma = 110{\cdot}90\ (1)$°. The structure is very similar to the one discussed above with two Cu ions on special positions and Ba^{2+} in a common site. Instead of six a total of seven water molecules were found. Further work on this form is not intended.

The support of the study by the Swiss National Science Foundation (Project No. 2.851-0.85) is gratefully acknowledged.

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Complexes of Strontium and Barium Dimethylpropanoates with Dicyclohexano-18-crown-6(*A*) Ether

By John H. Burns and Samuel A. Bryan

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, *USA*

(*Received* 28 *March* 1988; *accepted* 31 *May* 1988)

Abstract. (1): Bis(2,2-dimethylpropanoato)strontium-*cis-syn-cis*-2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0^{9,14}]-hexacosane monohydrate, $[Sr(C_{20}H_{36}O_6)(C_5H_9O_2)_2].H_2O$, $M_r = 680{\cdot}39$, triclinic, $P\bar{1}$, $a = 14{\cdot}528\ (2)$, $b = 13{\cdot}966\ (2)$, $c = 9{\cdot}0403\ (9)$ Å, $\alpha = 95{\cdot}967\ (8)$, $\beta = 103{\cdot}035\ (6)$, $\gamma = 87{\cdot}75\ (8)$°, $V = 1777{\cdot}1\ (7)$ Å^3, $Z = 2$, $D_x = 1{\cdot}27$, $D_m = 1{\cdot}28$ g cm^{-3}, λ(Mo $K\alpha$) = 0·70926 Å, $\mu = 15{\cdot}2$ cm^{-1}, $F(000) = 724$, $T = 293$ K, $R(F) = 0{\cdot}071$ for 1992 reflections ($F_o > 3\sigma$). (2): 2,2-Dimethylpropanoato(diaqua)barium-*cis-syn-cis*-2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0^{9,14}]-hexacosane 2,2-dimethylpropanoate hydrate, $[Ba(C_{20}H_{36}O_6)(C_5H_9O_2)(H_2O)_2][C_5H_9O_2].H_2O$, $M_r = 766{\cdot}13$, triclinic, $P\bar{1}$, $a = 12{\cdot}716\ (2)$, $b = 14{\cdot}231\ (2)$, $c = 12{\cdot}024\ (4)$ Å, $\alpha = 94{\cdot}18\ (1)$, $\beta = 96{\cdot}82\ (1)$, $\gamma = 116{\cdot}72\ (1)$°, $V = 1910\ (2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}33$, $D_m = 1{\cdot}38$ g cm^{-3}, λ(Mo $K\alpha$) = 0·70926 Å, $\mu = 10{\cdot}1$ cm^{-1}, $F(000) = 800$, $T = 291$ K, $R(F) = 0{\cdot}025$ for 4136 reflections ($F_o > \sigma$). The Sr^{2+} ion in (1) is coordinated by all six O atoms of the crown ether and by two bidentate dimethylpropanoate ions (dmp), and the resulting complex molecules are linked by H_2O molecules through H bonding. Complex (2) crystallizes as ion pairs, $[Ba(dmp).(H_2O)_2.DC18C6]^+$ and $(dmp)^-$, separated by H_2O molecules to which they are H bonded.

0108-2701/88/101742-05$03.00

Introduction. Since Pedersen (1967) first suggested a correlation between the size of the ring opening in crown ethers and the stability of the complexes they can form with cations, there have been many efforts towards separating ions on the basis of size by complexing them with crown ethers. The fact that crown ethers can solubilize cations in organic media has led to their use in solvent-extraction systems. Specifically, dicyclohexano-18-crown-6 (DC18C6) has been used to extract Sr^{2+} (and sometimes Ba^{2+}) ions as nitrates (Filippov, Yashkin, Abashkin, Fomenkov & Serebryakov, 1982; Blasius, Klein & Schön, 1985), organophosphates (Kinard & McDowell, 1981), picrates (Kimura, Iwashima, Ishimori & Hamada, 1979) and neocarboxylates (McDowell, Case & Aldrup, 1983; Moyer, McDowell, Ontko, Bryan & Case, 1986) from various media. In many cases the stoichiometry of the extracted species has been determined, but the structure is unknown. Previously we showed that Sr and Ba complexes with 18-crown-6 and the dibutylphosphate anion have the same molecular structure, differing only a little in the shape of the crown, and concluded that the size of the ring opening is of minor importance relative to other energy considerations and other variables of the solvent-extraction system (Burns, 1985; Burns & Kessler, 1987).

