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The Crown Ether Complex Ca(benzo-15-crown-5)$_2$(3,5-dinitrobenzoate)$_2$.3H$_2$O

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Abstract. $Ca(C_7H_3N_2O_6)_2(C_{14}H_{20}O_5)_2.3H_2O$, space group $P2_1/m$; $a = 7{\cdot}29\,(2)$, $b = 14{\cdot}56\,(2)$, $c = 22{\cdot}63\,(2)$ Å, $\beta = 94{\cdot}0\,(5)°$; $M_r = 1053{\cdot}0$, $D_c = 1{\cdot}46$ g cm^{-3}. The structure was solved by the heavy-atom method and refined to $R = 0{\cdot}095$ for 2654 observed reflexions. The coordination about the Ca atom is not the expected sandwich of two molecules of benzo-15-crown-5 (hereafter referred to as CROWN-5), but one molecule of CROWN-5 and two dinitrobenzoate (DNB) ions. The second CROWN-5 molecule is hydrogen bonded to water molecules.

Introduction. The bright-yellow complex (m.p. 77–78 °C) can be crystallized from an ethanolic mixture of Ca(DNB)$_2$ and CROWN-5 in the ratio 1:2, provided the solution contains 15–20% water. Since the characteristic peak of the IR spectrum (980 cm^{-1}; Poonia & Truter, 1973) of uncomplexed CROWN-5 is absent, suggesting a sandwich-type complex, the crystal structure determination was undertaken to provide information on the Ca coordination. Intensities were collected on Weissenberg film packs with the crystal rotating about **a** (and, later, **b**), and were measured by the SRC microdensitometer service† giving a merged data set of 2654 observed reflexions (for details of intensity estimation see Machin & Elder, 1974).

The space group $P2_1$ was initially assumed but the heavy-atom Fourier synthesis showed that all the organic ligands were bisected by the symmetry plane that results when one atom is placed in $P2_1$; so the space group was changed to $P2_1/m$ for the initial refinement. With the benzene rings specified as rigid bodies and isotropic temperature factors for all atoms, the structure was refined to an R of $0{\cdot}113$ with the least-squares program *RBLS* (Cradwick, 1976). It was further refined to $R = 0{\cdot}095$ with the *SHELX* program system at the Atlas computer laboratory by removing the rigid-body restrictions and giving anisotropic factors to appropriate atoms. H atoms contributed to the structure factors from their calculated positions. During refinement it was apparent that one nitro group and two of the water molecules were disordered. The atom sites concerned were therefore given occupancies of 0·5, and occupancies of the four atom sites used to represent the nitro group, O(32), O(33), O(34), O(35), were refined in the final cycles.

Refinement was then attempted in space group $P2_1$, in which these atoms need not be disordered, but no satisfactory model could be found involving full-weight atoms. This refinement terminated at an R of 0·077, and although the improvement in R is significant on the basis of Hamilton's test, the resulting model was rejected because of implausible geometry. A similar situation has been reported for the refinement of potassium hydrogenmalonate (Parthasarathy, Sime & Speakman, 1969) where a choice had to be made between space groups $C2$ and $C2/m$. Refinement in the noncentrosymmetric space groups was very similar for the two structures; both were slow to converge and both gave larger standard deviations than the refinement in the centrosymmetric space groups – five times larger for the malonate and three times for the crown ether. Comparison of the pairs of bonds that were equivalent in $P2_1/m$ but not in $P2_1$ (although the chemical environments are still the same) showed that the members of twelve such pairs differed from each other by more than three standard deviations. Four of these belonged to benzene rings and five had assumed unrealistic values, *e.g.* C—C bonds of 1·72, 1·29 and 1·67, 1·29 Å. It was therefore concluded that the true space group is $P2_1/m$.

