338. *Hydrated Oxalates of Some Rare-earth Elements.*

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The preparation of the "interstitial hydrates" of some cerium-group oxalates and of yttrium oxalate is described. A 6-*hydrate* and a 2-*hydrate* of lanthanum oxalate and a 2-*hydrate* of yttrium oxalate have been prepared. Some properties of these compounds, including optical properties, have been studied, and the structure of the hydrates discussed.

Although numerous hydrates of the rare-earth oxalates have been reported in the literature (Beilstein, "Handbuch der Organischen Chemie", 4th edtn.), confusion persists as to the identity of many of them. Further information about these compounds seems desirable in view of their importance in the chemistry of the rare-earth elements.

It was shown by Löwenstein (*Z. anorg. Chem.*, 1909, **63**, 69, 113) that oxalates of lanthanum, cerium, and yttrium containing between 9 and 12 mols. of water per mol. of oxalate varied continuously in composition at a given temperature with the pressure of aqueous vapour. This behaviour is characteristic of a group of hydrates containing what is sometimes termed "zeolitic" water. Although conveniently classing together those hydrates which give a bivariant system

on dehydration, the designation " zeolitic hydrate " is misleading, in that salts such as the rare-earth oxalates of the above-mentioned composition contain none of the interstitial cations present in the natural and synthetic zeolites. Barrer and Ibbitson (*Trans. Faraday Soc.*, 1944, **40**, 195) and Barrer (*Ann. Reports*, 1944, **41**, 31) consider that the state of water and other solutes in the zeolites is best described as an " interstitial solid solution ", and since water in the rare-earth oxalates and similar compounds may also be regarded as being in interstitial solid solution, it is proposed to distinguish such compounds as " interstitial hydrates ".

The work of Löwenstein and others indicates that substances previously classed at 9-, 10-, and 11-hydrates are to be regarded as interstitial hydrates, to which no definite composition can be attributed, but it is not clear from the literature whether a number of other substances containing considerably more or less water than indicated above are to be included in this category or regarded as separate entities. That the latter alternative is correct is shown subsequently, for the range of composition of interstitial hydrates precipitated from solution and isolated by the usual methods has been found to vary from 9·6 to 10·9 mols. of water per mol. of oxalate.

Well-formed crystals of the interstitial hydrates may readily be obtained by slow precipitation in nitrate solutions at 70°. Chemical and crystallographic evidence shows that these hydrates are identical with an isomorphous series of 11-hydrates described by Wyrouboff (*Bull. Soc. franç. Min.*, 1901, **24**, 105, 111; 1902, **25**, 66). Identification is most readily made by optical methods owing to variable development of crystal faces and a tendency to adopt different habits according to the mode of preparation.

Conditions for the precipitation of the interstitial hydrates differ from one oxalate to another. For instance, in 3% nitric acid the cerium compound is obtained at temperatures between 0° and 100°. The lanthanum and the yttrium compound, however, are formed only below 80°, 6-hydrates being obtained at higher temperatures. Although lanthanum forms the interstitial hydrate at 0°, yttrium forms a 17- or higher hydrate below 15°. " Didymium " oxalate and the mixed rare-earth oxalates in which cerium predominates resemble the pure cerium compound in behaviour.

The isolation of a 6-*hydrate* of lanthanum oxalate raises the question of analogous cerium-group oxalates, though no such compounds could be prepared. Since the 6-hydrates of both lanthanum and yttrium oxalate appear to form 2-*hydrates* on heating, formation of the latter type of hydrate may be general in the case of the 6-hydrates of the yttrium-group oxalates prepared by Marsh (*J.*, 1944, 40). No 17-hydrate other than $Y_2(C_2O_4)_3,17H_2O$ (Brauner, *J.*, 1898, **73**, 951; Marsh, *loc. cit.*) has been reported for oxalates of the rare earths, but in view of the behaviour of the so-called 17-hydrate either alone or when mixed with other hydrates, it is possible that a similar or higher hydrate was present in the material described by Wirth (*Z. anorg. Chem.*, 1912, **76**, 174) as a 14-hydrate of erbium oxalate. The degree of hydration of such compounds is unusually high for oxalates.

