Table 2. *Observed and calculated interplanar spacings and intensities for* $Cu_2La - Cr\ K\alpha$ *radiation*

hk·l	d_o†	d_c	I_o*	I_c
00·1	n.o	3·807	—	0·5
10·0	3·742	3·764	vw	1·93
10·1	2·670	2·677	vs	30·73
11·0	2·169	2·173	s	15·15
00·2	1·905	1·904	w-m	3·28
11·1	n.o	1·887	—	0·75
20·0	n.o	1·882	—	0·20
10·2	n.o	1·699	—	0·29
20·1	1·6863	1·6871	m	7·06
11·2	1·4339	1·4319	S	10·72
21·0	n.o	1·4226	—	0·20
20·2	n.o	1·3384	—	0·20
00·3	n.o	1·2691	—	0·06
21·1	1·3326	1·3326	s	11·36
30·0	1·2546	1·2546	m	6·75
10·3‡	1·2044	1·2026	ms	8·99
30·1	n.o	1·1916	—	0·58

* s = strong m = medium w = weak v = very.

† n.o = not observed.

‡ *d* values for α_1 and α_2 averaged.

planar spacings are shown in Table 2. In the calculations of intensities, the Thomas and Umeda (1957) atomic scattering factors corrected for dispersion (Dauben & Templeton, 1955) were used. Corrections for absorption were not made. The good agrrement between observed and calculated interplanar spacings and intensities supports the correctness of the proposed structure.

Larson and Cromer have discussed the close relationship between the AlB_2 type and orthorhombic structure of $CeCu_2$. The fact that $LaCu_2$ has the AlB_2 structure corroborates this close relationship. Attempts were made to convert $LaCu_2$ to the orthorhombic form and convert YCu_2 to the hexagonal AlB_2 structure even though the available phase diagram information indicated no phase changes. $LaCu_2$ was quenched in ice water from 740 °C (melting point 834 °C) which YCu_2 was annealed at 400 °C for 70 hours. These compounds did not change structure after these treatments. However, we do not believe these experiments negate the possibility of the existence of phases with the AlB_2 structure type in the XCu_2 compounds.

The authors wish to express their appreciation to J. H. Wernick for helpful discussions, D. Dorsi for preparation of the compounds and to Mrs V. B. Compton for calling their attention to the work of Larson and Cromer and for help with the IBM intensity program.

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The water molecules in (+)-demethanolaconinone hydroiodide trihydrate.

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In the course of a survey of organic hydrate structures (Clark, 1963), the crystal structure for (+)-demethanolaconinone hydroiodide, $C_{19}H_{17}N.C_2H_5(OH)_4.O.(OCH_3)_3.HI.3H_2O$, described by Przybylska (1961), was examined with respect to the water molecules. The three water molecules (O9, O10 and O11) and the iodine atom (I″) form a sub-structure (Fig. 1) that is discussed briefly in the present note.

The sub-structure viewed along the *a* direction has a trapezoidal shape. Trapezoids related by the 2_1 axis parallel to *c* are linked to one another by a short hydrogen bond (2.50 Å) between two water molecules to form a zigzag chain along the *c* direction. The chain is held among neighboring alkaloid molecules by four hydrogen bonds, one involving hydroxyl (O8) to water (O9), and three involving hydroxyls to the iodine atom (Tables 1, 2).

Assignment of water-molecule protons among the hydrogen bonds is complicated by the close contacts (3.5 to 3.6 Å) to one iodine by five oxygen atoms, *i.e.* two water and three hydroxyl oxygens, all noted by Przybylska (1961). The following comment has been made by Przybylska (written communication, 1963) about the assignment of the hydroiodide proton: *Considering the very low ionic character of* HI *and the fact that the iodine atom is*

Table 1. *Hydrogen bond distances*

Atoms† *X*	*Y*	Location of *Y*	Distance‡ *X* − *Y*
O9	I″	1/2+*x*, 1/2−*y*, 1−*z*	3·58 Å
O10	I″	1/2+*x*, 1/2−*y*, 1−*z*	3·53
I	O5′	1/2−*x*, 1−*y*, *z*−1/2	3·52
I	O6′	1/2−*x*, 1−*y*, *z*−1/2	3·52
I	O7	1−*x*, *y*−1/2, 1/2−*z*	3·62
O9	O8′	3/2−*x*, 1−*y*, *z*+1/2	2·84
O10	O6	1−*x*, *y*−1/2, 1/2−*z*	2·83
O10	O11	*x*, *y*, *z*	2·81
O11	O9	*x*, *y*, *z*+1	2·81
O11	O9′	3/2−*x*, 1−*y*, *z*−1/2	2·50

† Atoms *X* are located at *x*, *y*, *z* (Table 1, Przybylska, 1961) except O9 which is at *x*, *y*, *z*+1. O5, O6, O7, O8 are hydroxyl oxygens; O9, O10, O11 are water molecules.