The present work examines another pair of Sr and Ba complexes, but these involve a substituted crown, DC18C6(*A*), and a highly branched carboxylate anion, dimethylpropanoate (dmp). This combination is intended to serve as a model for the extraction complexes in the DC18C6–neocarboxylate system mentioned above. There have been no structures previously reported involving DC18C6 and the Sr^{2+} ion and only one with the Ba^{2+} ion, $Ba(SCN)_2.H_2O$.DC18C6 (Dalley, Sypherd & George, 1984).

Experimental. The *cis-syn-cis, A,* and *cis-anti-cis, B,* isomers of DC18C6 were separated by the method of Izatt, Haymore, Bradshaw & Christensen (1975), and the *A* isomer was reacted with $Sr(dmp)_2$ and $Ba(dmp)_2$ in $MeOH/H_2O$ solution to yield $Sr(dmp)_2$.DC18C6.H_2O, (1), and $Ba(dmp)_2$.DC18C6.$3H_2O$, (2), respectively. Crystal densities were measured by flotation. A colorless platelet (0·30 × 0·28 × 0·12 mm) of (1) and a colorless prism (0·30 × 0·45 × 0·22 mm) of (2) were sealed in glass and, in turn, mounted on a Huber four-circle diffractometer equipped with Mo $K\alpha$ (λ = 0·70926 Å) and a graphite monochromator.

Compound (1) was analyzed as follows: Unit-cell dimensions at 293 K determined from settings of 14 reflections ($2\theta = 19$–$21°$). Intensity data collected using $\theta/2\theta$ scans to $(\sin\theta)/\lambda = 0{\cdot}482$ Å^{-1}, $h = -13$ to 13, $k = -13$ to 13, $l = 0$ to 8. A reference reflection, measured hourly, declined a total of 4%. Data corrected for Lorentz and polarization factors, for changes in reference intensity, and for calculated transmission factors: $T_{\rm min} = 0{\cdot}66$, $T_{\rm max} = 0{\cdot}83$. Collected 4024 reflections, 3666 unique, $R_{\rm int}(F) = 0{\cdot}026$. Structure determined by Patterson and Fourier methods. All atoms in twofold sites of $P\bar{1}$. Atomic scattering factors, including anomalous-dispersion contributions for heavy atoms, from *International Tables for X-ray Crystallography* (1974). All calculations were performed with Oak Ridge computer programs [see Agron & Busing (1986) for listing]. All non-hydrogen atoms refined with anisotropic thermal parameters; 379 parameters varied. H atoms not found but included in idealized positions, with $B = B_{\rm eq}$ of the atom(s) to which they are attached, but omitted 18 methyl H's. $\sum w(F_o^2 - F_c^2)^2$ minimized, where $w = [\sigma_c^2 + (sF_o^2)^2]^{-1}$; σ_c^2 is variance of F_o^2 due to counting statistics, $s = 0{\cdot}03$. Largest $\Delta/\sigma = 0{\cdot}88$ for C(23); most values $< 0{\cdot}1$. Agreement factors $R(F_o) = 0{\cdot}071$, $wR(F_o) = 0{\cdot}148$, $S = 2{\cdot}57$ for 1992 observed reflections ($F_o > 3\sigma$). Final difference Fourier map had $(\Delta\rho)_{\rm max} = 1{\cdot}04$, $(\Delta\rho)_{\rm min} = -0{\cdot}52$ e Å^{-3}.