Properties of the Interstitial Hydrates.—Preservation of crystal form and transparency after dehydration is characteristic of this class of hydrate. Density measurements on the cerous compound reveal that dehydration is accompanied by a volume contraction exceeding 27%. The observation that certain inter-edge angles change markedly upon dehydration while other inter-edge angles remain almost unchanged suggests that contraction parallel to the (010) plane exceeds that in other directions. This contention is supported by cleavage of many dehydrated crystals parallel to the (010) plane.

Rapid yet incomplete expulsion of water from these crystals on heating, and resorption of water vapour at lower temperatures by the partly hydrated substances, indicates that transference of water to and from the crystal lattice is readily reversible in the early stages of dehydration. Very slow escape of residual water and similar slow resorption of water vapour by a sufficiently dehydrated product may be attributed to contraction of the interstitial channels. The sorption–desorption mechanism under either of these conditions possibly follows the process of activated diffusion visualised for the natural zeolites by Emmett and De Witt (*J. Amer. Chem. Soc.*, 1943, **65**, 1253) and by Barrer (*Trans. Faraday Soc.*, 1944, **40**, 206, 555). This contrasts with the simpler and more speedy diffusion process operative when the diameter of the channel exceeds the effective diameter of the solute molecules.

The action of water on the partly dehydrated oxalates varies with the extent of dehydration. If this is sufficient to cause extensive changes in the lattice *viz.*, greater than about 90% in the cerium-group oxalates and greater than about 70% in yttrium oxalate, less energy is required to move ions from the lattice to the solution than is involved in transferring a water molecule from solution to an appropriate position in the crystal; solution effects therefore predominate

over sorption effects. An immediate consequence of the entry of ions into solution is the deposition of the fully hydrated interstitial hydrate, which is the appropriate solid phase at the temperature of the system. If the extent of dehydration and lattice rearrangement is less, lattice forces are sufficiently strong to prevent escape of ions and sorption of water by the lattice predominates.

Conversion of rare-earth oxalates into " hydroxides " is usually accomplished by boiling with sodium hydroxide. It has been found that reaction with the interstitial hydrate proceeds rapidly in cold 15% sodium hydroxide. With suitable crystals migration of the phase boundary between newly-formed " hydroxide " and residual crystalline hydrate can readily be followed under the microscope. Initially the process is assumed to involve transfer of hydroxyl and oxalate ions across the ingoing surface :

$$6OH^- + [Ce_2(C_2O_4)_3,nH_2O]_{solid} \longrightarrow [Ce_2(OH)_6,nH_2O]_{solid} + 3C_2O_4^-$$

Since the product appears to be non-crystalline when examined in visible light, possessing only a " relic " structure, it is further assumed that subsequent rearrangement of cerous and hydroxyl ions and of interstitial water molecules occurs, leading to formation of a hydrous oxide or hydroxide of cerium in a gelatinous or microcrystalline condition.

By ignition of the interstitial hydrates in air at 900°, particles of oxides are formed which still retain the sharp outlines of the original hydrate crystals (cf. Urie and Wylie, *J. Soc. Chem. Ind.*, in the press). The channels in the dehydrated oxalate crystal must therefore be sufficiently wide to allow decomposition products of the oxalate radical to escape without disintegration of the structure. Furthermore, the mobility of the anions and cations of the residual oxide must be small at 900°, though sufficient at 1200° to bring about collapse of the relic structure and relatively speedy formation of a thermally stable form of oxide.

Limiting Composition and Structure of Interstitial Hydrates.—The highest values found in this investigation for the molar ratio of water in the lanthanum and cerium hydrates approach 11, a value found by James and Robinson (*J. Amer. Chem. Soc.*, 1913, **35**, 754) for pure neodymium oxalate at 25° in water and solutions of neodymium nitrate. For yttrium oxalate this molar ratio approaches 10 in samples known to be homogeneous. No study of the composition of this solid in contact with water or aqueous solutions has been reported. If the interstitial hydrates were strictly isomorphous, the number of interstitial positions available to water molecules should be the same in each hydrate and the maximum molar ratio should be 11 for oxalates of both the cerium and the yttrium group. Yttrium oxalate, however, differs in a number of respects from the cerium-group oxalates and strict isomorphism cannot be assumed. These differences must ultimately be traced to differences in the ionic radii and polarisabilities of the cations.

