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FORMATES OF YTTRIUM AND THE RARE-EARTH ELEMENTS AND THEIR DIHYDRATES: A REVIEW AND NEW DATA

ADOLF PABST
Department of Geology and Geophysics,
University of California, Berkeley, California 94720, U.S.A.

ABSTRACT

The rhombohedral formates of Y, Gd, Ho, Er and Tm were synthesized; all except Tm formate were obtained in good crystals with *R*3*m* morphology, confirming the previously determined structure of $Gd(HCOO)_3$ in the space group *R*3*m*. The small water content reported for some of the formates, obviously isostructural to the surely anhydrous formates of Eu and Gd, is not to be considered "structural water". The dihydrates of the formates of Y, Ho and Er are all orthorhombic and isostructural. The data for $Y(HCOO)_3 \cdot 2H_2O$ are: $P2_12_12_1$, *a* 8.332, *b* 12.269, *c* 7.481 Å, *Z* = 4, density (obs.) 2.24(1), (calc.) 2.258 g/cm³: apparent symmetry from morphology *mmm*; optical properties, α 1.535//*c* β 1.552//*b*, γ 1.597//*a*, 2*V*(+) (obs.) 66(1)°, (calc.) 62(5)°. The dihydrate of Tm formate is remarkably different. Its data are: triclinic, point group probably $\bar{1}$; *a* 6.686, *b* 9.547, *c* 6.510 Å, α 91.25°, β 98.76°, γ 71.91°, *Z* = 2, density (obs.) 2.88, (calc.) 2.880 g/cm³; there is evidence of stacking disorder and of a superlattice or superlattices in some crystals; {110} cleavage perfect; optical properties: α [⊥ (110)] 1.466, β 1.491, γ (// *c*) 1.662, 2*V* (calc.) + *ca.* 42°.

SOMMAIRE

On a synthétisé les formates rhomboédriques de Y, Gd, Ho, Er et Tm. Tous, sauf celui de Tm, donnent de bons cristaux montrant la morphologie *R*3*m*, ce qui confirme la détermination antérieure de la structure de $Gd(HCOO)_3$ dans ce même groupe spatial. La faible teneur en eau signalée dans certains formates isostructuraux des formates indubitablement anhydres de Eu et Gd, ne peut être considérée comme eau structurale. Les dihydrates des formates de Y, Ho et Er sont tous orthorhombiques et isostructuraux. Pour $Y(HCOO)_3 \cdot 2H_2O$, les données sont les suivantes: $P2_12_12_1$, *a* 8.332, *b* 12.269, *c* 7.481 Å, Z = 4; densité (obs.) 2.24(1), (calc.) 2.258; pseudo-symétrie morphologique *mmm;* propriétés optiques: α 1.535 // *c*, β 1.552 // *b*, γ 1.597 // *a*, 2*V*(+) (obs.) 66(1)°, (calc.) 62(5)°. Le dihydrate du formate de Tm est très différent: triclinique, groupe ponctuel probable $\bar{1}$; *a* 6.686, *b* 9.547, *c* 6.510 Å α 91.25°, β 98.76°, γ 71.91°, *Z* = 2; densité (obs.) 2.88, (calc.) 2.880; indices de désordre d'empilement et d'un (ou de plus d'un) surréseau dans certains cristaux; clivage {110} parfait; propriétés optiques: α [⊥ (110)] 1.466, β 1.491, γ (// *c*) 1.662, 2*V*(calc.) *ca.*+42°.

(Traduit par la Rédaction)

INTRODUCTION

Preliminary remarks

In the first edition of *Crystal Data* (Donnay & Nowacki 1954) Gd formate was listed under H-0.3818 and the space group given as *R*32 or *R*3*m* in spite of the fact that a structure had been reported in *R*3*m* (S.R. 9, 313). In the second edition (Donnay 1963) Gd formate is again listed under H-0.3818, the space group is given as *R*3*m* and in the column on crystal structure appears the notation "quant.". In the third edition (Donnay & Ondik 1973), the formates of Y and the rare-earth elements appear in the first volume, that for organic compounds. On page H-4 Ce formate and 10 Re formates are listed on the basis of data from Plyushchev *et al.* (1964, 1966) and Mayer *et al.* (1962). Unfortunately Y formate appears on page H-3 due to miscopying the value for *a* as 10.98Å, rather than 10.38Å as given in Plyushchev *et al.* (1966). In the column headed *Structure,* "none" appears in every case, even for Gd formate. Five of these rhombohedral formates are referred to as hydrates because a small water content (0.1-0.5 H_2O) had been reported for them. In some cases (*e.g.*, $Tb(HCOO)_3 \cdot 0.1H_2O$) this is indicated in the formula, in others (*e.g.*, Y, Er formates) a notation such as "Possibly contains up to 0.5 H_2O" is given.

Historical notes

Apparently the first report of a RE formate was by Cleve (1886). He synthesized samarium formate as a "white heavy crystalline powder, slightly soluble in water" and stated the Sm_2O_3 content to be 61.28%. Based on modern atomic weights the ideal value would be 61.05%. Cleve also reported the density to be 3.733. Based on the cell dimensions reported by Mayer *et al.* (1962) and cell content of 3 $Sm(HCOO)_3$

for the hexagonal cell, the calculated density would be 3.633.