Compound (2) was analyzed in a completely analogous manner to (1) with the following variables and results: Unit-cell dimensions at 291 K from settings of 18 reflections ($2\theta = 32$–$35°$). Intensity data to $(\sin\theta)/\lambda = 0{\cdot}516$ Å^{-1}, $h = -13$ to 12, $k = -14$ to 12, $l = 0$ to 12. Reference reflection declined 17% during data collection. Transmission factors were $T_{\rm min} = 0{\cdot}72$, $T_{\rm max} = 0{\cdot}81$. Collected 4646 reflections, 4340 unique, $R_{\rm int}(F_o) = 0{\cdot}009$. All non-hydrogen atoms refined with anisotropic thermal parameters and all H atoms included in fixed idealized positions with $B = B_{\rm eq}$ of attached atom(s); 397 parameters varied. Weighted as before, but $s = 0{\cdot}05$. Largest $\Delta/\sigma = 0{\cdot}80$ for C(29), most values $< 0{\cdot}1$. Agreement indices $R(F_o) = 0{\cdot}025$, $wR(F_o) = 0{\cdot}070$, $S = 1{\cdot}23$ for 4136 ($F_o > \sigma$) reflections. Final difference Fourier map had $(\Delta\rho)_{\rm max} = 0{\cdot}46$, $(\Delta/\rho)_{\rm min} = -0{\cdot}58$ e Å^{-3}. Relatively high agreement factors for (1) compared with (2) attributed to high background scattering due to fluorescence of Sr and to poorer-quality crystal sample.

Discussion. Final positional and thermal parameters for (1) and (2) are given in Tables 1 and 2. Bond lengths are given in Tables 3 and 4, and torsion angles in the crown molecules are deposited.*

The structure and thermal motions of one molecule of $Sr(dmp)_2.H_2O$.DC18C6 are represented in Fig. 1, and the intermolecular contacts including the hydrogen bonds are pictured in Fig. 2. The Sr^{2+} ion is coordinated by all six O atoms of the crown ether and by two bidentate $(dmp)^-$ ions. These complex molecules are

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* Lists of structure factors, anisotropic thermal parameters, best planes, calculated H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51088 (47 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Coordinates and equivalent isotropic thermal parameters for* (1)

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Sr	0·2239 (1)	0·2561 (1)	0·3240 (2)	3·92 (8)
O(1)	0·1098 (7)	0·2313 (9)	0·0466 (12)	5·6 (6)
O(2)	0·1946 (7)	0·0647 (7)	0·1836 (13)	5·1 (6)
O(3)	0·2723 (8)	0·1011 (9)	0·4790 (15)	6·5 (7)
O(4)	0·2840 (10)	0·2741 (10)	0·6344 (14)	7·7 (8)
O(5)	0·2698 (8)	0·4321 (7)	0·4609 (14)	5·7 (6)
O(6)	0·1869 (7)	0·4170 (8)	0·1587 (12)	4·9 (7)
O(7)	0·0755 (11)	0·1866 (11)	0·3793 (7)	9·7 (10)
O(8)	0·0496 (9)	0·3403 (11)	0·3841 (13)	7·7 (8)
O(9)	0·3384 (8)	0·2334 (7)	0·1292 (12)	5·5 (6)
O(10)	0·4061 (7)	0·2476 (8)	0·3695 (13)	6·2 (7)
O*w*	−0·0482 (12)	0·5247 (12)	0·3229 (16)	15·2 (12)
C(1)	0·119 (1)	0·138 (1)	−0·037 (2)	7·3 (11)
C(2)	0·111 (1)	0·063 (1)	0·066 (2)	7·3 (11)
C(3)	0·189 (2)	−0·008 (1)	0·287 (2)	6·1 (11)
C(4)	0·197 (1)	−0·108 (1)	0·203 (2)	7·0 (11)
C(5)	0·286 (2)	−0·125 (1)	0·146 (2)	7·9 (12)
C(6)	0·375 (1)	−0·108 (2)	0·276 (3)	8·5 (13)
C(7)	0·369 (1)	−0·009 (1)	0·355 (2)	7·0 (11)
C(8)	0·281 (2)	0·007 (1)	0·411 (2)	5·7 (11)
C(9)	0·302 (2)	0·108 (1)	0·638 (3)	9·3 (14)
C(10)	0·296 (2)	0·195 (2)	0·707 (3)	12·2 (17)
C(11)	0·287 (2)	0·364 (2)	0·695 (2)	10·0 (16)
C(12)	0·319 (2)	0·426 (2)	0·617 (2)	9·4 (13)
C(13)	0·279 (1)	0·510 (1)	0·372 (2)	5·9 (10)
C(14)	0·368 (1)	0·494 (1)	0·310 (2)	6·0 (9)
C(15)	0·376 (1)	0·577 (1)	0·208 (3)	8·6 (13)
C(16)	0·286 (2)	0·579 (1)	0·078 (2)	7·4 (11)
C(17)	0·199 (1)	0·593 (1)	0·146 (2)	7·0 (11)
C(18)	0·193 (1)	0·514 (1)	0·244 (2)	4·9 (9)
C(19)	0·098 (1)	0·403 (1)	0·043 (2)	6·5 (10)
C(20)	0·109 (1)	0·308 (1)	−0·049 (2)	6·6 (11)
C(21)	0·020 (2)	0·255 (2)	0·380 (2)	7·1 (16)
C(22)	−0·086 (1)	0·242 (2)	0·365 (3)	9·1 (15)
C(23)	−0·098 (3)	0·132 (3)	0·343 (6)	35·6 (42)
C(24)	−0·116 (2)	0·275 (2)	0·502 (3)	14·1 (18)
C(25)	−0·135 (2)	0·280 (3)	0·232 (4)	24·7 (33)
C(26)	0·411 (1)	0·236 (1)	0·234 (2)	4·7 (10)
C(27)	0·509 (1)	0·224 (2)	0·194 (2)	7·0 (12)
C(28)	0·518 (2)	0·121 (2)	0·126 (4)	17·7 (22)
C(29)	0·582 (2)	0·238 (3)	0·335 (3)	20·9 (26)
C(30)	0·515 (1)	0·290 (2)	0·077 (3)	13·3 (15)

