Table 2. Observed and calculated structure factors for $YbZn_2$

hkl	F_o	F_c	hkl	F_o	F_c
040	113	104	015	100	107
060	114	-107	035	31	-32
080	27	19	055	96	106
0·10·0	62	-64	075	37	-36
0·12·0	27	25	095	38	36
011	10	6	0·11·5	42	-42
031	109	-99	006	33	31
051	32	-26	026	61	63
071	46	-41	046	17	-16
091	21	20	066	16	-4
0·11·1	11	4	086	38	-40
002	56	51	0·10·6	7	-6
022	111	-122	017	35	40
042	82	71	037	70	-80
062	51	-43	057	13	15
082	69	61	077	42	-47
0·10·2	25	-22	097	32	30
0·12·2	26	26	008	63	-63
013	88	87	028	20	35
033	79	-80	048	36	-43
053	67	60	068	39	42
073	59	-50	088	22	-20
093	41	37	019	12	13
0·11·3	30	-26	039	14	-18
004	17	-13	059	9	9
024	60	-57	079	11	-12
044	23	21	00·10	66	-62
064	7	-4	02·10	24	30
084	35	33	04·10	34	-40
0·10·4	4	-1			

Table 3. *Interatomic distances in* $YbZn_2$

Yb–2Yb	3·790 ± 0·006 Å	Zn–2Yb	3·329 ± 0·005 Å
Yb–2Yb	3·741 ± 0·003	Zn–1Yb	3·241 ± 0·008
Yb–4Zn	3·329 ± 0·005	Zn–2Yb	3·134 ± 0·005
Yb–2Zn	3·241 ± 0·008	Zn–1Yb	3·128 ± 0·007
Yb–4Zn	3·134 ± 0·005	Zn–1Zn	2·802 ± 0·013
Yb–2Zn	3·128 ± 0·007	Zn–2Zn	2·630 ± 0·007
		Zn–1Zn	2·629 ± 0·014

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Crystal data on *o*-phenanthroline hydrate.

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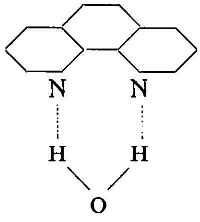
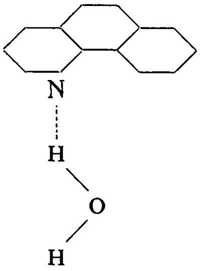
The bidentate ligand *o*-phenanthroline crystallizes from hot water as a monohydrate. The water molecules may be nonbonded, or hydrogen-bonded to the nitrogen atoms of the phenanthroline molecule. It is unlikely that the water is entirely in the non-bonded form, since the nitrogen atoms of the ligand are good proton acceptors; one molecule of water may be readily accommodated as shown in configuration *A*.

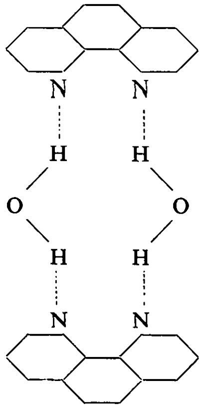
Configuration *B* is less likely because only one hydrogen donor and one hydrogen acceptor are used and because the dihydrate, which should exist if the configuration were *B*, has not been reported in the literature. Configuration *C* may be regarded as a special case of $(C_{12}H_8N_2 . H_2O)_n$ with $n=2$; *n*-membered rings of any size, as well as infinite chains, are consistent with this formulation. The predicted dimensions of a planar phenanthroline molecule are 8·98 Å in length and 5·51 Å in width, using accepted bond lengths (Sutton, 1958).



(*A*)



(*B*)



(*C*)

Infrared spectroscopy should indicate a single hydrogen-bonded OH band for structures *A* and *C*, or two OH bands (hydrogen-bonded OH and free OH) for structure *B*. However, solution spectra in dry carbon tetrachloride indicate displacement of the water molecule by the solvent, and solid state spectra (KBr) are unsatisfactory.

A sample obtained from the G. Frederick Smith Chemical Company in Columbus, Ohio, was recrystallized twice from hot water. Its melting point was determined as 93–94 °C. Elementary analyses are consistent with the formula $C_{12}H_8N_2 . H_2O$ with F.W. 198·226. The crystals, a few millimeters long, are colorless and fragile. They belong to the hexagonal system. In habit they are acicular **c** and singly terminated. Recrystallized on a glass slip from a drop of solution, they show plumose habit and subspherulitic aggregates, with bright interference colors between crossed nicols.

Optically the crystals are positive. The indices of refraction are roughly estimated as $nO \sim 1·55$, $nE \sim 1·77$, with very large birefringence $B \sim 0·22$. As a consequence of the positive optical character, the molecules can be predicted to lie parallel to **c**, an arrangement that will also agree with the prismatic cleavage.