Sarkar (1926, 1927) described the synthesis of Gd formate and reported 61.96% Gd_2O_3, the calculated value for $Gd(HCOO)_3$ being 62.00%, and stated "Le sel est par conséquent anhydre." Nutting (1934, see also Spedding & Nutting 1933) also prepared gadolinium formate. As the single crystals he obtained were not of adequate size for the study of absorption spectra, he resorted to "conglomerate pictures" and stated "The thickness of the crystals ranged from 0.4 to about 2.5 mm. In establishing the composition of the compounds, molecular weight determinations, carried out by converting weighed quantities of the salts into gadolinium oxide, were made." A report on the morphology and optics of the crystals grown by Nutting was published by Pabst (1933) and ten years later the same crystals were used for the structure determination (Pabst 1943, S.R. 9, 313).

Subsequently various authors reported syntheses of the formates of the rare-earth elements. Sahoo *et al.* (1960) synthesized the formates of lanthanum and cerium and stated only that "The formates settled down in granular form." They suggested that these are hydrated and, without reporting analytical results, concluded that "Of all the analyses for the constituents of the hydrated formate, the determination of metallic oxide is the most accurate one, and so in consideration of this fact, we are in favour of 0.25 molecules of water to be associated with each molecules of the rare earth formate." This conclusion is contrary to the reported analytical results of Cleve, Sarkar, and Nutting mentioned above.

Mayer *et al.* (1962) concluded that the formates of Ce(III), Pr, Nd and Sm they prepared "are all in accord with the formula $La(HCOO)_3 \cdot 0.2H_2O$. The results are in good agreement with an earlier report" and referred to Sahoo *et al.* (1960). They reported powder diffraction data for all of their phases and for Nd formate reported a few observed and calculated intensities based on the positional parameters that had been reported by Pabst (1943) for the Gd formate.

Plyushchev *et al.* (1964), referring to most of the workers mentioned above, reported powder diffraction data and cell dimensions for the formates of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Ho and illustrated the systematic change of the lattice within this series due to the "lanthanide contraction". They agree that many of the rhombohedral RE formates appear to contain "a small amount of water". But finding that the supposedly slightly hydrous formates are "isomorphous" with those that are surely anhydrous, such as Gd formate and La formate "completely dehydrated by heating to 230°", they state "that the water present in the formates of lanthanum and cerium is crystal hydrate water has not been definitely proved." In a further study (Plyushchev *et al.* 1966) these authors, using only unindexed powder diffraction patterns to characterize their products, reported the recognition of two groups of dihydrates, those of Ho, Y and Er and those of Tm (they write Tu), Yb and Lu. They further reported cell dimensions and indexed powder patterns for the formates of Y and Er showing them to belong to the large group of rhombohedral formates. Heated Tm and Lu formates, for which interplanar spacings only were reported, were referred to as "anhydrous β-formates" supposedly not belonging to the rhombohedral group. So in their summary there is reference to "the existence of four isostructural series". As a result of all this activity the Powder Diffraction File now includes at least two unindexed cards for rare-earth formates and six such cards for dihydrates of rare-earth formates, added as recently as 1972.

In a study with quite a different purpose Leipziger *et al.* (1964) described the "morphology of the rare earth formates" and in this connection referred to Pabst (1933, 1943), Sahoo *et al.* (1960) and to Mayer *et al.* (1962). They emphasized the rapid precipitation of the formates in tiny spherulites. These were considered to be so characteristic as "to enable their use as a microscopical method of identification."

OBJECTIVES AND PROCEDURES

This study was undertaken with a view towards reducing some of the uncertainties concerning the formates of yttrium and the rare-earth elements and their hydrates. As gadolinium formate was the only phase so far obtained and examined as single crystals, the aim has been to grow single crystals of several more of the formates in the hope of obtaining morphological confirmation of the polar nature of the structure and to throw some light on the question of the presumed small water content of some of the formates. Yttrium formate was to be included as it would be more suitable for a structure refinement, to be published separately by Dr. Joan Fitzpatrick. At least one of the heavy rare-earth formates was to be included to resolve the question of the so-called β-formates. Finally, it was hoped to obtain crystals representative of both series of dihydrates hitherto known only from analyses and powder data and to characterize all the crystalline phases as fully as possible.

As only a few months were available to carry out this plan, a selection of substances had to be made and in view of the high cost of most of the rare earths it was desirable to work with very small amounts of material. Yttrium, gadolinium, holmium, erbium and thulium were chosen for this study. Starting materials in each case were the 99.9% pure sesquioxides. The only other reagents used in the syntheses were formic acid of analytical grade and doubly distilled water.

In each case the initial step was treatment of powdered sesquioxide with formic acid, recommended by Sarkar (1927), though several other methods have been used by various workers. In each case the formation of the formate was very rapid, and the products had the form of minute spherulites as described by Leipziger *et al.* (1964). In only one case, that of thulium formate, did the initial product include a trace of the dihydrate, instantly recognizable in the powder pattern by a few spotty lines in addition to the perfectly smooth lines of the formate. All X-ray observations on polycrystalline materials were made by means of photographic patterns, Fe radiation being used for greater resolution in some cases.

Following initial crystallization, products were subjected to further treatment by formic acid or water + formic acid and to heating for extended periods, days or weeks, at various temperatures up to *ca.* 80°C. Several months of trials were required before measurable crystals of Y formate were obtained. Eventually excellent crystals of Y, Gd, Ho and Er formates, suitable for full optical, X-ray and morphological study were obtained. Tm formate was obtained only in microcrystalline form, but in this form yielded the best powder patterns. It seems unlikely that further trials would yield separable crystals of the Tm formate as well.