Table 2. *Coordinates and equivalent isotropic thermal parameters for* (2)

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Ba	0·02053 (2)	0·24173 (2)	0·33941 (2)	3·08 (1)
O(1)	0·0252 (2)	0·2310 (2)	0·0970 (2)	4·5 (1)
O(2)	0·2127 (2)	0·3990 (2)	0·2584 (2)	4·8 (1)
O(3)	0·2148 (2)	0·4148 (2)	0·4963 (2)	4·8 (1)
O(4)	−0·0069 (2)	0·3106 (2)	0·5518 (2)	4·8 (2)
O(5)	−0·2114 (2)	0·1695 (2)	0·4053 (2)	4·1 (1)
O(6)	−0·1849 (2)	0·1368 (2)	0·1820 (2)	4·5 (1)
O(7)	0·2001 (2)	0·1874 (2)	0·3546 (2)	5·3 (1)
O(8)	0·7362 (3)	0·3184 (3)	0·1346 (3)	6·8 (2)
O(9)	0·1426 (2)	0·0306 (2)	0·4137 (2)	5·5 (1)
O(10)	0·8137 (3)	0·4296 (3)	0·0149 (3)	7·3 (2)
O*w*(1)	−0·0700 (2)	0·0360 (2)	0·3806 (3)	5·5 (1)
O*w*(2)	−0·0535 (2)	0·3880 (2)	0·2792 (2)	5·1 (1)
O*w*(3)	0·9646 (3)	0·4434 (2)	−0·1500 (2)	6·3 (2)
C(1)	0·1261 (5)	0·3206 (4)	0·0694 (4)	6·6 (3)
C(2)	0·2312 (4)	0·3533 (4)	0·1583 (4)	6·2 (2)
C(3)	0·3194 (4)	0·4524 (3)	0·3408 (4)	5·9 (2)
C(4)	0·2917 (4)	0·4986 (3)	0·4418 (4)	6·5 (3)
C(5)	0·1918 (4)	0·4510 (3)	0·6019 (4)	5·8 (2)
C(6)	0·3039 (5)	0·4995 (5)	0·6945 (5)	8·6 (3)
C(7)	0·3470 (5)	0·4198 (7)	0·7226 (5)	9·8 (4)
C(8)	0·2496 (5)	0·3222 (6)	0·7572 (5)	9·6 (3)
C(9)	0·1392 (4)	0·2731 (4)	0·6658 (4)	6·5 (2)
C(10)	0·0965 (4)	0·3548 (3)	0·6393 (3)	5·1 (2)
C(11)	−0·1171 (4)	0·2555 (3)	0·5911 (3)	5·6 (2)
C(12)	−0·2157 (3)	0·2359 (3)	0·4965 (4)	5·4 (2)
C(13)	−0·3084 (3)	0·1380 (3)	0·3140 (3)	5·1 (3)
C(14)	−0·2923 (3)	0·0721 (3)	0·2217 (4)	5·7 (3)
C(15)	−0·1830 (4)	0·1083 (3)	0·0661 (3)	5·1 (4)
C(16)	−0·1632 (4)	0·0117 (3)	0·0470 (4)	6·3 (2)
C(17)	−0·1586 (5)	−0·0130 (4)	−0·0775 (5)	8·6 (3)
C(18)	−0·0659 (6)	0·0838 (4)	−0·1210 (4)	7·9 (3)
C(19)	−0·0875 (5)	0·1792 (4)	−0·0987 (4)	7·1 (2)
C(20)	−0·0872 (4)	0·2050 (3)	0·0272 (3)	5·0 (2)
C(21)	0·2217 (3)	0·1190 (3)	0·3959 (3)	4·0 (2)
C(22)	0·3528 (3)	0·1421 (3)	0·4269 (4)	5·0 (2)
C(23)	0·3958 (6)	0·1966 (9)	0·5467 (6)	15·5 (8)
C(24)	0·3615 (5)	0·0397 (4)	0·4178 (7)	11·2 (5)
C(25)	0·4297 (4)	0·2126 (4)	0·3508 (6)	8·7 (4)
C(26)	0·7296 (4)	0·3531 (3)	0·0445 (4)	5·1 (2)
C(27)	0·6086 (4)	0·3004 (4)	−0·0351 (4)	6·8 (3)
C(28)	0·6280 (8)	0·3047 (11)	−0·1532 (7)	20·0 (1)
C(29)	0·5439 (7)	0·3632 (8)	−0·0104 (9)	15·7 (7)
C(30)	0·5360 (7)	0·1916 (6)	−0·0143 (9)	18·4 (9)

