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The Structures of Polymorph I at 181 K and Polymorph II at 297 K of the Bis(water–dichloropicric acid)–1,4,7,10,13,16-Hexaoxacyclooctadecane Complex, $2[H_2O.C_6(NO_2)_3Cl_2(OH)].(CH_2CH_2O)_6$

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(*Received* 28 *May* 1987; *accepted* 3 *September* 1987)

Abstract. $2C_6HCl_2N_3O_7.C_{12}H_{24}O_6.2H_2O$. Polymorph I, $M_r = 896{\cdot}35$, monoclinic, $P2_1/a$, $a = 8{\cdot}519\,(12)$, $b = 24{\cdot}901\,(14)$, $c = 9{\cdot}592\,(6)$ Å, $\beta = 113{\cdot}46\,(9)°$, $Z = 2$, $V/Z = 933{\cdot}2\,(30)$ Å^3, $D_x = 1{\cdot}595\,(5)$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 4{\cdot}07$ cm^{-1}, $F(000) = 920$, $T = 181\,(5)$ K, $R = 0{\cdot}046$ for 4084 reflections. Polymorph II, $M_r = 896{\cdot}35$, monoclinic, $C2/c$, $a = 23{\cdot}069\,(7)$, $b = 12{\cdot}078\,(3)$, $c = 15{\cdot}740\,(2)$ Å, $\beta = 120{\cdot}65\,(2)°$, $Z = 4$, $V/Z = 943{\cdot}2\,(8)$ Å^3, $D_m = 1{\cdot}589\,(3)$, $D_x = 1{\cdot}578\,(2)$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 4{\cdot}03$ cm^{-1}, $F(000) = 1840$, $T = 297\,(2)$ K, $R = 0{\cdot}043$ for 1747 reflections. The structure of polymorph I at room temperature [Britton, Chantooni, Wang & Kolthoff (1984). *Acta Cryst.* C**40**, 1584–1587] is disordered and the H atoms near the O atom of the water molecule could not be found. The complex was reported as the hydronium picrate complex on chemical grounds. Polymorph II at room temperature and polymorph I at low temperature are both ordered and the H atoms have been located. Both are properly described as the water–picric acid complex. The principal difference between the two polymorphs is in the orientation of the picric acid portions with respect to the crown ring; there are no significant chemical differences. In each polymorph the complex is centrosymmetric with each water molecule weakly hydrogen bonded to two O atoms of the crown ether and strongly hydrogen bonded to the H atom of a dichloropicric acid molecule. There are no unusual bond distances or angles.

Introduction. In a previous paper (Britton, Chantooni, Wang & Kolthoff, 1984) we reported the room-temperature crystal structure of polymorph I of the title compound, which we then described, on chemical grounds, as the hydronium dichloropicrate complex (all of the H atoms involved in hydrogen bonding were disordered and not located in the structure determination). In an attempt to prepare the known complex with one water and one dichloropicric acid per crown ether we obtained crystals of a second polymorph, polymorph II, whose structure we determined and which we report here. To anticipate, the structure of polymorph II is ordered, the H atoms in the hydrogen bonds could be located and the observed structure is the water–dichloropicric acid complex. Given this result it appeared desirable to repeat the determination of the structure of polymorph I at low temperature (which was not available locally at the time of the original determination). This has been done and we also report this structure here.

Experimental. Crystals of polymorph II suitable for diffraction were obtained by dissolving the compound previously prepared from aqueous solution in a hot 1:7 1,2-dichloroethane:cyclohexane mixture and allowing the mixture to cool. D_m was measured by flotation in aqueous KI solution. Crystals of polymorph I suitable for diffraction were obtained by recrystallization from hot water; well formed crystals of both polymorphs were present in the recrystallized sample. D_m was not measured for I.