As Plyushchev *et al.* (1966, p. 687) have reported, in part "crystals of the compounds are deposited from extremely supersaturated solutions." The final solutions with which the crystals are in contact are so viscous as to be a syrup and when dried form a thin coating over the bottom of the crystallizing dish which can be broken into tiny, optically isotropic splinters. Such glassy, splintery residue was encountered during synthesis of Y, Er and Ho formate. An isotropic splinter, removed from a dish which had contained Ho formate solution was mounted for X-ray examination and during exposure crystallized to the dihydrate. Left undisturbed, such syrupy or glassy residue, actually a supersaturated solution, remains optically isotropic for a long time, at least several months. In a few cases slow crystallization into thin sheaves or sprays of dihydrate could be initiated locally by scratching the glassy residue.

The dihydrate of Y formate was first obtained accidentally as a few small crystals alongside a crop of formate crystals. Eventually excellent crystals of the dihydrates of Y, Ho, Er and Tm formate were obtained, the largest crystals measuring 3 or 4 mm in length, far larger than crystals of most of the anhydrous formates. No hydrate of Gd formate was obtained, confirming the findings of various earlier workers.

Conditions for formation of the hydrates cannot be specified exactly. In most cases they grew with the anhydrous formates, though sometimes in separate areas within a crystallizing dish. In general high acid concentration and higher temperature favor the crystallization of the anhydrous forms but maintaining a given pH in an evaporating solution is difficult. Yttrium formate was obtained in good crystals at various temperatures from 20° to 100° C. Crystallization at room temperature was very slow and only small crystals were obtained after several weeks. Crystals of Y formate dihydrate were grown between 20° and 62° C and a very small amount of the dihydrate crystallized with a larger amount of the anhydrous formate at 68° C. Similar results, but based on less extensive series of crystallizations, were obtained for Ho and Er formates and their dihydrates. Gd formate was grown at various temperatures from 62 to 82° C and no dihydrate was formed. Tm formate dihydrate was obtained in single crystals at 42, 50 and 70° C, always together with the microcrystalline anhydrous formate.

Several crystals of Y formate and of Y formate dihydrate were subjected to successive heatings. After 15 hours at 50° C, no change was observed; after 22 hours at 80°, incipient change could be seen in the dihydrate crystals which were still largely intact; upon further heating to 80° for 28 hours the dihydrate was completely decomposed to one or more unidentified phases, not the formate or oxide of of yttrium. Upon further heating for 41 hours at 97° plus 48 hours at 112° no further change occurred. Throughout the crystals retained their initial shape. It may be that the decomposition temperature is near the maximum temperature, 68° C, at which Y formate dihydrate crystals were grown. The Y

TABLE 1. NEWLY DETERMINED CELL DIMENSIONS, DENSITIES AND REFRACTIVE INDICES OF FIVE RHOMBOHEDRAL RARE-EARTH FORMATES

	a	c	ρ_{obs}	ρ_{calc}	n_e	n_o
Y	10.371(4)Å	3.9439(15)Å	3.02(2)	3.037	1.694(2)	1.716(2)
Gd	10.471(5)	3.983(2)	n. d.	3.850	1.701(3)	1.730(2)
Ho	10.375(6)	3.942(3)	n. d.	4.066	1.704(3)	1.734(3)
Er	10.352(4)	3.935(2)	4.13(3)	4.143	1.705(3)	1.735(3)
Tm	10.325(1)	3.9187(4)	n. d.	4.191	n. d.	n. d.

The space group is *R*3*m* for each, and the structure type that of $Gd(HCOO)_3$ (S.R. 9, 313); for the hexagonal cell $Z = 3RE(HCOO)_3$.

TABLE 2. POWDER DIFFRACTION DATA FOR THULIUM FORMATE

	Newly determined			Plyushchev†	
$hk{\cdot}l$	I	d_{obs}	d_{calc}*	I	d
11 0	100	5.15	5.163	s	5.069
				w	4.223
10 1	60	3.586	3.587	w	3.556
				w	3.261
				w	3.074
30 0	40	2.978	2.981		
02 1	65	2.943	2.945	m	2.917
22 0	75	2.580	2.581		
21 1	80	2.556	2.558	s	2.538
				w	2.334
				w	2.185
13 1	65	2.094	2.095	m	2.079
41 0	35	1.949	1.951		
40 1	35	1.939	1.941	w	1.934
01 2	35	1.913	1.913	w	1.900
32 1	40	1.816	1.817	m	1.804
20 2	25	1.794	1.793		
33 0	25	1.721	1.720		
12 2	25	1.695	1.694		
05 1	15	1.626	1.626		
24 1	35	1.551	1.551		
31 2	35	1.536	1.537		
60 0	35	1.487	1.490		
51 1			1.486		
04 2	12	1.473	1.473		
52 0	20	1.432	1.431		
23 2	25	1.416	1.416		

† Plyushchev *et al.* (1966): pattern of so-called "β-$Tu(HCOO)_3$" (see text).

* Calculated spacings correspond to *a* 10.325, *c* 3.9187Å.

formate crystals, subjected to the same series of heatings up to 112° C, were unchanged and a small crystal retained such good surfaces after protracted heatings that it could be precisely adjusted for an oscillation pattern on a Stoe 2-circle reflecting goniometer. Mayer *et al.* (1962) reported that their rare-earth formates, supposedly containing $0.2H_2O$ per formular unit, required heating to 300° C to drive off the water "with simultaneous decomposition of the formate".

THE ANHYDROUS FORMATES

Table 1 presents newly determined cell dimensions, densities and refractive indices of five rhombohedral formates. Cell dimensions of all except the Tm formate were determined by least squares from doubly quartz-calibrated Weissenberg patterns using only high-angle reflections with Cu$K\alpha_1$ and $K\alpha_2$ spots well-resolved. The indicated uncertainties correspond to the sigma values derived from each of these calculations, the lowest uncertainty having been attained for the Y formate. Cell dimensions for the Tm formate were obtained by least squares from a powder pattern made with Fe radiation and Mn filter, using lines in the high angle range, 139 to 160° 2θ. The standard error was about 1/13,000.