The final atom parameters are shown in Table 1 and the molecular geometry in Table 2,† Fig. 1 and Table 1 give the disordered water molecules, O*W*(2), O*W*(3), on

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† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31978 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final atomic parameters*

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(2)	−0·0945 (7)	0·0932 (4)	0·2394 (2)	0·051 (3)	0·063 (3)	0·039 (3)	−0·021 (3)	0·008 (2)	−0·016 (2)
O(41)	0·3245 (7)	0·1738 (3)	0·3063 (2)	0·052 (3)	0·041 (3)	0·034 (2)	−0·001 (2)	−0·006 (2)	−0·002 (2)
O(42)	0·7380 (9)	0·0821 (4)	0·5506 (2)	0·099 (5)	0·069 (4)	0·032 (3)	0·010 (3)	−0·014 (3)	0·013 (3)
O(43)	0·6768 (8)	0·0124 (4)	0·4670 (2)	0·084 (4)	0·042 (3)	0·055 (3)	0·012 (3)	−0·001 (3)	0·006 (3)
N(31)	0·2861 (2)	0·0849 (8)	−0·0524 (5)	0·314 (18)	0·085 (8)	0·069 (6)	−0·058 (10)	0·012 (9)	−0·035 (6)

	x	*y*	*z*	*U*		*x*	*y*	*z*	*U*
Ca	0·0661 (3)	0·25	0·2484 (1)	0·0304 (5)	N(41)	0·6835 (8)	0·0815 (4)	0·4988 (3)	0·045 (2)
O(1)	−0·235 (1)	0·25	0·1870 (4)	0·063 (2)	C(41)	0·371 (1)	0·25	0·3287 (4)	0·032 (2)
C(1)	−0·340 (1)	0·1669 (7)	0·1882 (5)	0·076 (3)	C(42)	0·484 (1)	0·25	0·3874 (4)	0·031 (2)
C(2)	−0·211 (2)	0·0892 (6)	0·1854 (4)	0·063 (2)	C(43)	0·5347 (9)	0·1679 (5)	0·4154 (3)	0·035 (1)
C(3)	−0·170 (1)	0·0471 (6)	0·2874 (3)	0·059 (2)	C(44)	0·6270 (9)	0·1696 (5)	0·4704 (3)	0·033 (1)
C(4)	−0·053 (1)	0·0662 (5)	0·3427 (3)	0·047 (2)	C(45)	0·676 (1)	0·25	0·5002 (4)	0·036 (2)
O(3)	−0·0541 (6)	0·1640 (3)	0·3481 (2)	0·038 (1)	O(31)	0·1776 (7)	0·1744 (3)	0·1605 (2)	0·047 (1)
C(5)	0·0158 (9)	0·2021 (4)	0·4005 (3)	0·032 (1)	O(32)*	0·174 (2)	0·023 (1)	−0·0363 (7)	0·105 (8)
C(6)	0·083 (1)	0·1539 (5)	0·4500 (3)	0·043 (2)	O(33)	0·399 (3)	0·017 (2)	−0·0147 (9)	0·134 (11)
C(7)	0·145 (1)	0·2032 (6)	0·5008 (3)	0·053 (2)	O(34)	0·247 (4)	0·100 (1)	−0·1105 (9)	0·078 (9)
O(21)	0·571 (1)	0·25	0·6708 (4)	0·065 (2)	O(35)	0·344 (2)	0·0755 (9)	−0·0970 (6)	0·071 (6)
C(21)	0·468 (1)	0·1667 (7)	0·6594 (4)	0·069 (2)	C(31)	0·195 (1)	0·25	0·1352 (4)	0·033 (2)
C(22)	0·583 (1)	0·0908 (6)	0·6844 (4)	0·065 (2)	C(32)	0·235 (1)	0·25	0·0708 (4)	0·034 (2)
O(22)	0·5184 (8)	0·0913 (4)	0·7465 (2)	0·061 (2)	C(33)	0·248 (1)	0·1680 (6)	0·0406 (3)	0·051 (2)
C(23)	0·733 (1)	0·0443 (7)	0·7737 (4)	0·071 (3)	C(34)	0·275 (1)	0·1715 (6)	−0·0198 (4)	0·059 (2)
C(24)	0·7461 (1)	0·0649 (7)	0·8385 (4)	0·067 (2)	C(35)	0·289 (2)	0·25	−0·0513 (5)	0·048 (3)
O(23)	0·7922 (8)	0·1610 (4)	0·8446 (2)	0·060 (2)	O*W*(1)	0·408 (1)	0·25	0·8032 (4)	0·603 (2)
C(25)	0·783 (1)	0·2026 (6)	0·8988 (3)	0·051 (2)	O*W*(2)	0·057 (2)	0·216 (1)	0·7558 (6)	0·104 (5)
C(26)	0·776 (1)	0·1551 (7)	0·9510 (4)	0·065 (2)	O*W*(3)	−0·024 (3)	0·291 (2)	0·6465 (9)	0·161 (9)
C(27)	0·768 (1)	0·2051 (7)	1·0048 (4)	0·073 (3)					