Since James and Robinson found that the " 11-hydrate " of neodymium oxalate behaved as a definite compound it must be assumed, in order to reconcile this result with the properties of the solid interstitial hydrates, that the substance $M_2(C_2O_4)_3,11H_2O$ (where M is a rare-earth element) forms a continuous series of solid solutions with its dehydration products. This interpretation requires that the *p–c* isotherms of the system oxalate–water vapour should extrapolate to the same composition for the interstitial hydrates of lanthanum, cerium, and neodymium. As the curves obtained by Löwenstein (*loc. cit.*) show little indication of behaving in this fashion at 25°, it is assumed that the systems investigated were not in equilibrium. It seems doubtful if the curve given for erbium oxalate was obtained with homogeneous material.

No *X*-ray determination of the crystal structures of rare-earth oxalates has been made. It is assumed that water molecules are held in the lattice of the interstitial hydrates in interstices between the cations and the larger oxalate ions, the latter of which have a predominating effect in determining the crystal structure. Forces restraining water molecules in the lattice presumably consist of electrostatic forces (ion-dipole and ion-induced dipole forces) and dispersion forces. In the fully saturated hydrates $M_2(C_2O_4)_3,11H_2O$ in which all available interstitial positions are occupied by water molecules an ordered arrangement of solute molecules may be assumed, whereas in the partly hydrated substances the distribution of water molecules is assumed to be statistical.

A survey of the optical properties of various forms of oxalic acid and its salts reveals that the great majority of these substances resemble the rare-earth oxalates in forming strongly birefringent monoclinic crystals. This behaviour may largely be attributed to the high refracting power and anisotropy of the oxalate ion (Evans, " Crystal Chemistry ", Cambridge Univ. Press, 1939, 24, 270; Wooster, *Z. Krist.*, 1931, **80**, 495; Robertson, *J.*, 1936, 1817). The optical data appear to exclude the possibility of a layer lattice in the interstitial hydrates. The

almost isotropic character of the crystals formed by expulsion of water from the lanthanum and cerium hydrates may be explained by assuming rotation of planar oxalate ions about a centre until, when 90% or more of the water is expelled, the anions of the lattice consist of oxalate groups inclined in all directions in space. A similar arrangement is not reached in yttrium oxalate owing to decomposition of the oxalate before sufficient water can be expelled to allow the necessary degree of rotation of the anions.

Experimental.

Purity of Materials.—Commercial brands of lanthanum, cerium, and yttrium nitrates "free from other rare earths" were employed as the hexahydrates. *Lanthanum nitrate.* The only impurities detected were phosphate (0·01%) and traces of calcium; the average atomic weight, calculated from the ratio $La_2O_3 : 3C_2O_4$, was 138·6. *Cerous nitrate.* Traces of phosphate were present; the average atomic weight, calculated from the ratio $2CeCO_2 : 3C_2O_4$, was 140·3. *"Didymium" nitrate.* A salt containing a preponderating amount of neodymium nitrate was used. *Yttrium nitrate.* A 10-cm. thickness of a 2M-solution showed faint absorption lines due to erbium and holmium; the average atomic weight was 89·4 and this value was used in calculating the composition of various hydrates of yttrium oxalate. *Mixed cerium-group nitrates.* These, containing thorium, were prepared from the mixed hydroxides by dissolving them in nitric acid and reducing ceric nitrate by addition of hydrogen peroxide.

Solutions for precipitation were placed in a thermostat, and 10% oxalic acid added in excess unless stated otherwise. The rate of precipitation was varied by controlling the rate of addition of oxalic acid. Products formed at 50° or above were digested in solution for 1 hour before being filtered; below 50° the digestion time was 4 hours. Each hydrate was washed four times with water at the temperature of precipitation, and after treatment with alcohol and ether was dried to constant weight in air and transferred to sealed jars.

All samples were examined under the microscope for homogeneity before analysis.