loosely joined into dimers in the crystal by rather weak H bonds from H_2O molecules. The Sr—O bond lengths to each (dmp)$^-$ ion are of unequal length because of the crowded 10-coordination, but Sr—O(8) is lengthened further because of the two H bonds to O(8). The C—C and C—O bond lengths (Table 3) are in the expected range except in the portion of the ether ring from C(9) to C(12), where they appear unusually short. This may be attributed to the higher thermal motion in that part of the ring (Table 1), or both effects may be the result of systematic errors in the data. Averaged bond angles and average deviations in the ether are: C—O—C 113·1 (25)° [omitting C(10)—O(4)—C(11) which is 127·5°]; C—C—O 108·9(34)° [omitting C(9)—C(10)—O(4) which is 123·2°], and C—C—C 110·7(19)°. The bond strain evidenced in some of these angles results from the simultaneous attraction of all six ether O atoms to the Sr^{2+} ion which does not quite fit the unstrained molecule. This is also seen in the O—C—C—O and C—O—C—C torsion angles, which are least strained when they have values near 60 and 180°, respectively; deviations by as much as 45° from these values are found. The array of crown O atoms can be viewed as lying, within 0·04 Å, in two planes having O(1) and O(4) in common and a dihedral angle of 26·4°. Thus the crown is partially wrapped around one side of the Sr^{2+} ion, which is 0·43 Å from each plane.

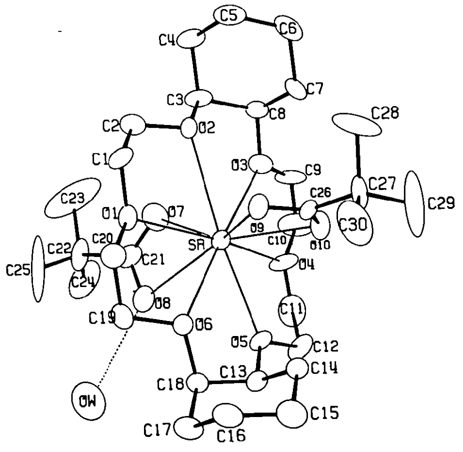

Fig. 1. One asymmetric unit of the structure of $Sr(dmp)_2.H_2O.DC18C6$ with 50% probability thermal ellipsoids.

