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Structure of the Bis(oxonium dichloropicrate)–Dicyclohexano-18-crown-6* Complex

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Abstract. $2[H_3O^+.C_6Cl_2N_3O_7^-].C_{20}H_{36}O_6$, M_r = 1004·54, triclinic, $P\bar{1}$, a = 7·855 (2), b = 10·048 (3), c = 14·927 (4) Å, α = 107·90 (2), β = 92·30 (2), γ = 91·62 (2)°, V = 1119·2 Å^3, Z = 1, D_x = 1·490 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 3·475 cm^{-1}, $F(000)$ = 1040, T = 293 K, R = 0·054 for 1650 reflections with $F^2 > 3\sigma(F^2)$. The complex consisting of two dichloropicrate ions, one dicyclohexano-18-crown-6 and two oxonium ions is centrosymmetric. Each oxonium ion is weakly hydrogen bonded to two ether O atoms and strongly to one dichloropicrate anion [OH···O distances of 2·775 (3), 2·796 (4) and 2·419 (3) Å respectively]. It lies 1·7 Å out of the ether O-atom mean plane. H_3O^+ has pyramidal geometry.

Introduction. Macrocyclic polyether complexes have received much attention as new types of extractants and ligands. Some structures of the crystalline extraction complexes of uranium(VI), uranium(IV) or thorium(IV) with dicyclohexano-18-crown-6 from hydrochloric acid or nitric acid systems have been reported (Zheng, Wang, Wang & Wang, 1986; Wang, Lin, Shen, Zheng, Wang & Wang, 1986; Wang, Wang, Zheng, Wang & Lin, 1988) and show that each H_3O^+ is anchored in the crown-ether cavity by three strong OH···O(ether oxygen) hydrogen bonds. The structure of the complex of dichloropicric acid, which is a relatively weaker acid compared with hydrochloric acid or nitric acid, with 18-crown-6 from water has been determined (Britton, Chantooni, Wang & Kolthoff, 1984). However, the details of the bonding between the crown ether, oxonium ions and dichloropicrate ions were confused by the disorder of the oxonium ion positions. In order to reveal these, we report the structure of the title compound.

Experimental. The compound was prepared in an aqueous solution of an equimolar mixture of dichloropicric acid and dicyclohexano-18-crown-6 (mixed isomer). Pale yellow crystal (0·33 × 0·2 × 0·13 mm). D_m not measured. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. 25 reflections with $10 < \theta < 16°$ to determine the cell parameters. 3932 unique reflections measured with $2\theta_{max}$ = 50°, h = 0 to 9, k = −11 to 11, l = −17 to 17, 1650 reflections with $F^2 > 3\sigma(F^2)$ used in the refinement. Three check reflections measured every 3600 s (5·0% variation). Lp and empirical absorption correction. No systematic absences. Structure solved by direct methods. All H atoms were located by difference Fourier syntheses. Full-matrix least-squares refinement on F with anisotropic temperature factors for non-H atoms and isotropic temperature factors for H atoms, 370 variables, $(\Delta/\sigma)_{max} < 0·02$, R = 0·054, wR = 0·059, where w = 1 for $F^2 > 3\sigma(F^2)$, w = 0 for $F^2 < 3\sigma(F^2)$, S = 1·355. No correction for isotropic extinction. Max. value in the final difference density map was 0·337 e Å^{-3}. Calculation performed on a PDP 11/44 computer with *SDP* program (Enraf–Nonius, 1983). Atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The final atomic parameters are given in Table 1. The structure is shown in Fig. 1. Table 2† gives the bond distances and angles.

The molecular ensemble of two dichloropicrate ions, one crown ether and two oxonium ions possesses a symmetry center. The dicyclohexano-18-crown-6 must be isomer *B* (Mercer & Truter, 1973). In the crown-ether ring, the C—C and C—O average bond distances are 1·482 and 1·430 Å respectively; the former appears to be abnormally short, but it is close to those of other crown-ether complexes (Zheng *et al.*, 1986; Wang *et al.*, 1988; Dunitz, Dobler, Seiler & Phizackerley, 1974). The torsion

* Dicyclohexano-18-crown-6 = 2,5,8,15,18,21-hexaoxatricyclo-[20.4.0.0^{9,14}]hexacosane.