The oxalate radical was determined by dissolving the compound in warm 10% sulphuric acid and titrating at 80° with 0·1N-potassium permanganate. Oxides were determined by igniting the oxalates to 1000°. Cerium, determined volumetrically by oxidation with ammonium persulphate followed by titration with ferrous ammonium sulphate (tri-*o*-phenanthrolinoferrous complex indicator), agreed satisfactorily with results obtained by the ignition method. The oxalate was first brought into solution by heating with ammonium persulphate, sulphuric acid, and silver nitrate (Axt, *J. Soc. Chem. Ind.*, 1941, **60**, 229).

Lanthanum Oxalate.—The solutions contained (*a*) lanthanum nitrate 10 g., 66% nitric acid 3 ml., water 100 ml., and (*b*) lanthanum nitrate 5 g., 66% nitric acid 3 ml., water 1 l.

Solution.	Temp.	Precipitation time, mins.	Molar ratio of water in product.	Remarks.
a	98—75°	120	6·00 *	Small granular crystals and aggregates
		3	7·5—8·6	Mixture
b	50	60	10·5	Interstitial hydrate,† well-formed crystals
		5	10·5	,, ,, poorly-formed crystals
	20	60	10·4, 10·4	,, ,, globular aggregates
	0	60	10·4, 10·6	,, ,, ,, ,,

* Found: La_2O_3, 50·1, 50·0; C_2O_4, 40·6, 40·6. $La_2(C_2O_4)_3,6H_2O$ requires La_2O_3, 50·1; C_2O_4, 40·6%.
† Also formed by adding just insufficient oxalic acid to cause precipitation at 75°, and cooling to 20°.

At 180° the *hexahydrate* appears to form a stable *dihydrate* [Loss of wt., 11·1—11·3. Required for loss of $4H_2O$, 11·1%. Found: C_2O_4, 45·7. $La_2(C_2O_4)_3,2H_2O$ requires C_2O_4, 45·7%].

The interstitial hydrate at 180° rapidly lost up to 85% of its water content. A further 10% was lost very slowly, even in a vacuum, the molar ratio of water in the residue falling to approximately 0·53 after 142 hours without constancy in composition being reached. At 280° the oxalate slowly decomposed. When dehydration was somewhat less than 85% complete, the residues resorbed water when placed in an atmosphere of water vapour at 20°, at first rapidly and then more slowly, resorption being eventually complete. When dehydration was more than 85% complete, reaction with water vapour was very slow, less than 7% of the total water content being resorbed after 100 hours.

When heated with 5·7N-sulphuric acid for 2 days at 25°, the interstitial hydrate formed rectangular, lath-shaped crystals belonging to the orthorhombic or tetragonal system. Although sulphate could not be completely removed by washing with water without decomposing the crystals, the composition approximated to the 7-hydrate described by Brauner and Pavlicek (*J.*, 1902, **81**, 1264) and by Wirth (*Z. anorg. Chem.*, 1908, **58**, 226).

Cerous Oxalate.—Solutions (*a*) and (*b*) were similar in composition to those used for preparation of lanthanum oxalate.

Solution.	Temp.	Precipitation time, hrs.	Molar ratio of water in product.	Remarks.
a	101°	3·5	8·5—9·2	Mixture of interstitial hydrate and lesser amount of small granular crystals
b	98	1	10·3	Interstitial hydrate, well-formed crystals
		2	10·6	,, ,, ,, ,,
a	80	1	10·3—10·6	,, ,, ,, ,,
	20	1	10·8, 10·9	,, ,, globular aggregates
	0	2	10·9	,, ,, ,, ,,

Attempts to prepare a pure 6-hydrate by boiling the interstitial hydrate for 17 hours in water or 1% nitric acid were unsuccessful.

The rates of dehydration of the interstitial hydrate at 180° and of resorption of water vapour at 20° were very similar to the rates observed for the analogous lanthanum hydrate. Prolonged heating in air caused slow formation of a yellow ceric compound, although approximately 92% of the water content could be removed in a vacuum at 180° without decomposition of the oxalate. Rapid oxidation in air occurred at 280°.

