is by exchange of the negative ions with an already existing cubic $Hg_2N^+$ framework. On the other hand, owing to the relatively smaller size of $Cl^-$, cubic $Hg_2NCl$ forms readily in chemical reactions in dilute aqueous ammonia.

The hexagonal form of $Hg_2NBr$ shows little or no tendency to exchange its negative ions, unlike the behavior of cubic $Hg_2NBr$. It seems probable that this difference is again to be associated with the relatively tighter packing of $Br^-$ as suggested by the abnormal axial ratio. In addition, there is only one possible direction of exchange, along the $c$ axis, in contrast with the several possible directions of exchange in the cubic form. It is, however, possible that the $Hg \cdots Br$ bonds are somewhat more covalent in the hexagonal form, and that our resulting long observed distances are merely some statistical average over shorter covalent distances. On the other hand the observed intensities seem sufficiently sensitive to the Br positions that we feel that the $Hg \cdots Br$ bonds are most probably predominantly ionic, as they are in the cubic form of $Hg_2NBr$.

Finally, we wish to correct an error in the related paper on the structure of $HgNH_2Br$ (Nijssen & Lips-

comb, 1952b). Owing to the use of an incorrect value of the wave length, all distances including the unit-cell values, spacings and bond distances should be increased by $1.58\%$. The correct cell constants are thus

$$a = 5.52, \quad b = 4.56 \quad \text{and} \quad c = 6.87 \text{ Å} .$$

The Hg–N bond length, based on the assumption of strictly tetrahedral bond angles about N, is $2.10$ Å, still in reasonable agreement with the values listed above. Fortunately, these changes are sufficiently small that our conclusions remain unchanged.

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# The Structure of Lanthanum Sulfate Enneahydrate*

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Lanthanum sulfate enneahydrate, $La_2(SO_4)_3 . 9H_2O$, is hexagonal, $a_0 = 10.98$, $c_0 = 8.13$ Å, $Z = 2$, space group $C6_3/m$. There are two types of lanthanum ions in the structure: two at $0, 0, 0$; $0, 0, \frac{1}{2}$ with twelve sulfate oxygens about them at $2.72$ Å, two at $\pm\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$ with six water molecules and three sulfate oxygens at $2.6$–$2.7$ Å. It is presumed that the failure of the heavier rare earth sulfates to form an enneahydrate is due to their inability to support a coordination number of twelve for oxygen.

## Introduction

It is noteworthy that the lighter rare earth chlorides and sulfates form higher hydrates than can be obtained with the similar heavier rare earth salts. Thus the sulfate enneahydrates, $M_2(SO_4)_3 . 9H_2O$, and chlo-

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rides, $MCl_3 . 7H_2O$, are known for the rare earths, lanthanum through praseodymium, while the heavier rare earths form the compounds $M_2(SO_4)_3 . 8H_2O$ and $MCl_3 . 6H_2O$ under similar conditions. Since ion size decreases with increasing number in the rare earth series, it seemed possible that this difference was due to a coordination difference of light and heavy rare earth ions for water and oxygen.

Several hydrates of trivalent rare earth salts have been examined structurally (Ketelaar, 1937; Helmholz, 1939). These and gadolinium formate (Pabst, 1943) have been consistent in showing an oxygen coordination number of nine, in which six oxygens form a trigonal prism, and the other three, equidistant from the rare earth ion, are found out from the prism

faces (Fig. 1). This configuration has been found for relatively heavy rare earth salts, so that an anomalous coordination number was to be sought in the highest
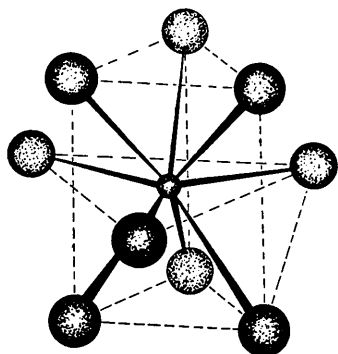


Fig. 1. Coordination polyhedron about La$_{II}$ atoms. The trigonal prism is formed by water molecules, while the three oxygens in prism faces are sulfate-oxygens. This polyhedron is common to several rare earth salt hydrates.

hydrates of the light rare earths. Of these, lanthanum sulfate enneahydrate was chosen because of its known hexagonal symmetry and availability.

## Structure determination

### Physical and X-ray data

Lanthanum sulfate enneahydrate crystallizes from water at room temperature, and is stable in air. Large (10.0) and smaller (11.0), (10.1), (10.2) and (00.1) faces develop on needle-like hexagonal crystals. Interfacial angles give an axial ratio, $a_0 : c_0$ of 1·35. Kraus (1901) reported 1·359.