II. A crystal $0{\cdot}30 \times 0{\cdot}30 \times 0{\cdot}35$ mm was coated with a thin layer of epoxy cement to prevent loss of

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0108-2701/88/020303-04$03.00

Table 1. *Polymorph* II: *atomic coordinates, e.s.d.'s and equivalent isotropic thermal parameters*

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

	x	y	z	B_{eq}(Å^2)
C1*C*	0·4032 (2)	0·1123 (3)	0·1501 (3)	5·9 (1)
C2*C*	0·3725 (2)	0·0973 (3)	0·2117 (3)	6·1 (1)
O3*C*	0·3285 (1)	0·1866 (2)	0·1955 (2)	5·15 (6)
C4*C*	0·2990 (2)	0·1811 (4)	0·2543 (3)	6·9 (1)
C5*C*	0·2604 (2)	0·2845 (4)	0·2407 (2)	7·2 (1)
O6*C*	0·2069 (1)	0·2900 (2)	0·1415 (2)	5·25 (6)
C7*C*	0·1706 (2)	0·3902 (3)	0·1163 (3)	6·4 (1)
C8*C*	0·1170 (2)	0·3872 (3)	0·0110 (3)	6·0 (1)
O9*C*	0·1458 (1)	0·3969 (2)	−0·0495 (2)	5·06 (6)
O1	0·3965 (1)	0·3969 (2)	0·0602 (2)	4·77 (6)
C1*R*	0·4209 (1)	0·4980 (3)	0·0797 (2)	3·48 (8)
C2*R*	0·3833 (1)	0·5945 (3)	0·0613 (2)	3·57 (8)
C3*R*	0·4111 (1)	0·6989 (3)	0·0775 (2)	3·74 (8)
C4*R*	0·4793 (1)	0·7088 (3)	0·1151 (2)	3·87 (8)
C5*R*	0·5193 (1)	0·6158 (3)	0·1373 (2)	3·88 (8)
C6*R*	0·4898 (1)	0·5133 (3)	0·1200 (2)	3·58 (8)
N2	0·3097 (1)	0·5857 (2)	0·0196 (2)	4·88 (8)
O2*A*	0·2879 (1)	0·6061 (3)	0·0732 (2)	7·58 (9)
O2*B*	0·2768 (1)	0·5573 (3)	−0·0654 (2)	7·59 (9)
Cl3	0·36080 (4)	0·81363 (8)	0·04870 (7)	5·63 (3)
N4	0·5089 (1)	0·8190 (3)	0·1279 (2)	5·54 (8)
O4*A*	0·4939 (1)	0·8722 (2)	0·0553 (2)	7·70 (8)
O4*B*	0·5486 (2)	0·8483 (3)	0·2121 (2)	9·5 (1)
Cl5	0·60328 (4)	0·6285 (1)	0·17733 (8)	6·79 (3)
N6	0·5312 (1)	0·4131 (2)	0·1440 (2)	4·76 (8)
O6*A*	0·5366 (2)	0·3684 (3)	0·0823 (2)	9·10 (9)
O6*B*	0·5598 (2)	0·3841 (3)	0·2263 (2)	12·6 (1)
O*W*	0·2901 (1)	0·3566 (2)	0·0550 (2)	6·28 (7)
H1	0·356 (2)	0·382 (4)	0·053 (3)	11 (1)*
H*WA*	0·296 (2)	0·312 (3)	0·096 (2)	9 (1)*
H*WB*	0·252 (3)	0·374 (5)	0·011 (4)	16 (2)*

* Atoms refined isotropically.

Table 2. *Polymorph* I (181 K): *atomic coordinates, e.s.d.'s and equivalent isotropic thermal parameters*