An indexed powder pattern for $Tm(HCOO)_3$ is presented in Table 2 together with the powder data reported by Plyushchev *et al.* (1966, Table 5) for "β-$Tu(HCOO)_3$", produced by heating thulium formate to 100° C for 24 hours. These authors did not record a pattern or cell dimensions for unheated thulium or lutetium formate. It is apparent from Table 2 that the strong lines in the pattern of so-called β formate correspond to those of rhombohedral $Tm(HCOO)_3$, but that the correspondence is imperfect and that at least five lines cannot be matched. In an attempt to duplicate the results of the Russian authors, several bits of the microcrystalline Tm formate that had been used for determination of the cell dimensions were heated to 100° C for about 24 hours. The powder pattern obtained from a heated fragment proved to be identical with that from the unheated material. Accordingly, no support could be found for the existence of the so-called β series of anhydrous formates.

Densities by Berman balance were newly determined only for the formates of Y and Er. They show departures from the calculated values for anhydrous crystals of the order of 0.6 and 0.3%. The good agreement of observed and calculated densities for the two formates offers an opportunity to check on their supposed water content. For this purpose Y formate is more suitable as a given amount of water present within the crystal structure will cause the greatest relative increase in density when the cation is lightest. From the formula $Y(HCOO)_3{\cdot}0.05H_2O$, reported by some authors, the calculated density becomes 3.159 and the departure of the calculated value from the observed value is about seven times the uncertainty of the observed value (*cf.*, Table 1). Thus the water cannot be considered to be "structural water". The well-established structure has, in any case, no open spaces of a size adequate to accommodate water molecules.

As the dihydrates commonly crystallize to-

TABLE 3. PHYSICAL PROPERTIES OF YTTRIUM, HOLMIUM AND ERBIUM FORMATE DIHYDRATES

	a (Å)	b (Å)	c (Å)	V (Å^3)	ρ_{obs}	ρ_{calc}	$\alpha//c$	$\beta-\alpha$	$\beta//b$	$\gamma-\beta$	$\gamma//a$	$\gamma-\alpha$	$2V_\gamma$calc	$2V_\gamma$obs	color
Y	8.332(9) +0.26%†	12.269(6) +0.08%	7.481(4) +0.17%	764.75 +0.65%	2.24(1)	2.258	1.535*	0.017	1.552	0.045	1.597	0.062	62(5)°	66(1)°	colorless
Ho	8.354(4) -0.31%	12.279(7) -0.38%	7.494(4) -0.35%	769.72 -1.17%	2.90(1)	2.903	1.546	0.016	1.562	0.045	1.607	0.061		64(1)°	pale yellowish green
Er	8.328(3)	12.233(2)	7.468(3)	760.81	2.93(2)	2.953	1.547	0.017	1.564	0.045	1.609	0.062		64(1)°	very pale pink

* The uncertainty in the recorded refractive indices throughout is of the order of 0.001.

† Percentage difference between a of Y formate dihydrate and a of Ho formate dihydrate, *etc.*

gether with the anhydrous formates a sample of the latter, contaminated with a bit of dihydrate, would yield an analysis suggesting a low state of hydration. If the sample is used for X-ray examination one would expect the dihydrate to be revealed, except, possibly, if the water present corresponds to only $0.1H_2O$ per formular unit as has been reported in a few cases. However, a better explanation emerges if one considers the extremely fine grain of most of the precipitates and especially their spherulitic character (Leipziger *et al.* 1964). The trapping of solution in such aggregates is to be expected. The high viscosity of the supersaturated solutions from which the formates are mostly obtained will also tend towards contamination of precipitates. Bits of glassy material were seen attached to single crystals obtained in the present study without affecting the X-ray patterns. Splinters of such "glass", with a few Y formate crystals formed at 70°C enclosed, have $n = 1.554(2)$ and a density of 2.22(4), very similar to the properties of Y formate dihydrate (*cf.*, Table 3) to which it devitrifies upon irradiation.

The reported cell dimensions, especially those of the formates of Ho (at. no. 67), Er (68) and Tm (69), show nicely the effect of the "lanthanide contraction" over this small range, whereas a larger range must be considered if cell dimensions are given only to 0.0x Å as hitherto.

Refractive indices were determined by the immersion method using mounted single crystals in a Jones device (Jones 1960), monochromatic light obtained by interference filters and freshly calibrated liquids. The refractive indices of Gd formate had been determined earlier by minimum deviation on natural 60° prisms, a method expected to yield superior results, and were reported to four decimal places at three wavelengths (Pabst 1933). Nevertheless, those values were found to be too high and the newly reported values are surely preferable. An explanation of the early error is to be found in the peculiarity of the hexagonal prisms of Gd formate. It was reported at the time of their description that opposite faces of the prisms "depart by more than 30′ from parallelism", the rho angle always differing from 90°. If this is not taken into account in using the supposed 60° prisms in the minimum deviation method the resulting apparent indices of refraction will be slightly high; in this case the error amounted to +0.009(2) for n_e and a similar error in the same sense for n_o.