The unit cell, as determined from Weissenberg diagrams, is

$$a_0 = 10\cdot98, \quad c_0 = 8\cdot13 \text{ Å}.$$

Iveronova, Tarasova & Umansku (1951) reported $a_0 = 10\cdot99$, $c_0 = 8\cdot08$ Å. The density calculated for $Z = 2$ (4 La ions per unit cell) is 2·85 g.cm.$^{-3}$, versus a reported density of 2·821 g.cm.$^{-3}$ (Kraus, 1901).

The Laue symmetry, as found from Weissenberg

photographs, is $C_{6h}$, and the only systematic absences are the odd orders of $(00.L)$, where $(00.L)$ data have been observed to $L = 10$. Possible space groups are $C6_3$ and $C6_3/m$. The latter is made probable by the face development and lack of pyroelectric effect when the crystal is dipped in liquid air.

X-ray data were obtained by the multiple-film technique with visually estimated intensities, using a crystal 0·0042 cm. in cross section and 0·1 cm. in length, except for $(H0.L)$ data which were obtained with a crystal whose cross section and length were 0·03 and 0·08 cm., respectively.

Substantially all the reflections observable with copper radiation have been examined. Table 3* contains observed and calculated structure factors for the 536 reflections observed, and calculated values for the 51 reflections too weak to be observed on our films.

Patterson and Fourier summations and structure-factor calculations were made on I.B.M. machines by methods essentially like those already published (Shaffer, Schomaker & Pauling, 1946; Donohue & Schomaker, 1949).

### Lanthanum positions

Patterson projections and simple intensity considerations require that the lanthanum positions be: 2 La in $2(b)$ of $C6_3/m$ at $0, 0, 0$; $0, 0, \frac{1}{2}$, 2 La in $2(c)$ of $C6_3/m$ at $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$. (An equivalent set of positions, $2(a)$ with $z = 0$, $2(b)$ with $z = \frac{1}{4}$, can be obtained in $C6_3$.) A promising degree of intensity agreement was obtained from these positions for lanthanum alone.

### Sulfur and oxygen positions

Two-dimensional Patterson and Fourier projections were misleading. In space group $C6_3/m$ the six sulfur
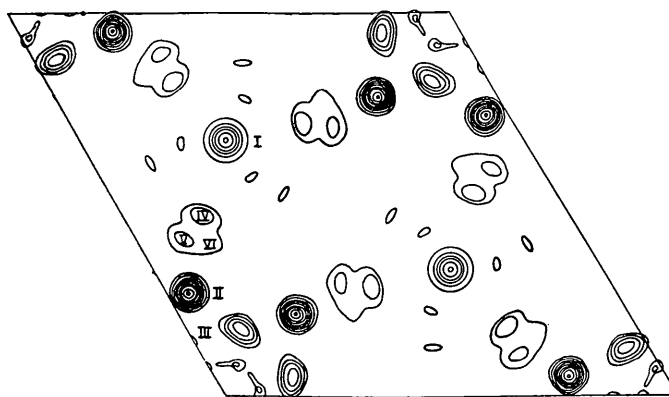
Fig. 2. Patterson section, $P(x, y, \frac{1}{4})$.
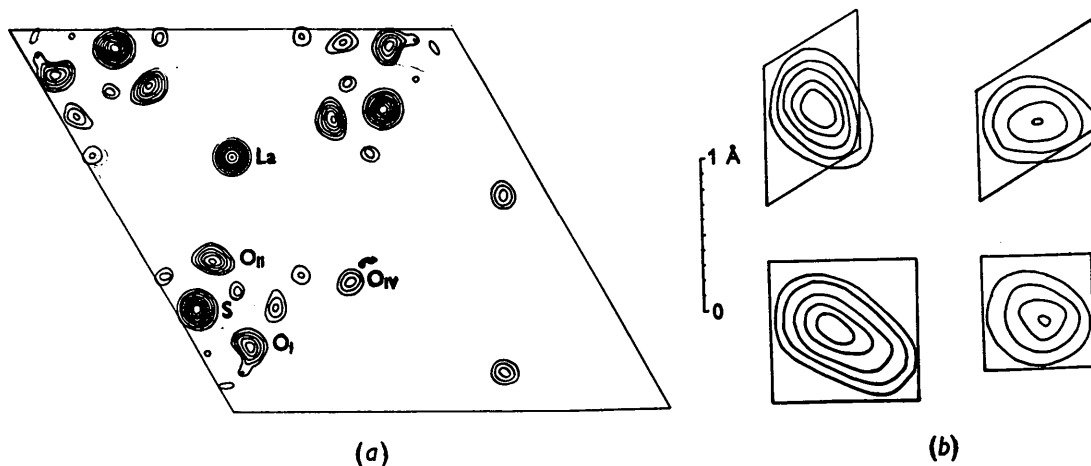
(a)                                        (b)

Fig. 3. Fourier sections. (a) $\varrho(x, y, \frac{1}{4})$. (b) Fourier sections through $O_{III}$ and $O_V$ atoms.