Table 3. *Bond distances* (Å) *in* (1)

Sr–O(1)	2·67 (1)	Ether	
Sr–O(2)	2·85 (1)	O(1)–C(1)	1·45 (2)
Sr–O(3)	2·68 (1)	C(1)–C(2)	1·49 (2)
Sr–O(4)	2·73 (1)	C(2)–O(2)	1·42 (2)
Sr–O(5)	2·68 (1)	O(2)–C(3)	1·46 (2)
Sr–O(6)	2·79 (1)	C(3)–C(8)	1·55 (2)
Sr–O(7)	2·57 (1)	C(8)–O(3)	1·41 (2)
Sr–O(8)	2·89 (1)	O(3)–C(9)	1·40 (2)
Sr–O(9)	2·67 (1)	C(9)–C(10)	1·31 (3)
Sr–O(10)	2·59 (1)	C(10)–O(4)	1·33 (2)
		O(4)–C(11)	1·31 (3)
Cyclohexyl		C(11)–C(12)	1·44 (2)
C(3)–C(4)	1·53 (2)	C(12)–O(5)	1·43 (2)
C(4)–C(5)	1·50 (2)	O(5)–C(13)	1·44 (2)
C(5)–C(6)	1·55 (2)	C(13)–C(18)	1·50 (2)
C(6)–C(7)	1·50 (2)	C(18)–O(6)	1·48 (2)
C(7)–C(8)	1·48 (2)	O(6)–C(19)	1·48 (2)
C(13)–C(14)	1·53 (2)	C(19)–C(20)	1·51 (2)
C(14)–C(15)	1·57 (2)	C(20)–O(1)	1·44 (2)
C(15)–C(16)	1·54 (2)		
C(16)–C(17)	1·53 (2)		
C(17)–C(18)	1·51 (2)		
tma		Hydrogen bonds	
C(21)–O(7)	1·23 (2)	O*w*···O(8)	2·93 (2)
C(21)–O(8)	1·27 (2)	O*w*···O′(8)	3·10 (2)
C(21)–C(22)	1·52 (3)		
C(22)–C(23)	1·54 (4)		
C(22)–C(24)	1·44 (2)		
C(22)–C(25)	1·40 (3)		
C(26)–O(9)	1·25 (2)		
C(26)–O(10)	1·24 (2)		
C(26)–C(27)	1·55 (2)		
C(27)–C(28)	1·52 (2)		
C(27)–C(29)	1·46 (2)		
C(27)–C(30)	1·49 (2)		

Table 4. *Bond distances* (Å) *in* (2)

Ba–O(1)	2·917 (3)	Ether	
Ba–O(2)	2·809 (3)	O(1)–C(1)	1·439 (5)
Ba–O(3)	2·910 (3)	C(1)–C(2)	1·474 (7)
Ba–O(4)	2·785 (3)	C(2)–O(2)	1·421 (5)
Ba–O(5)	2·887 (2)	O(2)–C(3)	1·430 (5)
Ba–O(6)	2·746 (3)	C(3)–C(4)	1·491 (7)
Ba–O(7)	2·712 (3)	C(4)–O(3)	1·423 (5)
Ba–O*w*(1)	2·731 (3)	O(3)–C(5)	1·446 (5)
Ba–O*w*(2)	2·750 (3)	C(5)–C(10)	1·507 (6)
		C(10)–O(4)	1·437 (5)
Cyclohexyl		O(4)–C(11)	1·424 (5)
C(5)–C(6)	1·541 (7)	C(11)–C(12)	1·498 (6)
C(6)–C(7)	1·507 (9)	C(12)–O(5)	1·416 (5)
C(7)–C(8)	1·515 (9)	O(5)–C(13)	1·427 (4)
C(8)–C(9)	1·519 (7)	C(13)–C(14)	1·492 (6)
C(9)–C(10)	1·526 (7)	C(14)–O(6)	1·424 (5)
C(15)–C(16)	1·512 (6)	O(6)–C(15)	1·429 (4)
C(16)–C(17)	1·526 (7)	C(15)–C(20)	1·523 (6)
C(17)–C(18)	1·535 (8)	C(20)–O(1)	1·442 (5)
C(18)–C(19)	1·513 (7)		
C(19)–C(20)	1·530 (6)		
tma		Hydrogen bonds	
C(21)–O(7)	1·245 (4)	O*w*(1)···O(9)	2·722 (3)
C(21)–O(9)	1·262 (4)	O*w*(1)···O′(9)	2·822 (4)
C(21)–C(22)	1·539 (5)	O*w*(2)···O′(8)	2·725 (4)
C(22)–C(23)	1·499 (8)	O*w*(2)···O*w*′(3)	2·824 (4)
C(22)–C(24)	1·507 (7)	O*w*(3)···O′(10)	2·784 (4)
C(22)–C(25)	1·502 (6)	O*w*(3)···O(10)	2·876 (5)
C(26)–O(8)	1·233 (5)		
C(26)–O(10)	1·247 (5)		
C(26)–C(27)	1·534 (6)		
C(27)–C(28)	1·471 (9)		
C(27)–C(29)	1·499 (9)		
C(27)–C(30)	1·462 (9)		