MORPHOLOGY OF THE RHOMBOHEDRAL FORMATES

In the initial report on Gd formate (Pabst 1933, p. 72 & Fig. 1) the crystals were pictured as bounded by {11$\bar{2}$0}, the dominant form, plus {10$\bar{1}$1} and {02$\bar{2}$1}, both apparently rhombohedra. Review of the 45-year-old notes on the goniometric measurements and inspection of G. C. Nutting's crystals, which had been preserved, show that this representation of the material was correct. As most of the dozen or so crystals measured at that time were terminated only at one end, the goniometric measurements were supplemented by etch-figure tests which failed to show 2-fold axes or planes of symmetry normal to the prism faces. This was

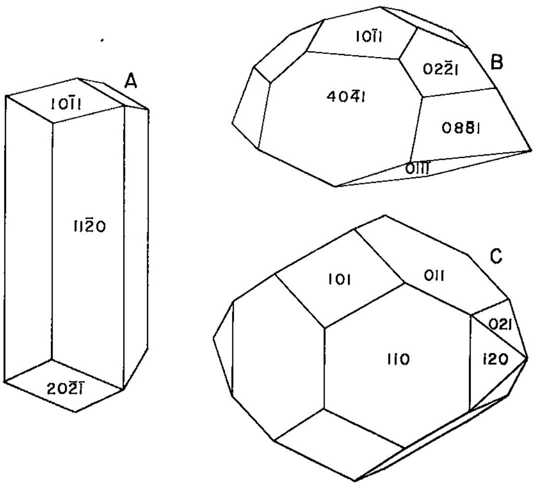

FIG. 1. Axonometric drawings of representative crystals. A. Gadolinium formate; B. Erbium formate; C. Yttrium formate dihydrate.

interpreted as indicating the class C_{3i} but is also compatible with the class C_{3v} shown to be the correct class by the structure determination (Pabst 1943). Figure 1A shows the morphology of Gd formate crystals obtained during the present study. They are dominated by the second-order prism, $\{11\bar{2}0\}$, and of a habit markedly different from that of the other formates examined. However, close inspection of many crystals showed that the newly obtained crystals are invariably terminated by different trigonal pyramids, arbitrarily indexed $\{10\bar{1}1\}$ and $\{20\bar{2}1\}$ on the drawing, at opposite ends, showing the expected polar character. These crystals formed in a solution obtained by redissolving the initially formed fine-grained formate in water with some formic acid. It is not known under what conditions the crystals provided by G. C. Nutting were grown so that they developed with the polar habit not readily apparent. However, the habit of those crystals is *not* incompatible with the structure. In fact, $\{10\bar{1}1\}$ and $\{02\bar{2}1\}$ trigonal pyramids occur together on all crystals of the other formates examined morphologically.

Crystals of Y, Ho and Er formate are all immediately recognizable as being polar. Though all but the smallest crystals are usually somewhat milky and some of the faces dull or rough, goniometric measurements could be carried out on all and these were supplemented by rough measurements on immersed crystals after the manner described by Gilbert & Turner (1949). Typically Y formate crystals are bounded by $\{10\bar{1}1\}$, $\{02\bar{2}1\}$, $\{40\bar{4}1\}$ and $\{05\bar{5}1\}$ at one end and by $\{\bar{1}0\bar{1}1\}$ together with large, irregular, striated $\{0001\}$ at the other. The four trigonal pyramids occurring together at one end are those with the lowest values of *h*, *l* being unity, compatible with a rhombohedral lattice, so that the lattice type is directly indicated by the morphology. Moreover, correlation with the indexing of Weissenberg patterns shows that the $(10\bar{1}1)$ faces correspond to the $(10\bar{1}1)$ reflections so that disposition of cations in the structure corresponds to the arrangement of corners of an ideal $\{10\bar{1}1\}$ rhombohedron. Figure 2 shows two crystals of Y formate of the type just described.

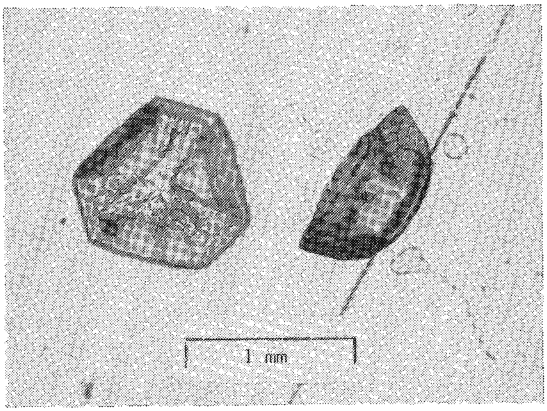

FIG. 2. Two crystals of yttrium formate, immersed in liquid 1.656; *c* axis normal to plane of picture in crystal at left, parallel to plane of picture in crystal at right.

Crystals of Er formate are generally similar to those of Y formate but with two interesting differences. The $\{05\bar{5}1\}$ trigonal pyramid is absent and the next steeper one compatible with a rhombhedral lattice, $\{08\bar{8}1\}$, takes its place, as shown in Figure 1B. With this combination the lateral edges of each of the first three pyramids are parallel so that the two similar combinations of pyramids are readily distinguished by mere inspection. The blunt end of the Er formate crystals is usually terminated by $\{\bar{1}0\bar{1}1\}$ with many reentrant angles. Crystals of Ho formate are somewhat similar to those of Y and Er formate but smaller. The blunt end is always terminated by $\{\bar{1}01\bar{1}\}$ with reentrant angles and bright faces, whereas the other end is dominated by $\{02\bar{2}1\}$ and no pyramids steeper than $\{40\bar{4}1\}$ were identified, but $\{03\bar{3}0\}$ is sometimes present as very small faces. Most Ho formate crystals are glomeratic, actually being small rosettes of slightly misaligned crystals with multiple subparallel edges, but the smallest, three of which were used for Weissenberg and precession photographs, are true single crystals.