atoms are required to lie in mirror planes at $z = \frac{1}{4}$ and $\frac{3}{4}$, and La–S peaks should be prominent on $P(x, y, \frac{1}{4})$, due to lanthanum atoms at 0, 0, 0; 0, 0, $\frac{1}{2}$. From this Patterson (Fig. 2), sulfur and two oxygens of the sulfate group were found as expected for sulfate, lying in a mirror plane (peaks II, III and VI). The S–O distance was about 1·5 Å, $\angle$ O–S–O was about 109$\frac{1}{2}$°. Peak III was about twice as high as expected for oxygen, and peaks IV and V remained to be accounted for. The interpretation which was consistent with all subsequent work was that twelve oxygens from water occupy set 12($i$), with $x = 0.53$, $y = 0.16$, $z = 0$, accounting for IV and the height of III, while six other water molecules occupy 6($h$), lying in the mirror planes, so as to account for peak V. The remaining sulfate oxygens are far from the mirror plane and do not appear on $P(x, y, \frac{1}{4})$. Their positions were estimated, however, by assuming the sulfate ion to be a tetrahedron.

$P(x, y, \frac{1}{4})$ leaves an ambiguity in $z$. Thus, for an atom at $(x, y)$ in the map, the $z$ parameter may be

$\frac{1}{4}$ or $\frac{3}{4}$. This ambiguity was resolved by $P(x, y, 0)$. The first set of parameters, obtained from the two Patterson sections, is given as set $A$ of Table 1.

### Refinement of parameters

Parameters were refined by Fourier sections, $\varrho(x, y, z)$. Since most of the atoms were on the mirror planes at $z = \frac{1}{4}, \frac{3}{4}$, it was necessary to calculate the density function only for the $z = \frac{1}{4}$ level, for a few levels near $z = 0$ to obtain the parameter of water atoms in the twelvefold set, and near $z = 0.09$ for the twelvefold sulfate oxygens. In making the first Fourier map, of 487 reflections, 70 weak ones were omitted since their signs were left uncertain by the parameters obtained from the Patterson sections. This first map led to the parameter set $B$ of Table 1. A second electron-density map was calculated using all reflections with signs determined from the second parameter set. These are listed as set $C$ in the same table, and significant sections from the Fourier are shown in Fig. 3. Intensities calculated using the positions $C$, led to a discrepancy factor $R$, taken as $\Sigma||F_o| - F_c|| \div \Sigma|F_o|$, of 0·24.

A series-termination correction (Booth, 1946) was obtained through a synthetic Fourier using calculated structure factors. The corrected parameters, set $D$ of Table 1, were used to calculate intensities of the 129 reflections of the type $h+k = 3n$, $l \neq 4n$, which contain no lanthanum contribution. Six of the weaker of these reflections changed sign in going from parameters $C$ to $D$. Over-all agreement of these special reflections was not improved by the series termination correction ($R = 0.43$ for these reflections in both cases, versus an over-all $R = 0.24$). The intensities of Table 3, and distances in Table 2 are based on set $C$.

It seems likely that only better intensity data would improve the present agreement. Reflections with no lanthanum contributions are all relatively weak, and, upon judging multiple films scaled so that there is a

### Table 1. *Parameter values*

|        |     | $A$    | $B$    | $C$    | $D$    |
|--------|-----|--------|--------|--------|--------|
| S      | $x$ | 0·050  | 0·052  | 0·047  | 0·045  |
|        | $y$ | 0·263  | 0·260  | 0·262  | 0·260  |
| $O_I$  | $x$ | 0·120  | 0·107  | 0·120  | 0·105  |
|        | $y$ | 0·167  | 0·178  | 0·165  | 0·154  |
| $O_{II}$ | $x$ | 0·167  | 0·162  | 0·150  | 0·144  |
|        | $y$ | 0·388  | 0·388  | 0·388  | 0·398  |
| $O_{III}$ | $x$ | 0·960  | 0·957  | 0·961  | 0·971  |
|        | $y$ | 0·222  | 0·222  | 0·218  | 0·228  |
|        | $z$ | 0·088  | 0·090  | 0·093  | 0·093  |
| $O_{IV}$ | $x$ | 0·405  | 0·427  | 0·437  | 0·437  |
|        | $y$ | 0·298  | 0·328  | 0·333  | 0·331  |
| $O_V$  | $x$ | 0·840  | 0·841  | 0·841  | 0·829  |
|        | $y$ | 0·367  | 0·370  | 0·373  | 0·361  |
|        | $z$ | 0·000  | 0·992  | 0·988  | 0·988  |