The average Sr–O bond length (to crown O's) of 2·73 Å is close to the 2·75 Å in Sr(dibutylphosphate)$_2$.H_2O.18-crown-6 (Burns & Kessler, 1987), to the 2·68 Å in Sr(ClO_4)$_2$.(H_2O)$_3$.benzo-18-crown-6 (Hughes, Mortimer & Truter, 1978), and to the 2·69 Å in Sr(ClO_4)$_2$.acetobenzo-18-crown-6 (Fenton, Parkin, Newton, Nowell & Walker, 1982).

The asymmetric unit of the structure of Ba(dmp)$_2$.3H_2O.DC18C6 is shown in Fig. 3. Included in the coordination of the Ba^{2+} ion are all six O atoms of the crown ether, two H_2O molecules, and a monodentate (dmp)$^-$ ion. Thus the structure consists of ion pairs, (Ba.dmp.DC18C6.2H_2O)$^+$ and (dmp)$^-$, linked in the crystal by H bonding. The third H_2O molecule participates in further H bonding, connecting the ions into a chain approximately along the [011] directions as seen in Fig. 4. All these H bonds are stronger than those in (1). The crown appears to be less strained than in (1), the greatest deviation of torsion angles from *gauche* or *anti* being 29°. Averaged bond angles in the other molecule, and average deviations, are: C–O–C 113·8(8), C–C–O 108·2(7) and C–C–C 110·9(9)°.

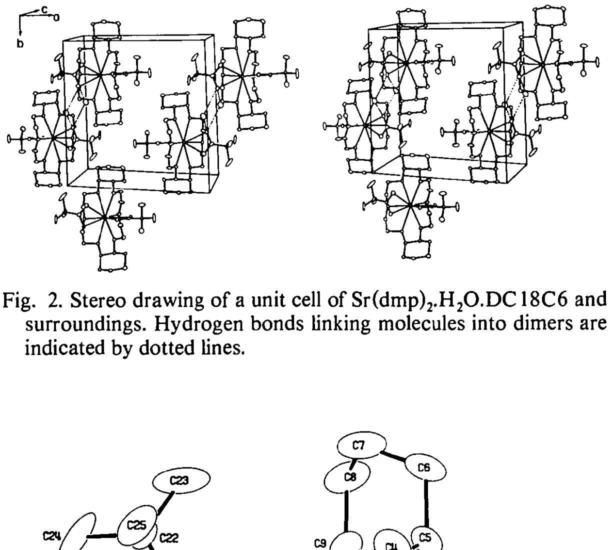

Fig. 2. Stereo drawing of a unit cell of Sr(dmp)$_2$.H_2O.DC18C6 and surroundings. Hydrogen bonds linking molecules into dimers are indicated by dotted lines.