The contraction of the interstitial hydrate during dehydration was followed by determining the density of well-formed crystals in bromobenzene at 25° ± 0·01°. This substance is known to be occluded to a negligible extent by dehydrated zeolites (Barrer, *Ann. Reports*, 1944, **41**, 44) :

Molar ratio of water	10·5	8·36	5·00	2·81	1·18
$d_{25°}^{25°}$	2·36, 2·36 *	2·47	2·72	3·02	3·27

* Determined in kerosene.

The density of the final product was equivalent to a contraction in volume of 27·9%.

Yttrium Oxalate.—The solution contained yttrium nitrate 3 g., 66% nitric acid 2 ml., water 100 ml. Duration of precipitation was 2 hours.

Temp.	Molar ratio of water in product.	Remarks.
98°	6·00 *	Short, thick, well-formed crystals
80	7·5—8·5	Mixture
70	9·62, 9·92	Interstitial hydrate, well-formed crystals
25	10·4, 12·9	Mixture of aggregate and poorly-formed crystals
15	16·8, 10·1	Globular aggregates of very small crystals
9	14·8	,, ,, ,, ,, ,,
0	15·5, 16·7, 15·8 †	,, ,, ,, ,, ,,

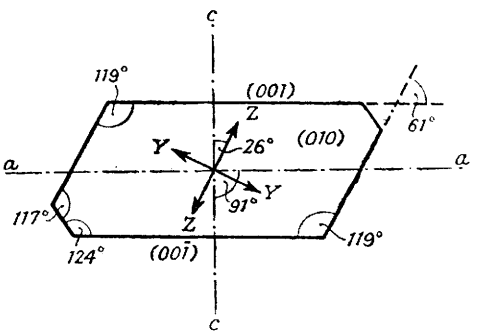
* Found : Y_2O_3, 41·1, 41·2; C_2O_4, 47·9, 48·0. Calc., for $Y_2(C_2O_4)_3,6H_2O$; Y_2O_3, 41·2; C_2O_4, 47·9%.
† Precipitate digested in mother-liquor for 72 hours.

Precipitates formed at 25° or below appeared to consist either of mixtures of the interstitial hydrate and a higher hydrate such as the 17-hydrate described by Brauner (*loc. cit.*) and by Marsh (*loc. cit.*) or else of a second interstitial hydrate containing approximately 17 or more mols. of water per mol. of oxalate. Physicochemical data are required to reveal the true nature of the solid phase.

Both the interstitial hydrate and the unidentified hydrate obtained below 25° gave the 6-hydrate when heated in water for 7 hours at 98°.

A *dihydrate* was formed from the hexahydrate at 180° [Found : C_2O_4, 55·0, 55·0. $Y_2(C_2O_4)_3,2H_2O$ requires C_2O_4, 55·1%. Loss of wt., 13·1. Required for $4H_2O$, 13·1%].

At 180° the interstitial hydrate readily lost approximately 57% of its water content. A further 20% was lost more slowly, leaving a residue in which the molar ratio of water was 2·1—2·2. The unidentified hydrate gave a similar residue at 180°. No further loss of water took place at 220°, and at 280° the oxalate slowly decomposed. Resorption of water vapour at 20° was comparatively rapid when dehydration of the interstitial hydrate was less than 57% complete; beyond this point water vapour was taken up much more slowly, less than 15% of the total water content being resorbed after 45 hours.



Optical orientation of interstitial hydrates.

"Didymium" Oxalate.—Between 50° and 98° only the interstitial hydrate was precipitated from didymium nitrate solutions comparable in composition to solution (*b*) used for the preparation of lanthanum oxalate.

Mixed Oxalates.—Solution (*a*) contained mixed nitrates 10 g., 66% nitric acid 38 ml., water 1 l. Solution (*b*) contained rare-earth oxides 5·1 g., thoria 0·6 g., sulphuric acid 18·0 g., phosphoric acid 3·2 g., water 100 ml., and was obtained by heating monazite with sulphuric acid, dissolving the sulphates in water and filtering the solution. The interstitial hydrate was the only hydrate obtained from either solution (*a*) (50—98°) or (*b*) (80—98°). Crystals precipitated in (*a*) differed in habit from those precipitated in (*b*), the former resembling crystals precipitated from lanthanum or cerous nitrate solution. The identity of these products was established by determining the optical properties of the crystals.