Cell dimensions were derived from precession photographs taken with Co $K\alpha$ radiation ($\lambda = 1{\cdot}79026$ Å): $a = 17{\cdot}67 \pm 5$, $c = 8{\cdot}55 \pm 3$ Å, so that $V = 2312$ Å^3 and $c/a = 0{\cdot}484 \pm 3$. The measured density, $D_m = 1{\cdot}25 \pm 5$ g.cm^{-3}, was determined by flotation in an aqueous solution of cadmium iodide. For $Z = 9$ molecules per cell, the calculated density is $D_x = 1{\cdot}28$ g.cm^{-3}. The Laue class is $\bar{3}2/m$. The condensed diffraction symbol (Donnay & Kennard, 1964) is either $P31*$, compatible with space groups $P\bar{3}1m$ (D_{3d}^1), $P312$ (D_3^1) and $P31m$ (C_{3v}^2), or $P3_{1,2}12$ ($D_3^{3,5}$). The uncertainty arises from the very weak intensities of the $000l$ reflections, only one of which, 0003, has definitely been observed. (Either the $000l$ reflections obey the space-group criterion $l = 3n$ or the absences are structural.)

The highest possible symmetry of the water and the phenanthroline molecules is $mm2$. In $P\bar{3}1m$ the only positions with acceptable point symmetries have multiplicities 6 [site symmetry 2 for 6(i) and 6(j), m for 6(k)] and 12 (symmetry 1), so that $P\bar{3}1m$ is ruled out. In the other four possible space groups the general position is sixfold, and threefold positions with permissible symmetries, namely m or 2, are available. Packing considerations do not allow a unique choice either of molecular configuration or of space group.

Can a morphological analysis remove the uncertainty of the space-group determination? In view of the X-ray results, the morphology is referred to the structural cell, for which the point group can only be 312 or $31m$. The observed forms do not recognizably express either hemihedry.

The prism $\{11\bar{2}0\}$ predominates. The longitudinal cleavage, $\{11\bar{2}0\}$, is easy and good. Faces of $\{11\bar{2}1\}$ occur at one end of the needle-shaped crystal. The polar angular distance of $(11\bar{2}1)$ is 44° 12′, whence (c/a)gon. $= 0{\cdot}486$, in agreement with the structural ratio. The other end of the crystal shows no measurable faces. Striations parallel to the elongation are due to line-faces that truncate the edges of the prism. They belong to $\{10\bar{1}0\}$. Some minute faces of $\{10\bar{1}1\}$ can be identified, from weak but measurable signals.

The list of nets in order of decreasing interplanar distances, in a primitive hexagonal lattice with c/a 0·486, is read directly from Mallard's (1879) graph: $10\bar{1}0.11\bar{2}0.0001.10\bar{1}1.11\bar{2}1.21\bar{3}0.20\bar{2}1.21\bar{3}\bar{1}.30\bar{3}1.10\bar{1}2$. Either the classical law of Bravais or its first generalization (Donnay & Harker, 1937) would predict this sequence to be that of the observed forms listed according to decreasing importance (*i.e.* frequency of occurrence, size), for any of the space groups in aspect $P***$. In $P3_{1,2}12$ the only change would be the thirding of $d(0001)$. Note that $10\bar{1}0$ is conspicuously out of place at the top of the list.

Recent work (Donnay & Donnay, 1964) enables one to distinguish between the space groups under consideration, thanks to the morphological effect of centrosymmetric projections (linear or planar). Briefly, the above Bravais sequence should hold for the centrosymmetric group $P\bar{3}1m$, which is thus ruled out again, this time by morphology. In $P31m$ the list is modified by the morphological halving of $d(10\bar{1}0)$: now written as $20\bar{2}0$, the prism $10\bar{1}0$ recedes to between 0001 and $10\bar{1}1$, a place more in keeping with its observed development. In $P312$ and $P3_{1,2}12$ the prism $10\bar{1}0$ remains first on the list, but all the forms $h.h.\bar{2}\bar{h}.l$ have their spacings halved and go down the list. The only difference between the two space groups is that $d(0001)$ is halved in $P312$ and thirded in $P3_{1,2}12$. The thirding would be better than the halving, since 0001 has not been observed, but it would not compensate for the misplacing of $10\bar{1}0$ on top of the list and the relegating to fifth rank of the dominant $11\bar{2}0$.

Space group $P31m$, without being perfect, is the one that best fits the facts. The point group should be $31m$ and the forms are described as follows: two trigonal prisms, $11\bar{2}0$ and $2\bar{1}\bar{1}0$, equally developed and dominant; two trigonal pyramids, $11\bar{2}1$ and $2\bar{1}\bar{1}1$, also nearly equal in size, but small; hexagonal pyramid $10\bar{1}1$, very subordinate; hexagonal prism $20\bar{2}0$, as line-faces. Of the nine formula units in the cell three have to lie in special position 3(c) with symmetry m. The hypothesis that three threefold positions could be occupied, to accommodate all nine molecules, is ruled out by packing considerations. Each of the three molecules in special position can either lie in a mirror or be perpendicular to it. In the first case the molecules must be rigorously planar (with no other requirements); configuration C is ruled out because the cell height cannot accommodate more than one organic molecule, when these molecules lie in a vertical plane. In the second case, configuration B and the chain hypotheses are ruled out. The two N–H bonds of one formula unit are mirror images of each other and must, therefore, be equivalent but the H_2O plane could be tilted with respect to the ring system.

We wish to thank Professor Emil White for proposing the problem and Professor David P. Shoemaker for suggesting the possibility of the chain configuration and for other helpful remarks. No further crystallographic work is planned on this compound.

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