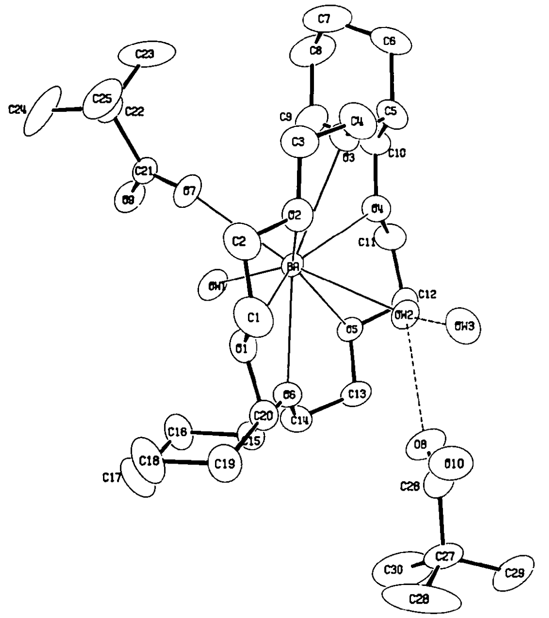

Fig. 3. One asymmetric unit of the structure of Ba(dmp)$_2$-(H_2O)$_2$.DC18C6.H_2O with 50% probability thermal ellipsoids.

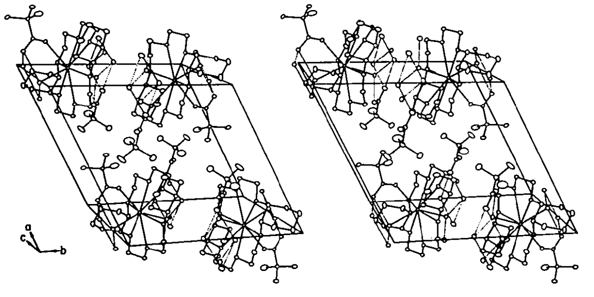

Fig. 4. Stereo drawing of $Ba(dmp)_2(H_2O)_2$.DC18C6.H_2O including a unit cell and some additional O atoms related by centers of symmetry at the midpoint of *b* and *c*. Dotted lines indicate the H-bond network which links molecules in chains along [011].

When the crown O atoms are described, as for (1), as lying in two planes (±0·1 Å) with O(2) and O(5) in common, the dihedral angle is only 11·7°, while the Ba^{2+} ion lies farther away from each plane (0·75 Å).

The average Ba—O distance to the crown is 2·84 Å, a value quite comparable to the equivalent averages in other compounds: 2·83 Å in $Ba(SCN)_2.H_2O$.DC18C6 (Dalley, Sypherd & George, 1984), 2·84 Å in Ba(dibutylphosphate)$_2$.H_2O.18-crown-6 (Burns, 1985), 2·82 Å in $Ba(ClO_4)_2.(H_2O)_2$.benzo-18-crown-6 (Hughes, Mortimer & Truter, 1978), and 2·82 Å in $BaBr_2.(H_2O)_2$.(15-crown-5)$_2$ (Feneau-Dupont, Arte, Declercq, Germain & Van Meerssche, 1979). The O···O distances close enough to indicate H bonding are also given in Table 4.

It is noteworthy that the two complexes (1) and (2) are quite different while the pair *M*(dibutylphosphate)$_2$.18-crown-6.H_2O (*M* = Sr,Ba), with the same two cations, are almost identical to each other (Burns & Kessler, 1987). This different complexing behavior is not expected to result from the crowns in (1) and (2) having cyclohexano substituents, because molecular mechanics calculations (Wipff, Weiner & Kollman, 1982; Burns & Kessler, 1987) have shown that these crowns can adapt to Sr^{2+} and Ba^{2+} ions without much strain. This flexibility is also apparent in reported structures of complexes between DC18C6 and ions ranging in size from Na^+ (Fraser, Fortier, Rodrigue & Bovenkamp, 1986) to $Tl(CH_3)_2^+$ (Hughes & Truter, 1983). Most likely, crystals of (1) and (2) differ primarily because there is a different balance (due to different Sr^{2+} and Ba^{2+} radii) among the contributions to the Coulombic energies from ion dehydration, dipolar attraction of the crown, $(dmp)^-$ attraction and H bonding. If this is the case, then different structures in crystals of complexes such as these would be expected more than would identical ones.

This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy under contract DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc. We thank G. M. Brown and W. R. Busing of ORNL for the use of their X-ray diffractometer.

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