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52798 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates and thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B_{eq}(Å^2)
Cl(1)	0·7028 (3)	0·2024 (2)	0·8978 (2)	6·97 (6)
Cl(2)	0·7967 (4)	0·7557 (3)	1·0751 (2)	7·43 (7)
O(1)	0·6625 (7)	0·4212 (5)	0·5632 (3)	5·1 (1)
O(2)	0·7207 (7)	0·5667 (5)	0·7244 (3)	4·9 (1)
O(3)	0·5411 (8)	0·2582 (6)	0·6880 (4)	7·4 (2)
O(4)	0·807 (1)	0·2204 (7)	0·6908 (5)	9·6 (2)
O(5)	0·913 (1)	0·8290 (7)	0·6908 (5)	12·4 (3)
O(6)	0·643 (1)	0·8503 (7)	0·8900 (6)	10·1 (2)
O(7)	0·8837 (8)	0·4583 (9)	1·1075 (4)	12·6 (2)
O(8)	0·6279 (8)	0·443 (1)	1·1016 (4)	12·9 (2)
O(9)	0·4658 (6)	0·1941 (5)	0·4488 (3)	3·7 (1)
O(10)	0·2480 (6)	0·4069 (5)	0·5449 (3)	4·1 (1)
O(11)	0·7237 (6)	0·3083 (4)	0·3625 (3)	3·4 (1)
N(1)	0·6849 (9)	0·2811 (6)	0·7224 (4)	5·2 (2)
N(2)	0·774 (1)	0·7873 (7)	0·8825 (5)	6·4 (2)
N(3)	0·7521 (8)	0·4553 (8)	1·0698 (4)	6·1 (2)
C(1)	0·7227 (9)	0·3715 (7)	0·8949 (5)	4·0 (2)
C(2)	0·7486 (9)	0·4849 (8)	0·9776 (5)	4·0 (2)
C(3)	0·7628 (9)	0·6162 (8)	0·9735 (5)	4·5 (2)
C(4)	0·7552 (9)	0·6417 (7)	0·8887 (5)	3·7 (2)
C(5)	0·7282 (9)	0·5343 (7)	0·8034 (4)	3·5 (2)
C(6)	0·7139 (9)	0·4004 (7)	0·8102 (5)	3·8 (2)
C(7)	0·6235 (9)	0·1854 (8)	0·3093 (5)	4·0 (2)
C(8)	0·729 (1)	0·0874 (8)	0·2333 (5)	4·9 (2)
C(9)	0·885 (1)	0·0442 (8)	0·2812 (6)	5·2 (2)
C(10)	0·833 (1)	−0·0256 (8)	0·3522 (6)	5·5 (2)
C(11)	0·719 (1)	0·0663 (7)	0·4261 (5)	4·3 (2)
C(12)	0·5696 (9)	0·1113 (7)	0·3762 (5)	3·8 (2)
C(13)	0·296 (1)	0·2066 (7)	0·4160 (5)	4·4 (2)
C(14)	0·189 (1)	0·2681 (7)	0·4965 (5)	4·4 (2)
C(15)	0·148 (1)	0·4738 (7)	0·6239 (5)	4·8 (2)
C(16)	0·245 (1)	0·5963 (7)	0·6883 (5)	4·5 (2)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cl(1)—C(1)	1·716 (8)	N(2)—C(4)	1·50 (1)
Cl(2)—C(3)	1·726 (8)	N(3)—C(2)	1·495 (9)
O(2)—C(5)	1·316 (8)	C(1)—C(2)	1·402 (9)
O(3)—N(1)	1·208 (8)	C(1)—C(6)	1·380 (8)
O(4)—N(1)	1·187 (8)	C(2)—C(3)	1·34 (1)
O(5)—N(2)	1·187 (9)	C(3)—C(4)	1·365 (9)
O(6)—N(2)	1·211 (9)	C(4)—C(5)	1·397 (8)
O(7)—N(3)	1·152 (7)	C(5)—C(6)	1·382 (9)
O(8)—N(3)	1·124 (7)	C(7)—C(8)	1·542 (9)
O(9)—C(12)	1·444 (7)	C(7)—C(12)	1·485 (9)
O(9)—C(13)	1·428 (8)	C(8)—C(9)	1·53 (2)
O(10)—C(14)	1·415 (8)	C(9)—C(10)	1·50 (1)
O(10)—C(15)	1·440 (8)	C(10)—C(11)	1·54 (2)
O(11)—C(7)	1·438 (8)	C(11)—C(12)	1·521 (9)
O(11)—C(16)	1·415 (7)	C(13)—C(14)	1·48 (1)
N(1)—C(6)	1·484 (9)	C(15)—C(16)	1·48 (2)