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

	x	y	z	B_{eq}(Å^2)
C1*C*	−0·1551 (3)	0·00947 (8)	0·3057 (2)	2·08 (4)
C2*C*	−0·0609 (3)	0·06104 (8)	0·3137 (2)	1·92 (4)
O3*C*	0·0780 (2)	0·05096 (6)	0·2693 (2)	1·94 (3)
C4*C*	0·1853 (3)	0·09699 (9)	0·2923 (2)	2·38 (4)
C5*C*	0·3294 (3)	0·08425 (9)	0·2450 (2)	2·35 (4)
O6*C*	0·2634 (2)	0·07822 (6)	0·0840 (2)	1·72 (3)
C7*C*	0·3988 (2)	0·06958 (8)	0·0331 (3)	2·29 (4)
C8*C*	0·3221 (3)	0·05603 (9)	−0·1328 (2)	2·32 (4)
O9*C*	0·2417 (2)	0·00514 (5)	−0·1500 (1)	1·72 (2)
O1	0·2619 (2)	−0·10941 (5)	0·0543 (1)	1·51 (2)
C1*R*	0·2796 (2)	−0·15322 (7)	0·1371 (2)	1·23 (3)
C2*R*	0·2980 (2)	−0·15499 (7)	0·2901 (2)	1·31 (3)
C3*R*	0·3113 (2)	−0·20348 (8)	0·3668 (2)	1·38 (3)
C4*R*	0·3094 (2)	−0·25112 (7)	0·2912 (2)	1·42 (3)
C5*R*	0·3026 (2)	−0·25141 (7)	0·1435 (2)	1·36 (3)
C6*R*	0·2837 (2)	−0·20285 (7)	0·0692 (2)	1·26 (3)
N2	0·3176 (2)	−0·10391 (7)	0·3728 (2)	1·57 (3)
O2*A*	0·2274 (2)	−0·09607 (6)	0·4428 (2)	2·55 (3)
O2*B*	0·4265 (2)	−0·07277 (6)	0·3670 (2)	2·28 (3)
Cl3	0·34442 (6)	−0·20606 (2)	0·55540 (5)	2·030 (8)
N4	0·3144 (2)	−0·30282 (6)	0·3675 (2)	1·77 (3)
O4*A*	0·1820 (2)	−0·31709 (7)	0·3762 (2)	3·37 (4)
O4*B*	0·4468 (2)	−0·32810 (7)	0·4126 (2)	3·48 (4)
Cl5	0·31276 (6)	−0·31039 (2)	0·05440 (5)	1·863 (8)
N6	0·2666 (2)	−0·20203 (6)	−0·0896 (2)	1·54 (3)
O6*A*	0·3990 (2)	−0·20163 (8)	−0·1107 (2)	3·02 (3)
O6*B*	0·1229 (2)	−0·20160 (7)	−0·1888 (2)	2·73 (3)
O*W*	0·0717 (2)	−0·04698 (6)	0·1189 (2)	1·87 (3)
H1	0·223 (3)	−0·088 (1)	0·081 (3)	3·6 (6)*
H*WA*	0·089 (3)	−0·016 (1)	0·157 (3)	3·0 (6)*
H*WB*	−0·019 (4)	−0·048 (1)	0·055 (3)	4·1 (7)*

* Atoms refined isotropically.

water. Data were collected on an Enraf–Nonius CAD-4 diffractometer with a graphite monochromator. 24 reflections with $9 < \theta < 19°$ were used to determine the cell parameters. Systematic extinctions (hkl, $h + k$ odd; $h0l$, l odd) indicated space group Cc or $C2/c$. The latter was used successfully for the solution and refinement. Data were collected in the range $0 < \theta < 24{\cdot}1°$ for one quadrant (ranges: h 0 to 26; k 0 to 13; l −18 to 18). 2983 unique reflections measured; 1747 with $I > \sigma(I)$ used in the calculations. Three check reflections, measured every 5000 s of exposure time, showed no systematic change with time. Empirical absorption corrections were made; the maximum variation in intensity was 10·5%. The structure was solved by direct methods (*MULTAN*; Germain, Main & Woolfson, 1971) and refined with full-matrix least-squares refinement of F's. A secondary-extinction coefficent of $2{\cdot}49\ (3) \times 10^{-6}$ was included in the refinement. Methylene H atoms were placed at idealized positions but with variable isotropic thermal parameters which were refined. The phenolic and the two water H atoms were located from a difference Fourier synthesis and were refined with isotropic thermal parameters. All remaining atoms were given anisotropic thermal parameters. Refinement converged with $wR = 0{\cdot}046$ and $S = 1{\cdot}481$; $w = 1/\sigma^2(F)$ calculated from $\sigma^2(I) = \sigma^2(I_c) + (0{\cdot}04I)^2$, where $\sigma(I_c)$ is the standard deviation in I based on the counting statistics alone. In the final cycle of refinement $(\Delta/\sigma)_{\max} = 0{\cdot}02$ for thermal and positional parameters. The extreme variation from zero on the final difference Fourier synthesis was 0·275 e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections for all atoms were taken from *International Tables for X-ray Crystallography* (1974). All computer programs were from the Enraf–Nonius *Structure Determination Package,* described by Frenz (1978).