* For O(32), O(33), O(34), O(35), *G* = 0·58 (3), 0·52 (3), 0·42 (4), 0·58 (4) respectively.

Table 2. *Bond lengths and angles*

O(1)–C(1)	1·43 (1)	O(21)–C(21)	1·44 (1)
C(1)–C(2)	1·47 (1)	C(21)–C(22)	1·48 (1)
C(2)–O(2)	1·44 (1)	C(22)–O(22)	1·41 (1)
O(2)–C(3)	1·419 (9)	O(22)–C(23)	1·40 (1)
C(3)–C(4)	1·49 (1)	C(23)–C(24)	1·49 (1)
C(4)–O(3)	1·429 (8)	C(24)–O(23)	1·44 (1)
O(3)–C(5)	1·374 (8)	O(23)–C(25)	1·374 (9)
C(5)–C(5′)	1·39 (1)	C(25)–C(25′)	1·38 (1)
C(5)–C(6)	1·38 (1)	C(25)–C(26)	1·37 (1)
C(6)–C(7)	1·41 (1)	C(26)–C(27)	1·42 (1)
C(7)–C(7′)	1·36 (1)	C(27)–C(27′)	1·31 (1)
O(31)–C(31)	1·251 (6)	O(41)–C(41)	1·256 (4)
C(31)–C(32)	1·51 (1)	C(41)–C(42)	1·515 (9)
C(32)–C(33)	1·382 (9)	C(42)–C(43)	1·390 (8)
C(33)–C(34)	1·40 (1)	C(43)–C(44)	1·37 (1)
C(34)–C(35)	1·36 (1)	C(44)–C(45)	1·386 (9)
C(34)–N(31)	1·47 (2)	C(44)–N(41)	1·480 (9)
N(31)–O(32)	1·28 (2)	N(41)–O(42)	1·211 (8)
N(31)–O(33)	1·51 (3)	N(41)–O(43)	1·236 (8)
N(31)–O(34)	1·34 (2)	N(31)–O(35)	1·13 (2)

C(6)–C(5)–O(3)	125·7 (6)	C(26)–C(25)–O(23)	123·6 (8)
C(5)–O(3)–C(4)	118·2 (5)	C(25)–O(23)–C(24)	119·2 (6)
O(3)–C(4)–C(3)	104·6 (6)	O(23)–C(24)–C(23)	106·7 (7)
C(4)–C(3)–O(2)	109·1 (7)	C(24)–C(23)–C(22)	109·2 (8)
C(3)–O(2)–C(2)	113·3 (6)	C(23)–O(22)–C(22)	111·9 (7)
O(2)–C(2)–C(1)	110·4 (8)	O(22)–C(22)–C(21)	109·6 (7)
C(2)–C(1)–O(1)	108·0 (8)	C(22)–C(21)–O(21)	106·9 (8)
O(31)–C(31)–C(32)	118·4 (4)	O(41)–C(41)–C(42)	117·9 (2)
N(31)–C(34)–C(33)	118·5 (8)	N(41)–C(44)–C(43)	118·8 (6)
O(32)–N(31)–C(34)	113·6 (13)	O(42)–N(41)–C(44)	118·5 (6)
O(33)–N(31)–C(34)	108·9 (12)	O(43)–N(41)–C(44)	117·0 (6)
O(34)–N(31)–C(34)	109·4 (12)	O(42)–N(41)–O(43)	124·5 (6)
O(35)–N(31)–C(34)	126·2 (13)	O(33)–N(31)–O(34)	137·0 (16)
O(32)–N(31)–O(35)	117·1 (14)		