C(12)—O(9)—C(13)	113·5 (5)	N(2)—C(4)—C(5)	116·4 (6)
C(14)—O(10)—C(15)	112·9 (5)	C(3)—C(4)—C(5)	122·1 (7)
C(7)—O(11)—C(16)	113·6 (5)	O(2)—C(5)—C(4)	118·8 (6)
O(3)—N(1)—O(4)	126·1 (8)	O(2)—C(5)—C(6)	125·5 (6)
O(3)—N(1)—C(6)	117·4 (8)	C(4)—C(5)—C(6)	115·7 (7)
O(4)—N(1)—C(6)	116·5 (8)	N(1)—C(6)—C(1)	117·9 (6)
O(5)—N(2)—O(6)	127·7 (9)	N(1)—C(6)—C(5)	118·6 (6)
O(5)—N(2)—C(4)	117·2 (8)	C(1)—C(6)—C(5)	123·4 (7)
O(6)—N(2)—C(4)	115·1 (9)	O(11)—C(7)—C(8)	110·9 (6)
O(7)—N(3)—O(8)	123·9 (7)	O(11)—C(7)—C(12)	107·6 (5)
O(7)—N(3)—C(2)	117·1 (7)	C(8)—C(7)—C(12)	109·3 (7)
O(8)—N(3)—C(2)	118·7 (7)	C(7)—C(8)—C(9)	109·1 (6)
Cl(1)—C(1)—C(2)	121·6 (5)	C(8)—C(9)—C(10)	111·3 (7)
Cl(1)—C(1)—C(6)	120·8 (6)	C(9)—C(10)—C(11)	112·3 (7)
C(2)—C(1)—C(6)	117·6 (6)	C(10)—C(11)—C(12)	109·2 (6)
N(3)—C(2)—C(1)	118·0 (8)	O(9)—C(12)—C(7)	113·2 (5)
N(3)—C(2)—C(3)	121·4 (7)	O(9)—C(12)—C(11)	106·7 (5)
C(1)—C(2)—C(3)	120·5 (6)	C(7)—C(12)—C(11)	112·9 (6)
Cl(2)—C(3)—C(2)	120·5 (6)	O(9)—C(13)—C(14)	110·3 (7)
Cl(2)—C(3)—C(4)	118·8 (6)	O(10)—C(14)—C(13)	109·9 (7)
C(2)—C(3)—C(4)	120·7 (7)	O(10)—C(15)—C(16)	110·0 (6)
N(2)—C(4)—C(3)	121·5 (6)	O(11)—C(16)—C(15)	107·4 (6)

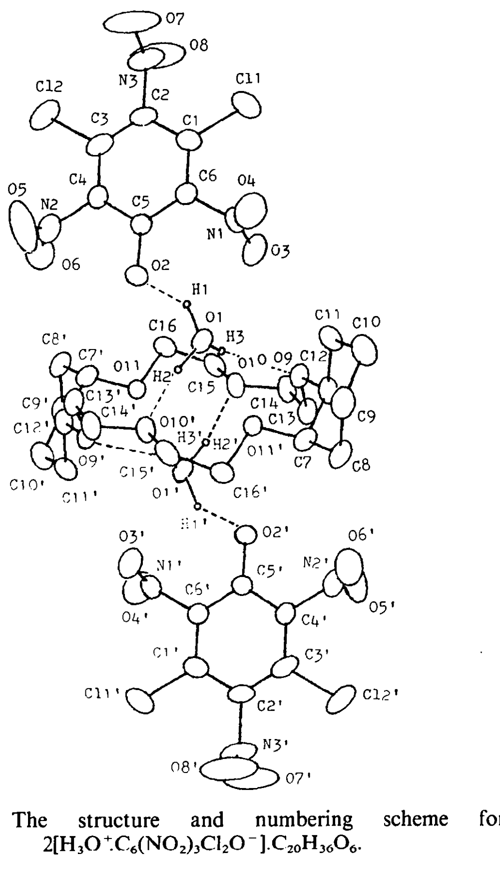

Fig. 1. The structure and numbering scheme for $2[H_3O^+.C_6(NO_2)_3Cl_2O^-].C_{20}H_{36}O_6$.

angles about C—C bonds are close to 60°, those about C—O bonds are mostly close to 180°. The six ether O atoms lie alternately about 0·20 Å above and below their mean plane, similar to those of the complex cation H_3O^+(dicyclohexano-18-crown-6), isomer *B* (Zheng *et al.*, 1986). The bond distances and angles of the dichloropicrate ion are close to those given by Britton *et al.* (1984). In the present compound, each H_3O^+ ion forms a strong hydrogen bond with the phenolate O atom of an adjacent dichloropicrate ion, as indicated by the short O(1)···O(2) distance of 2·419 (3) Å and two weaker hydrogen bonds with the ether O(9) and O(10′) atoms located on both sides of the cyclohexane group, at distances of 2·775 (3) and 2·796 (4) Å respectively. These distances are close to those found in a similar complex (Britton *et al.*, 1984). Further stabilization may arise from ion–dipolar interactions [O(1)···O(11) distance of 2·923 (3) Å] (Behr, Dumas & Moras, 1982). All the distances between the oxonium ion O(1) atom and crown-ether O atoms are longer than the corresponding ones in the structure of H_3O^+(dicyclohexano-18-crown-6), isomer *B* (Zheng *et al.*, 1986). This may be attributed to each H_3O^+ ion forming a strong hydrogen bond with the phenolate O atom which is 3·4 Å above the mean plane of the six ether O atoms. The oxonium ion is not able to penetrate deeply into the crown-ether cavity (1·7 Å out of the mean plane of ether O atoms), because it is not anchored in the crown-ether cavity by hydrogen bonds to three ether O atoms as in the structures of strong acids.