THE ORTHORHOMBIC DIHYDRATES

Plyuschev *et al.* (1966) recognized two series of dihydrates, one including those of Y, Ho and Er, the other those of Tm, Yb and Lu, the members of each series being characterized by unindexed powder patterns only. During the present study the first crystals of $Y(HCOO)_3 \cdot 2H_2O$ were obtained accidentally, but in the course of further work excellent crystals of each of the dihydrates were obtained. They are mostly larger than crystals of the corresponding anhydrous formates and better suited for goniometric examination.

The properties of the three orthorhombic

TABLE 4. POWDER DIFFRACTION DATA FOR YTTRIUM FORMATE DIHYDRATE

hkl	*I*	d_{obs}	d_{calc}	Plyushchev* *I*	Plyushchev* *d*
020	17	6.13 Å	6.135Å		
101	100	5.54	5.566	vs	5.585Å
111	<5	5.07	5.069		
120	60	4.94	4.940		
021	50	4.74	4.744	vs	4.857
200	<5	4.16	4.166	w	4.123
210	<5	3.95	3.945		
002	8	3.75	3.741		
031	22	3.584	3.588		
012			3.578	w	3.558
220	20	3.452	3.446	w	3.427
131	17	3.299	3.296		
022	20	3.193	3.194		
221	25	3.136	3.130	s	3.138
122	25	2.988	2.982	s	2.974
140	8	2.881	2.878		
202	18	2.787	2.783	w	2.767
231	10	2.722	2.719		
141	22	2.685	2.686	w	2.663
132	8	2.616	2.620		
311	8	2.538	2.547		
222			2.535		
240	18	2.470	2.470	w	2.462
013	6	2.444	2.444		
321	12	2.396	2.397		
103			2.389		
042	5	2.373	2.372		
241	15	2.346	2.345		
023	15	2.309	2.310		
142	15	2.281	2.281		
151	8	2.246	2.245		
123	8	2.228	2.226		
331	8	2.200	2.196		
322	25	2.097	2.096	w	2.100
242	25	2.063	2.061	w	2.055
340			2.059		
223	25	2.021	2.020	w	2.011
152	15	1.989	1.992		
420	8	1.975	1.972	w	1.977
043	10	1.935	1.935		
161	12	1.919	1.919	w	1.911

* Plyushchev *et al.* (1966, Table 1).

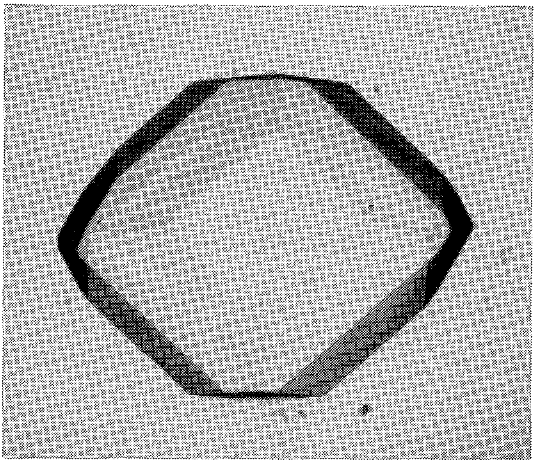

FIG. 3 Yttrium formate dihydrate crystal immersed in liquid of *n* 1.523, lying on (101). Overrall length 3.5 mm.

dihydrates are summarized in Table 3 and an indexed powder pattern for $Y(HCOO)_3 \cdot 2H_2O$ is shown in Table 4 together with the powder data for this dihydrate reported by Plyushchev *et al.* (1966). The powder patterns for the Ho and Er formate dihydrates, represented by PDF cards 22-327 and 22-267 respectively, can be similarly indexed in view of the close similarity of the cell dimensions. Comprehensive sets of single-crystal diffraction patterns were obtained for each of these dihydrates to define the space group. Each set shows the systematic absences indicating that the binary axes are screw axes. At first glance it also seems that *h*0*l* reflections appear only with $h+l$ even which would require an *n* plane normal to *b*, a combination incompatible with three 2_1 axes. However, close inspection shows that there are very weak *h*0*l* reflections with $h+l$ odd on the patterns of each of these dihydrates, the same in each case, 104, 401, 106, 601 and a few others. The space group therefore must be given as $P2_12_12_1$, but the structure is such as to nearly have a glide plane parallel to (010). *Z* equals 4, and all atoms must be in 4-fold positions so that the structure description will involve 57 positional parameters, including those of hydrogen. The effect of the lanthanide contraction is nicely shown in the near constancy of the change of *a*, *b* and *c* from the Ho to the Er formate dihydrate. It seems that there can be only minimal differences between the structural parameters of the three orthorhombic dihydrates and that those for the Ho and Er formates will be closely predictable from the structure of Y formate dihydrate, the most suitable for structure determination. Close agreement of measured and calculated densities leaves no doubt as to the state of hydration.

Crystal habits of the three dihydrates are similar. Prismatic forms are dominant and only such forms were identified with assurance. Pinacoids are lacking. The three unit prisms are usually present, with {101} dominant; {120} and {021} are also present on some crystals and the combination of all of these forms is shown in Figure 1C and in the photograph of a $Y(HCOO)_3 \cdot 2H_2O$ crystal in Figure 3. Many crystals are extended along *b* and bounded mostly by {101} with a chisel-edge termination by {011}. Such a habit is anomalous in that the direction of longest translation is also the direction of maximum dimension of the crystal. This cannot be ascribed to some special effect of external conditions as nearly all crystals of the three dihydrates have their greatest dimension in the *b* direction.