‡ All data taken from Przybylska (1961) for calculations of bond distances using SILLIAC program V-21 by Dr F. M. Lovell, University of Sydney. Errors estimated by present author: O–I ± 0·05 Å; O–O ± 0·10 Å. The crystals have space group $P2_12_12_1$, $a = 14{\cdot}69 \pm 0{\cdot}03$, $b = 22{\cdot}08 \pm 0{\cdot}03$, $c = 8{\cdot}33 \pm 0{\cdot}02$ Å.

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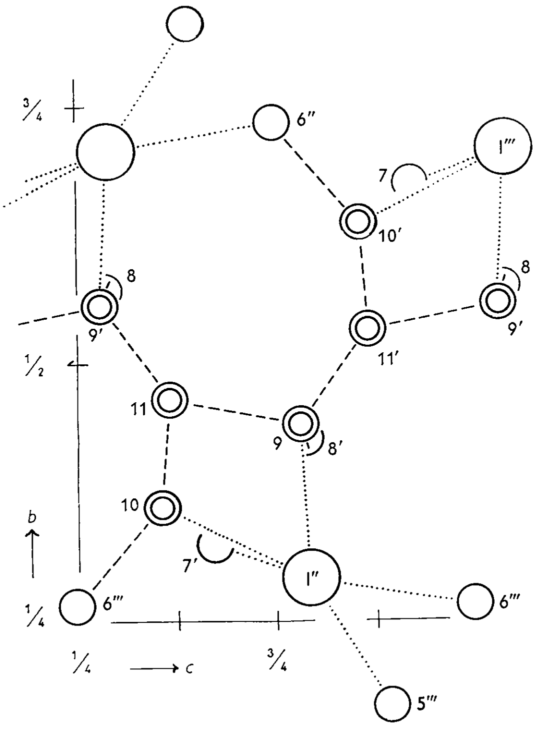

Fig. 1. Zigzag chain of water molecules and iodine atoms in (+)-demethanolaconinone hydroiodide trihydrate (Przybylska, 1961), viewed along the *a* direction (+*a* into paper), origin of figure at 1/4 *b*, 1/4 *c*. Labelling of atoms as in Tables 1 and 2. Large circles, iodine atoms; small single circles, hydroxyls; small double circles, water molecules. Dashed lines show hydrogen bonds among oxygens; dotted lines show hydrogen bonds to iodine.

situated at a distance of 5 Å *from the nitrogen atom of the alkaloid, it seems unlikely that the hydrogen of* HI *is attached to nitrogen. It follows that one of the oxygen atoms associated with iodine may be an acceptor of the hydroiodide proton. Since* ∠C9–O6···O10 *is* 112°, *it is possible that hydroxyl* (O6) *is donating a proton to* O10 *and accepting the proton of* HI. Following this reasoning, water (O9) presumably accepts a proton from hydroxyl (O8′)(∠C12–O8′–O9 = 116°), and donates one to the iodine. Water (O10) donates one proton to the iodine. There remain four water protons, one on O9, one on O10, and two on O11, to be assigned among the remaining three hydrogen bonds around the water molecules. Further refinement of the structure might clarify the proton assignment in this interesting hydrogen-bond scheme.

Table 2. *Bond angles around water molecules and iodine atom*

Water molecules		Iodine atom	
Atoms†	Angle‡	Atoms†	Angle‡
I″–O9–O11	100°	O5‴–I″–O6‴	52°
I″–O9–O11′	141	O7′–I″–O9	59
I″–O9–O8′	105	O7′–I″–O10	66
I″–O10–O6‴	100	O9–I″–O10	67
I″–O10–O11	101	O9–I″–O6‴	103
O8′–O9–O11	101	O7′–I″–O6‴	128
O8′–O9–O11′	87	O10–I″–O5‴	133
O11–O9–O11′	114	O7′–I″–O5‴	140
O11–O10–O6‴	124	O9–I″–O5‴	153
O9–O10–O9′	134	O10–I″–O6‴	157
O9–O11–O10	89		
O9′–O11–O10	134		

† Atoms located as described in the footnote of Table 1; see also Fig. 1.

‡ All data taken from Przybylska (1961) for calculations of bond angles using SILLIAC program V-19 by Dr F. M. Lovell, University of Sydney. Errors estimated by present author: I–O–O ± 6°; O–O–O ± 10°.

Similar zigzag chains involving water molecules and halogen atoms have been found in other halogeno alkaloid hydrates, *e.g.* codeine hydrobromide dihydrate (Lindsey and Barnes, 1955; Kartha, Ahmed and Barnes, 1962), and strychnine hydrogen bromide dihydrate (Robertson and Beevers, 1951). Such chains may prove to be a frequent feature in structures containing large organic molecules among which halogen atoms and several crystallographically distinct water molecules must be fitted.

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An analysis of possible methods for refining a non-centrosymmetric structure containing a partial centre of symmetry.

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Srinivasan (1961) has shown that, in non-centrosymmetric structures containing a partial centre of symmetry, 'inverse overlap' can occur between one atom and another related to it by inversion through this centre. He has demonstrated that the diagonal approximation to the least-squares matrix will not be valid when inverse