I. A crystal 0·20 × 0·35 × 0·50 mm was mounted and coated with STP. The same diffractometer was used. 25 reflections with $9 < \theta < 17°$ were used to determine cell parameters. Systematic extinctions ($0k0$, k odd; $h0l$, h odd) uniquely determined space group $P2_1/a$. Data collected in the range $0 < \theta < 30°$ for one quadrant (ranges: h 0 to 11; k 0 to 35; l −13 to 13). 5379 unique reflections were measured; 4084 with $I > \sigma(I)$ were used in the calculations. Three check reflections, measured every 5000 s of exposure time, showed a 1·1% decay over the time of the entire data collection; a linear correction was made. Empirical absorption corrections were made; the maximum variation in intensity was 4·7%. The trial structure was taken from the room-temperature determination and refined with full-matrix least-squares refinement of F's. A secondary-extinction coefficient of $5\ (4) \times 10^{-8}$ was included in the refinement. Methylene H atoms were placed at idealized positions but the isotropic thermal parameters were refined. In contrast to the room-temperature results there was no disorder in the position of the water molecule and the water and phenolic H atoms could be found from a difference Fourier synthesis; they were included in the refinement with isotropic thermal parameters. All remaining atoms were given anisotropic thermal parameters. Refinement converged with $wR = 0{\cdot}047$ and $S = 1{\cdot}342$; w defined as for II. In the final cycle of refinement $(\Delta/\sigma)_{\max} = 0{\cdot}05$ for positional parameters and 0·26 for thermal parameters. The extreme variation from zero in the final difference Fourier synthesis was 0·580 e Å^{-3}; the four highest peaks were near the centers of bonds. Scattering factors and programs as for II.

Discussion. The final positional parameters and the equivalent isotropic thermal parameters are given in Tables 1 and 2.* In both polymorphs the complex of one crown ether, two water molecules and two dichloropicric acid molecules is located at a center of symmetry. In Figs. 1 and 2 the entire crown ether, one water, and one dichloropicric acid are shown with atom labelling for each of the polymorphs. In Figs. 3 and 4 stereodrawings of the entire complexes are shown. In all

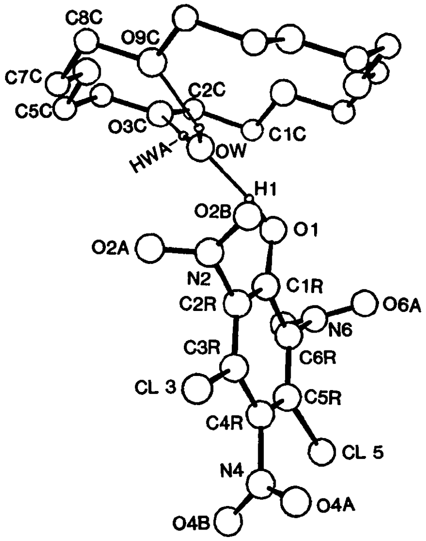

Fig. 1. Atom labelling for polymorph II. One asymmetric unit plus the symmetry-related remainder of the crown-ether ring is shown in the same orientation as in the lower half of Fig. 3. O6*C*, C4*C* not labelled because of crowding. H atoms are omitted for clarity.

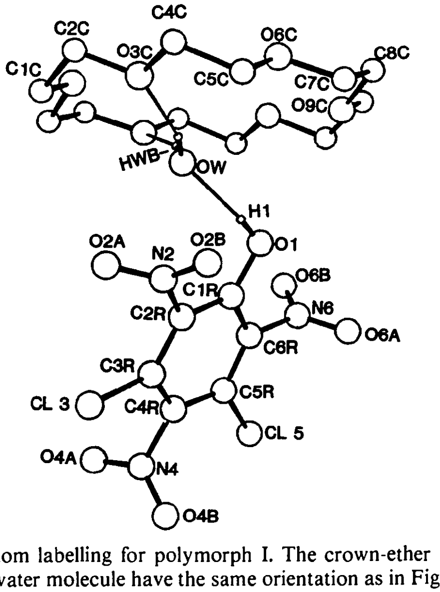

Fig. 2. Atom labelling for polymorph I. The crown-ether ring and the water molecule have the same orientation as in Fig. 1.