Optical properties of the three are also closely similar. The anomalous habit with {101} dominant was advantageous for direct determination of 2*V* on crystals immersed in a liquid with $n = \beta$ using a Jones device. Repeated

TABLE 5. PHYSICAL PROPERTIES OF THULIUM FORMATE DIHYDRATE

Triclinic, space group probably $P\bar{1}$		Optical properties
a 6.686 Å	α 91.25°	α 1.466(2) ⊥ (110)
b 9.547	β 98.74	β 1.491(1) // (110) ⊥ c
c 6.510	γ 71.91	
V 390.29 $Å^3$; Z = 2		γ 1.662(2) // c
Density (meas.) 2.88		$\gamma - \alpha$ 0.196
(calc.) 2.880		$2V(+)$ *ca.* 42° (calc)
		pale green; no marked pleochroism

measurements yielded values with an uncertainty of one degree or less in each case. The near-identity of refractive indices of the Ho and Er formate dihydrates corresponds to the relations between the anhydrous formates. The colors of these dihydrates are similar to those of the oxides. Though the colors are faint and small crystals appear nearly colorless in immersion, they are easily recognized and distinctive in larger crystals or aggregates.

THULIUM FORMATE DIHYDRATE

Only one representative of the second series of dihydrates recognized by Plyushchev *et al.* (1966) was studied. Data for $Tm(HCOO)_3{\cdot}2H_2O$ are set forth in Table 5. In all its properties this dihydrate differs remarkably from the orthorhombic dihydrates. Though it is easily grown in relatively large crystals, it is difficult to handle as it is soft, has perfect {110} cleavage and the crystals are easily bent about c, evidently due to translation gliding. There are probably also cleavages or partings in two directions yielding steps or striations on {110} parallel to its edges with {010} and {001}. In all these features this dihydrate is reminiscent of gypsum.

TABLE 6. POWDER DIFFRACTION DATA FOR THULIUM FORMATE DIHYDRATE

hkl	*I*	d_{obs}	d_{calc}	Plyushchev* *I*	Plyushchev* *d*
110	vs	6.14 Å	6.133 Å	vs	6.074 Å
011	m	5.32	5.315	s	5.207
$0\bar{1}1$	w	5.19	5.181		
$11\bar{1}$	w	4.78	4.761		
020	s	4.54	4.536	s	4.568
120	wb	4.25	4.380		
101			4.185		
$1\bar{1}\bar{1}$	wb	3.86	3.960		
$12\bar{1}$			3.764		
121	vw	3.46	3.492		
$1\bar{2}0$	mw	3.23	3.231		
200	s	3.146	3.140	vs	3.120
130			3.132		
030	vw	3.036	3.024		
$2\bar{1}0$	w	2.717	2.718	w	2.691
201	w	2.664	2.666		
022	vw	2.605	2.591		
$1\bar{3}0$	mw	2.435	2.444		
$\bar{1}31$	vvw	2.352	2.349		
231			2.345		
$2\bar{2}0$	m	2.272	2.272	w	2.252
040			2.268		
310	ms	2.199	2.195	w	2.198
013	w	2.100	2.099		
300	w	2.092	2.094		
321	w	1.972	1.975		
$\bar{2}22$			1.975		
$0\bar{2}3$	m	1.918	1.918	m	1.911
123	w	1.868	1.867		
151	w	1.823	1.821		
312	wb	1.759	1.761	w	1.756
051			1.759		
$0\bar{5}1$	vw	1.734	1.734	w	1.728
$\bar{3}20$	vw	1.709	1.709		
203	w	1.656	1.657		
$1\bar{4}2$	m	1.617	1.617	m	1.613
$\bar{2}40$			1.616		

* Plyushchev *et al.* (1966).

The cell constants as stated correspond to a reduced cell with right-handed axes conforming to the conventions set forth in Crystal Data III, vol. 2, page 2 (Donnay & Ondik 1973). It would be possible to choose another cell such that the dominant form, which is parallel to the {110} cleavage, is designated {100}. Such a cell was initially chosen; its constants are a 6.686, b 9.809, c 6.510 Å α 94.72, β 98.74, γ 67.70°, the only difference from the conventional cell being in the b axis and the associated angles α and γ. The transformation matrix is $\bar{1}00/\bar{1}\bar{1}0/00\bar{1}$ and the inverse matrix is the same. Table 6 records an indexed powder pattern for $Tm(HCOO)_3{\cdot}2H_2O$ to $d = 1.61$ only, and the unindexed powder data reported by Plyushchev *et al.* (1966, Table 2) for this phase. It is clear that the Russian authors observed or recorded only the principal lines.

A dozen crystals were mounted and eight of these were examined by X-ray diffraction. Patterns from several crystals showed streaks along certain reciprocal lattice rows. Figure 4 shows zero-layer Weissenberg patterns from two of these crystals, numbers 12 and 6. The rotation axis for these patterns is [$\bar{1}$10], 9.809Å, which had initially been chosen as the b axis, parallel to the cleavage, now designated {110}. Both patterns show streaks along the *hh*2 locus and fainter streaks along some of the parallel loci. Similar streaks are faintly discernible on some precession patterns and barely detectable on a few oscillation patterns. Additional spots in Figure 4B (number 6), not present in Figure 4A, require reindexing 110 to 220, *etc.*, and a few spots along the *hh*1 and *hh*3 loci would require quartering of the reciprocal lattice spacing in this direction. Besides these spots, apparently related to the streaks and seen in Figure 4B only, both films show tiny sharp spots along an oblique locus connecting 441 and $\bar{4}\bar{4}3$ and along some parallel loci. These spots, barely visible in the reproduction, indicate yet another superlattice. The cell dimensions here reported for thulium formate dihydrate and the indexing associated therewith correspond to the readily recognizable system of spots common to Figures 4A and 4B, as only spots corresponding to this lattice are consistently present on the patterns of all eight of the crystals examined by X-rays.