H_3O^+ has a pyramidal geometry with HOH valence angles [117 (7), 111 (8) and 113 (8)°] close to tetrahedral ones. The distances of O(1)—H(1)···O(2), O(1)—H(2)···O(10) and O(1)—H(3)···O(9) bonds are 1·0 (2), 1·51 (7), 0·97 (9), 1·84 (9) and 0·78 (9), 2·16 (6) Å respectively. The angles at the H atoms are 143 (8), 166 (7) and 137 (6)° respectively. They are not so widely spread as those reported by Behr, Dumas & Moras (1982).

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The Structures of Two Sesquiterpene Lactones

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Abstract. Helenalin, 6α,8β-dihydroxy-4-oxo-ambrosa-2,11(13)-dien-12-oic acid 12,8-lactone, (1), $C_{15}H_{18}O_4$, $M_r = 262{\cdot}31$, monoclinic, $P2_1$, $a = 7{\cdot}469$ (2), $b = 8{\cdot}568$ (2), $c = 10{\cdot}094$ (1) Å, $\beta = 90{\cdot}30$ (1)°, $V = 645{\cdot}4$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}348$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71072 Å, $\mu = 0{\cdot}91$ cm^{-1}, $F(000) = 280$, $T = 298$ K, $R = 0{\cdot}0351$ for 1446 observed reflections. Mexicanin I, 6β,8α-dihydroxy-4-oxoambrosa-2,11(13)-dien-12-oic acid 12,8-lactone, (2), $C_{15}H_{18}O_4$, $M_r = 262{\cdot}31$, triclinic, $P1$, $a = 6{\cdot}549$ (1), $b = 6{\cdot}649$ (1), $c = 8{\cdot}063$ (1) Å, $\alpha = 77{\cdot}91$ (1), $\beta = 81{\cdot}59$ (1), $\gamma = 70{\cdot}67$ (1)°, $V = 322{\cdot}9$ (1) Å^3, $Z = 1$, $D_x = 1{\cdot}349$ g cm^{-3}, λ(Mo $K\alpha$), $\mu = 0{\cdot}91$ cm^{-1}, $F(000) = 140$, $T = 298$ K, $R = 0{\cdot}0410$ for 1431 reflections. Compounds (1) and (2) are diastereoisomers which are reported to differ significantly in melting points and solubilities in $CHCl_3$. Both compounds reported herein form hydrogen-bonded chains involving the hydroxyl group and the lactone carbonyl of an adjacent molecule; however, there is a reported polymorphic form of (1) with intermolecular H bonds between the hydroxyl and the ketone O atom of the five-membered ring. In (2) the molecules exhibit a flattened conformation and the H-bonded chain is almost linear while (1) adopts a more bent conformation and the H-bonded chains zigzag through the solid. Differences in solvent interactions are estimated to be small and the melting point and solubility differences must be related to the different polymeric forms of (1)

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Introduction. While investigating *Hymenoxy scaposa* var. *villosa* (Gao, Wang, Mabry & Bierner, 1990), it was noted that the C(6) and C(8) diastereoisomers helenalin (1) and mexicanin I (2) differed significantly in melting points and in their solubilities in $CDCl_3$. Compound (1) (Herz, Romo de Vivar, Romo & Viswanathan, 1963) has a reported melting point of 439–440 K and is readily soluble in $CDCl_3$ while compound (2) (Dominguez & Romo, 1963) melts at 530–533 K and is only slightly soluble in $CDCl_3$. X-ray analysis of samples supplied by Professor Mabry gave calculated densities of 1·348 and 1·349 g cm^{-3} for (1) and (2), respectively. The X-ray structure of (1) has been reported previously (Fronczek, Ober & Fischer, 1987); however, unit-cell dimensions and a calculated density of 1·271 g cm^{-3} indicated a polymorphic relationship. The structure of (2) and the new polymorph of (1) are described in this paper.

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