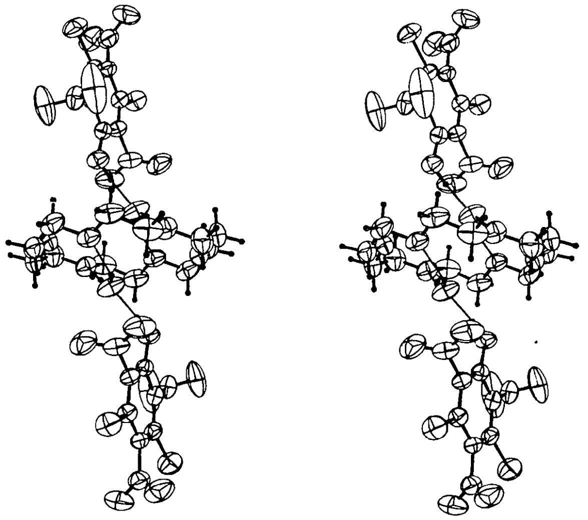

Fig. 3. Stereodrawing of the entire complex in polymorph II, showing the thermal ellipsoids (50% probability), the assumed H-atom positions in the crown ether, and the hydrogen bonds (light lines).

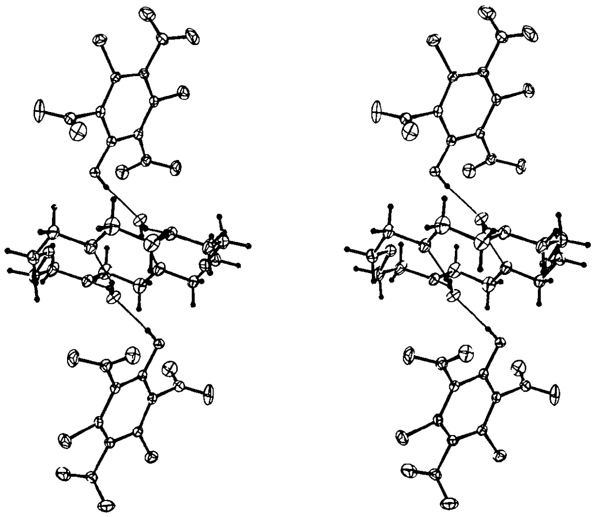

Fig. 4. Stereodrawing of the entire complex in polymorph I.

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* Tables of methylene H-atom parameters, anisotropic thermal parameters, torsion angles in the crown ethers, bond lengths and bond angles, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44347 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Observed distances* (Å) *and angles* (°) (*with e.s.d.'s*) *for the hydrogen-bonding system in both polymorphs*

	II	I
O1···O*W*	2·462 (3)	2·495 (2)
O1–H1	0·91 (5)	0·73 (3)
H1···O*W*	1·56 (3)	1·79 (3)
O*W*···O3*C*	2·809 (4)	2·823 (2)
O*W*–H*WA*	0·80 (5)	0·85 (3)
H*WA*···O3*C*	2·02 (5)	2·01 (3)
O*W*···O9*C*(O6*C*′)*	2·904 (4)	2·850 (2)
O*W*–H*WB*	0·82 (5)	0·77 (3)
H*WB*···O9*C*(O6*C*′)	2·15 (8)	2·12 (3)
O*W*···O6*C*(O9*C*′)	2·975 (4)	2·989 (2)
C1*R*–O1···O*W*	119·6 (2)	107·2 (1)
C1*R*–O1–H1	120 (3)	111 (2)
O3*C*···O*W*···O9*C*(O6*C*′)	112·3 (2)	113·3 (1)
H*WA*–O*W*–H*WB*	122 (5)	109 (3)
O1···O*W*···O3*C*	102·0 (2)	141·5 (1)
O1···O*W*···O9*C*(O6*C*′)	145·1 (2)	103·5 (2)
O1–H1···O*W*	173 (3)	163 (2)
O*W*–H*WA*···O3*C*	167 (3)	163 (2)
O*W*–H*WB*···O9*C*(O6*C*′)	153 (3)	159 (2)