The habit of thulium formate dihydrate crystals is rather variable. The form $\{110\}$ is always dominant and the crystals tend to be tabular. Two crystals are shown in Figure 5. However, the modifying forms vary greatly. For two crystals these forms were checked directly against appropriate zero-layer Weissenberg or precession patterns or both. Crystal number 12, represented by its Weissenberg pattern in Figure 4A, showed the forms $\{110\}$, $\{\bar{1}30\}$, $\{\bar{1}32\}$ $\{1\bar{3}2\}$ and $\{001\}$, whereas crystal number 11, also used in determination of the lattice, showed the markedly different combination $\{110\}$, $\{010\}$, $\{100\}$, $\{1\bar{1}0\}$, $\{112\}$, $\{\bar{1}\bar{1}2\}$ and $\{001\}$.

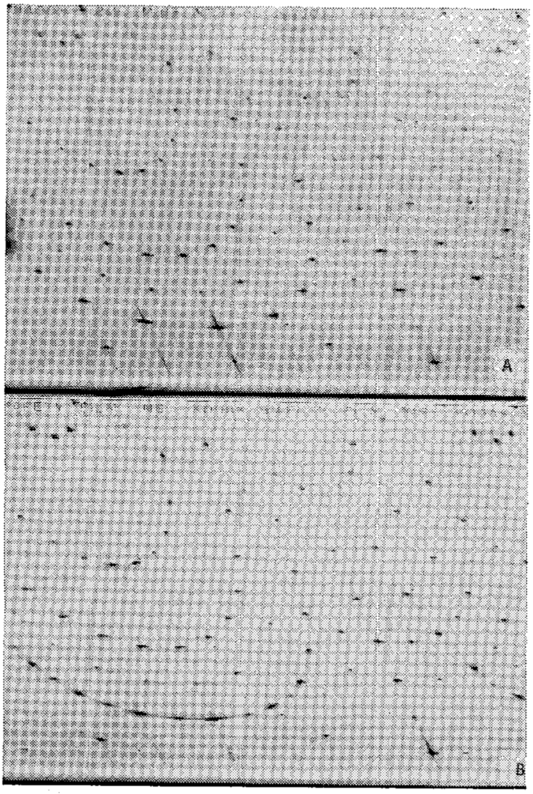

FIG. 4. Zero-layer Weissenberg patterns of two thulium formate dihydrate crystals. Rotation axis $[\bar{1}10]$; Cu radiation, Ni filter, 14 hours exposure. A. Crystal 12, showing faint streaks along the *hh*2 locus. B. Crystal 6, more conspicuous streaks and additional spots on *hh*2 locus.

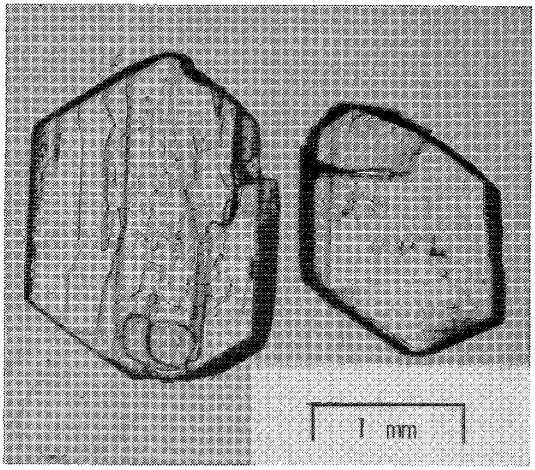

FIG. 5. Two typical crystals of thulium formate dihydrate. Both crystals are lying on (110) with *c* vertical.

The optical orientation of thulium formate dihydrate is simply related to the lattice or morphology. The mean index, $(\alpha+\beta+\gamma)/3$, is 1.540, substantially below that of Er formate dihydrate, 1.573, as one would expect from the difference in density. The volumes per formular unit are: 195.14 Å^3 for $Tm(HCOO)_3 \cdot 2H_2O$ and 190.20 for $Er(HCOO)_3 \cdot 2H_2O$. However, the birefringence of the Tm formate dihydrate, 0.196, is thrice that of the orthorhombic dihydrates and exceeds even the birefringence of calcite or aragonite, 0.182 and 0.155.

In connection with the structure determination of sodium formate, Zachariasen (1940) pointed out that the optical properties of formates are largely determined by the orientation of the formate groups and that "the normal to the plane of the formate group is the direction of smallest polarizability" (*i.e.*, the "vibration direction corresponding to the smallest refractive index"). At the time of Zachariasen's work the optical properties of Na(HCOO) had not been recorded. Mitchell (1949) reported data of W. M. D. Bryant on the optical properties of sodium formate, which is monoclinic, optically positive with large $2V$ and $\gamma-\alpha = 0.193$, very close to the value for Tm formate dihydrate. Unfortunately Bryant did not report the optical orientation of Na(HCOO) fully so that Zachariasen's prediction cannot be checked. However, from the known optical orientation of $Tm(HCOO)_3 \cdot 2H_2O$, α normal to the $\{110\}$ cleavage, it can be predicted with confidence that the planes of the formate groups are aligned parallel to the cleavage and that "the connection line between the two oxygen atoms", which is "the direction of greatest polarizability" (Zachariasen 1940, p. 1013), is parallel to *c*. It can further be predicted that no corresponding alignment of formate groups exists in the orthorhombic formate dihydrates that have a comparatively moderate birefringence.

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