Microscopical Examination of Interstitial Hydrate and Reaction Products.—Crystals 40—400 μ in length, surfaces often curved. Inclusions numerous if rapidly precipitated. Flattened perpendicular to *b* axis if deposited by cooling saturated acid solutions.

For lanthanum, cerium, and yttrium hydrates with molar ratios of water 10·3, 10·4, and 9·92, respectively, optical properties were: crystals monoclinic, optically—, $X = b$, $Z \wedge c = 26° \pm 2°$, $2V$ large. Elongation, — in nitrate solution, + in sulphuric–phosphoric acid solution. Refractive indices : α 1·47(5), β 1·55, γ 1·61 [except for the yttrium hydrate : α 1·48(5), β 1·55, γ 1·61]. No changes in α, β, or γ were detected for variations of ± 2% in the above values of the molar ratio of water. Cleavage was distinct parallel to (010). The (001) face often showed striæ parallel to the 010 edge. "Didymium" and the mixed rare-earth compounds were almost optically identical with the lanthanum and cerium compounds.

None of these observations conflicts with a meagre description of a series of 11-hydrates of cerium-group oxalates given by Wyrouboff (*loc. cit.*) with the exception of the angle $Z \wedge c$, which was said to be 18°. The figure gives the optical orientation of the interstitial hydrates, $c \wedge a$ being the axial angle given in Wyrouboff's paper for the lanthanum compound.

Transparent crystals preserving the outline of the parent substance were obtained when 90% of the water of hydration was removed (180°) from lanthanum or cerous oxalate. Although no change was detected in profile views of the (010) face (see fig.), yet profile views of the (001) face disclosed marked changes in inter-edge angles. Cleavage of a number of crystals along the 010 plane was noted. The dehydrated crystals were weakly birefringent and the average refractive index was 1·68—1·69. When treated with water at 20°, these crystals were gradually changed into a mass of small (2—10 μ) acicular crystals, the optical properties of which, as far as could be determined, resembled those of the fully hydrated interstitial hydrate. The recrystallisation process was slightly exothermic. The optical properties of the partly (40—70%) dehydrated oxalates were of an intermediate character, smaller or thinner crystals being apparently dehydrated to a greater extent than others in the same sample. The former reacted with water only if the extent of dehydration approached 90%.

Transparent crystals resembling the parent substance were obtained at 180° only from thin crystals of yttrium oxalate, thicker specimens disintegrating on heating. After loss of 75% of the total water content, a brittle residue was obtained with approximate refractive indices: α 1·50, β 1·67, γ 1·67—1·68. Treatment with water changed this residue into small rectangular laths of the interstitial hydrate.

After ignition for 1 hour at 900°, the interstitial hydrates formed coherent particles of oxides closely resembling the parent crystals, providing these were thin. The particles were highly refractive and the majority showed aggregate polarisation. Prolonged ignition completely destroyed the outline of the original crystals and resulted in formation of opaque, sintered products.

By boiling with 15% aqueous sodium hydroxide the interstitial hydrates were converted into "hydroxides" consisting of discrete particles similar in shape to the parent substance. The particles were isotropic or faintly birefringent. By observing the process on a microscope slide the rate of attack was seen to be rapid even at 20°. The sodium oxalate produced separated from solution in radiating clusters of acicular crystals.

Microscopical Examination of Hexahydrate of Yttrium Oxalate.—Crystals monoclinic, 20—60 μ in length, often pinacoidal parallel to c axis and flattened parallel to (100). Cleavage distinct parallel to (010). Optically—, $X = b$, $Z \wedge c = 40°$, $2V$ small, α 1·47, β 1·61, γ 1·62. A granular mass of small birefringent fragments was formed on heating to 180°. The crystals swelled and disintegrated when treated with 15% sodium hydroxide.

Crystals of the hexahydrate of lanthanum oxalate were too small for satisfactory optical examination.

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