* Atom labels in parentheses are given when the labelling in I is not identical to that in II.

of the figures the crown ether and water molecules have the same orientation; the difference in the relative orientation of the dichloropicric acid molecules in the two polymorphs can be seen. The bond distances and angles are normal and are given in the supplementary tables except for those involving the hydrogen bonding, which are given in Table 3. The association into the complex through hydrogen bonding is essentially the same in the two polymorphs. There is a short hydrogen bond between the phenolic O and the water O atoms, 2·462 (3) Å in II and 2·495 (2) Å in I. The torsion angle between the OH group and the benzene ring is slightly smaller in II [torsion angles 20 (3)° for ether O···H1 and 25·7 (3)° for O1···O*W* in II and 26 (2)° for ether O···H1 and 38·3 (2)° for O1···O*W* in I], and the difference in the overall orientation of the benzene rings with respect to the crown ethers is even greater (see Figs. 3 and 4), but this appears to be a packing effect with no chemical significance. The water molecule in each case forms two longer hydrogen bonds with two ether O atoms. The O*W*···O(ether) distances [2·809 (4) and 2·904 (4) Å in II and 2·823 (2) and 2·850 (2) Å in I] are slightly different from each other but all are significantly longer than the O1···O*W* distances. These distances are also only slightly shorter than the shortest O*W*···O(ether) distance not involving hydrogen bonding [O*W*···O6*C*, 2·975 (4) Å in II and O*W*···O9*C*′, 2·989 (2) Å in I]. With respect to the hydrogen-bond angles, in each case there is one distorted angle near 145° while the rest are normal. All things considered, the complexes in the two polymorphs do not look particularly different, and the differences could be attributed to packing effects. Nevertheless, the differences are sufficient to allow the water molecule in polymorph I to be disordered at room temperature while it is not in polymorph II. The most significant conclusion is that the present complex in both polymorphs involves picric acid and water rather than picrate ion and hydronium ion.

Table 4. *Hydrogen-bond distances* (Å) *in* 2:2:1 *adducts; substituted phenols:water:*18-*crown*-6

Adduct		pK_a of phenol in water	Reference	O1···O*W*	Average of O*W*···O(ether)*	Reference
18-Crown-6(H_2O.dichloropicric acid)$_2$	I	–0·7	(*a*)	2·495 (2)	2·84 (2)	This work
	II			2·462 (3)	2·85 (4)	This work
18-Crown-6(H_2O.2,4-dinitrophenol)$_2$		4·09	(*b*)	2·552 (4)	2·89	(*c*)
18-Crown-6(H_2O.3-nitrophenol)$_2$		8·38	(*b*)	2·635	2·895	(*d*)
18-Crown-6(H_2O.4,4′-biphenyldiol)$_2$		9·95†	—	2·669 (8)	2·92 (4)	(*e*)

References: (*a*) Pearce & Simpkins (1968); (*b*) Kortum, Vogel & Andrussow (1961); (*c*) Caira, Watson, Vögtle & Müller (1984); (*d*) Watson, Galloy & Grossie (1984); (*e*) Grossie, Watson, Vögtle & Müller (1982).

* Average of the two hydrogen-bonded O(crown ether)–O(water) distances.

† The pK_a of phenol is used as an estimate for the unknown pK_a of 4,4′-biphenyldiol.

From a comparison of hydrogen-bond lengths of 2:2:1 substituted phenol:water:18-crown-6 adducts in Table 4, it is apparent that the O(phenolic)–O(water) distance (O*W*···O1) increases regularly with decreasing acid strength. The O(water)–O(crown ether) hydrogen-bond lengths appear to increase slightly with decreasing acid strength, but the increase is too small to be certain.

A unit-cell determination of the analogous 2:2:1 dimethylpicric acid–water–crown ether complex [monoclinic, $a = 8{\cdot}03\ (2)$, $b = 26{\cdot}50\ (1)$, $c = 9{\cdot}45\ (1)$ Å, $\beta = 106{\cdot}1\ (2)°$, $V/Z = 965\ (3)$ Å^3, $T = 297\ (2)$ K] suggests that this complex is isomorphous with I.

IMK thanks the National Science Foundation for grant NSF/CHE 8401840 in support of this work.

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