### Table 2. *Bond distances*

(Based upon parameter set *C*)

| | N | Z | R (Å) |
|---|---|---|---|
| LaI | OI | 6 | 2·60 |
| | OIII | 6 | 2·74 |
| LaII | OII | 3 | 2·70 |
| | OV | 6 | 2·74 |
| S | OI | 1 | 1·62 |
| | OII | 1 | 1·28 |
| | OIII | 2 | 1·52 |
| OI | LaI | 2 | 2·60 |
| | S | 1 | 1·62 |
| | OI | 2 | 2·81 |
| | OII | 1 | 2·30 |
| | OIII | 2 | 2·46 |
| | OIV | 1 | 3·02 |

| | N | Z | R (Å) |
|---|---|---|---|
| OII | LaII | 1 | 2·70 |
| | S | 1 | 1·28 |
| | OI | 1 | 2·30 |
| | OIII | 2 | 2·36 |
| | OIV | 1 | 3·49 |
| | OV | 2 | 2·89 |
| | OV | 2 | 3·22 |
| OIII | LaI | 1 | 2·74 |
| | S | 1 | 1·52 |
| | OI | 1 | 2·46 |
| | OII | 1 | 2·36 |
| | OIII | 1 | 2·55 |
| | OIV | 1 | 3·09 |
| | OIV | 1 | 3·50 |
| | OV | 1 | 2·76 |

| | N | Z | R (Å) |
|---|---|---|---|
| OIV | OI | 1 | 3·02 |
| | OII | 1 | 3·49 |
| | OIII | 2 | 3·09 |
| | OIII | 2 | 3·50 |
| | OV | 2 | 2·83 |
| | OV | 2 | 3·25 |
| | OV | 2 | 3·36 |
| OV | LaII | 1 | 2·74 |
| | OII | 1 | 2·89 |
| | OII | 1 | 3·22 |
| | OIII | 1 | 2·76 |
| | OIV | 1 | 2·83 |
| | OIV | 1 | 3·25 |
| | OIV | 1 | 3·36 |
| | OV | 1 | 3·01 |
| | OV | 1 | 3·28 |

*N*: Neighboring atom; *Z*: number; *R*: distance.

good coverage of both strong and weak reflections, tend to be put into one class with little differentiation made among them. Since the structural features of principal interest were already clear, we did not feel justified in attempting further refinement.

### Discussion of the structure

Lanthanum ions, La$_{II}$, at $\pm(\tfrac{1}{3}, \tfrac{2}{3}, \tfrac{1}{4})$ are surrounded by six water oxygens in the form of a trigonal prism with three sulfate oxygens in the prism faces, giving a coordination number of nine and the same polyhedron (Fig. 1) found several times previously. All nine La–O distances are very nearly the same, about 2·72 Å (Table 2).

Lanthanum ions, La$_{I}$, at 0, 0, 0; 0, 0, $\tfrac{1}{2}$ are crystallographically different from the above set and have twelve sulfate oxygens about them. The arrangement of these oxygens is illustrated in Fig. 4. We presume
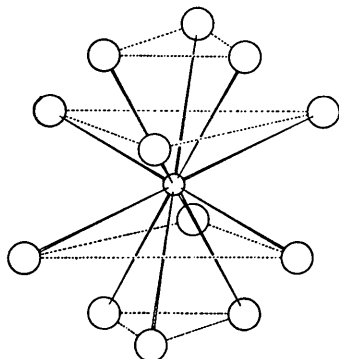


Fig. 4. Coordination polyhedron about La$_{I}$. All oxygens (large circles) are sulfate oxygens.

that it is this unusually large coordination number which cannot be maintained by heavier (and smaller) rare earth ions, so that the heavier rare earth sulfates

form lower hydrates. La–O distances for twelve-fold coordination are as small as those for nine-fold. In both cases La–O distances are longer than expected from La$_2$O$_3$ where La–O = 2·42–2·69 Å, and from Nd(BrO$_3$)$_3$.9H$_2$O where Nd–O = 2·50 Å.

Each sulfate ion has one oxygen in the polyhedron about La$_{II}$ and the other three about La$_{I}$. Of the eighteen water molecules in the unit cell, twelve are in the coordination polyhedra about La$_{II}$, while the other six fill a hole in the structure.

After the coordination of lanthanum ions for oxygen of water and sulfate, hydrogen bonding might be expected to be the next most important structural feature in a hydrate of this type. As can be seen from Table 2, however, the number of nearest neighbors about each oxygen, 8–12, and the number of O–O distances above 3 Å, is more characteristic of close-packing than of an open structure based on hydrogen bonding. There are, to be sure, a number of O · · · O distances in the neighborhood of 2·7–2·9 Å, and the infra-red spectra of a mull of the crystals in hexachlorobutadiene gives a broad O–H peak in the region of 3300 cm.$^{-1}$, characteristic of moderately strong hydrogen bonds. Hydrogen bonding is, then, neither negligible nor so predominant as to preclude a close-packed structure.

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