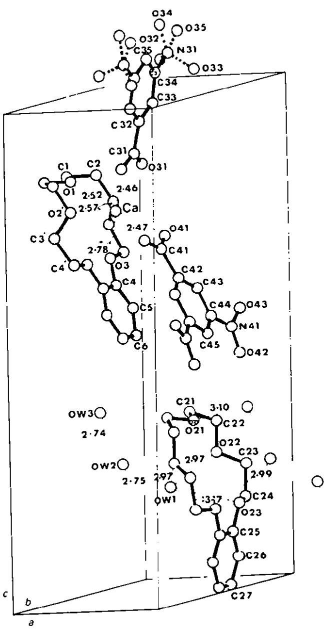

Fig. 1. The environments of the CROWN-5 molecules. The four oxygens of the disordered nitro group are shown with broken N—O bonds. Atom numbers with primes are mirror-related to those in Table 1.

opposite sides of the mirror plane at $y=\frac{1}{4}$, as their separation (2·78 Å) then makes a plausible hydrogen-bonding distance. The alternative positions are mirror related to those shown but, as the atoms to which they are hydrogen-bonded [O(21), O*W*(1)] lie on the mirror plane, the geometry of the two alternatives is identical.

Discussion. Contrary to expectations, Ca(DNB)$_2$(CROWN-5)$_2$.3H$_2$O is a 1:1 complex of Ca with CROWN-5. The second molecule of CROWN-5, instead of displacing the two organic anions from the cation, is involved in weak interactions with the protons of two bent hydrogen-bonded chains each made up of three water molecules, one chain approaching CROWN-5 from an adjacent unit cell. The Ca atom is coordinated to the four benzoate O atoms (Ca—O, 2·46, 2·47 Å) and the five O of a CROWN-5 molecule (Ca—O, 2·52, 2·57, 2·78 Å); this gives a coordination number of nine.

As a result of direct cation–anion interactions, the Ca atom is displaced further from the plane of the CROWN-5 O atoms (1·38 Å) than the similar sized ion in the complex NaI(CROWN-5) (0·75 Å, Bush & Truter, 1972). This reflects the relatively high charge density of the Ca ion since, in complexes of lower charge density, complete ionic separation is achieved – by H$_2$O in the NaI complex, and by a second CROWN-5 molecule in KI(CROWN-5)$_2$ (Mallinson & Truter, 1972).

An explanation for the disorder of the nitro group is suggested by the observation that the plane of the ordered nitro group, O(42), N(41), O(43), is rotated about the C—N bond by 14° with respect to the plane of the benzene ring. On the basis of the ONO angle (124° for the ordered nitro group), two orientations can be resolved for the disordered group, defined by O(32), N(31), O(35) (117°) and O(33), N(31), O(34) (137°). The planes through these two groups are rotated about the C—N bond with respect to the benzene plane by +35, −41°, considerably larger than for the ordered nitro group, but less than the 54° reported for *o*-nitrobenzoic acid (Kurahashi, Fukuyo & Shimada, 1967). Thus the disorder can be envisaged as a choice between two out-of-plane orientations. The sums of the angles about N(31) for these two orientations are 357 and 355°, indicating that C(34) is close to or on the ONO planes. Attempts to restrict the disordered group to a two-oxygen model led to very distorted anisotropic thermal ellipsoids for these atoms with very large components along **a**.

The two CROWN-5 rings have different conformations, as can be seen from Fig. 1. In particular, there is a difference of 125° in the torsion angles about C(4)—C(3) and C(24)—C(23), which allows O(22) and O(21) to coordinate to opposite sides of the molecular plane. The hydrogen bonds are sufficiently strong to bring about these conformational changes.

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