the calculated with the experimental curves it is necessary to know the value of p for the state of the specimen when each photograph was taken. Since the positions of the diffraction maxima move as p changes, it is possible to estimate p for any photograph from the positions of any of the maxima. From the curve shown in Fig. 2(a) the value of p corresponding to each photograph was obtained from the measured apparent spacings of the reflexion in the region of 9 kX. Using this p value the calculated spacings of the other diffraction maxima were read off from Fig. 2(b) and (c), and Table 1 shows that agreement is good between these values and the observed values.

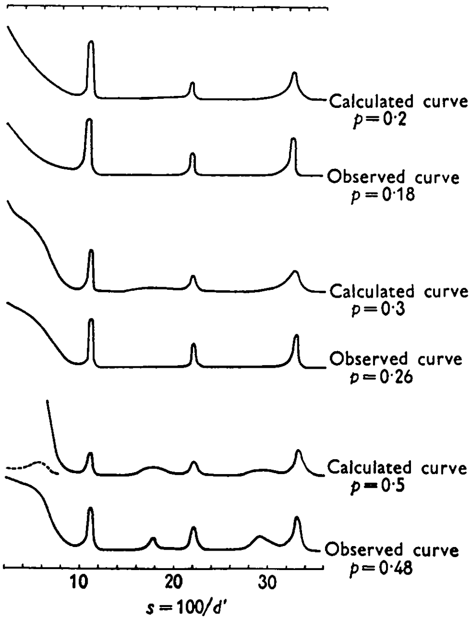

Fig. 3. Experimental microphotometer traces and calculated intensities of the diffraction maxima.

The spacings in Table 1 marked with an asterisk are for $p = 0{\cdot}5$ as they cannot be obtained from Fig. 1 or 2 for $p = 0{\cdot}48$.

Fig. 3 shows the experimental microphotometer traces after subtraction of background and calculated intensities of the diffraction maxima. The experimental traces for photographs 1, 2 and 3 are compared with the calculated intensity distribution curves for $p = 0{\cdot}2$, $p = 0{\cdot}3$ and $p = 0{\cdot}5$ already shown in Fig. 1. Here again agreement is good.

The material used for the third photograph appears to have a p value of about 0·5, i.e. half the layers can be expanded by glycerol. It is interesting to note that pyridine sorption measurements on samples of lithium montmorillonite heated to 190° C. showed about half the uptake of unheated samples.

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A Hexagonal Modification of a Salt of Millon's Base

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A hexagonal modification of Hg_2NBr has an Hg_2N^+ framework based upon the idealized tridymite (SiO_2) structure, with Br^- in the interstices. The unit-cell dimensions are $a = 6{\cdot}65$ and $c = 11{\cdot}26$ Å. The deviation of the axial ratio $c/a = 1{\cdot}693$ from the ideal value of $1{\cdot}633$ is probably related to the slightly greater stability of this hexagonal modification as compared with the cubic form in which the Hg_2N^+ framework is based upon the cristobalite structure. The Hg–N bond distance is 2·06 Å.

A correction of 1·6 % in the lattice constants of the $HgNH_2Br$ structure is given.

An interesting analogy exists between the idealized SiO_2 structures and the Hg_2N^+ framework in Millon's base and its salts. In the cubic modification (Lipscomb, 1951a) the Hg_2N^+ framework has the idealized cristobalite structure. In the hexagonal modification described here a similarly idealized tridymite structure exists for Hg_2N^+ in which Si is replaced by N, thus forming regular tetrahedral bonds and Hg replaces O, forming linear bonds at 180° angles. The bromide ions fit into the interstices of this framework, as described below.

This study is part of a more general program of studies of the compounds produced in reactions of various Hg(I) or Hg(II) salts with ammonia. A general summary, not including the present results, has recently appeared (Lipscomb, 1953).

Experimental results and discussion

The sample of Hg_2NBr was prepared by reaction of Hg_2Br_2 with dilute aqueous ammonia, washing the precipitate intermittently for several days with ammonia until no further changes were observable in the diffraction pattern, and then evaporation of the free mercury at 110° C. Our analytical results are: Hg, 80·4%; N, 3·0%; Br, 16·4%; in good agreement with the values 81·0%, 2·8% and 16·2% calculated from the formula Hg_2NBr.

Only a powder specimen was available for the diffraction analysis. The pattern was obtained by means of a General Electric XRD-3 unit with the use of a Geiger counter for recording the diffracted Cu $K\alpha$ radiation. Integrated intensities and spacings were measured from a tracing of this pattern by the usual method.

As a first attempt towards the analysis of the pattern a radial distribution function was prepared from the summation (Waser & Schomaker, 1945),

$$rD(r) = \sum_i \frac{I_i \sin 2\theta_i}{1+\cos^2 2\theta_i} \exp\left[-B \sin^2 \theta/\lambda^2\right] \sin 2\pi h_i r ,$$

where $h_i = 2 \sin \theta_i/\lambda$. The summation (Fig. 1) was made for values of $B = 0$ (broken line) and $B = 4$ Å^2 (solid line). The resulting large peaks at 3·4, 5·6 and 6·5 Å indicate that the Hg · · · Hg distances are essentially the same as in the cubic form and that the structures must be very closely related. Many unsuccessful attempts were made to index the pattern on some small distortion of the cubic structure, because such reversible distortions had previously been observed by us for the cubic Hg_2NCl structure (Nijssen & Lipscomb, 1952*a*).

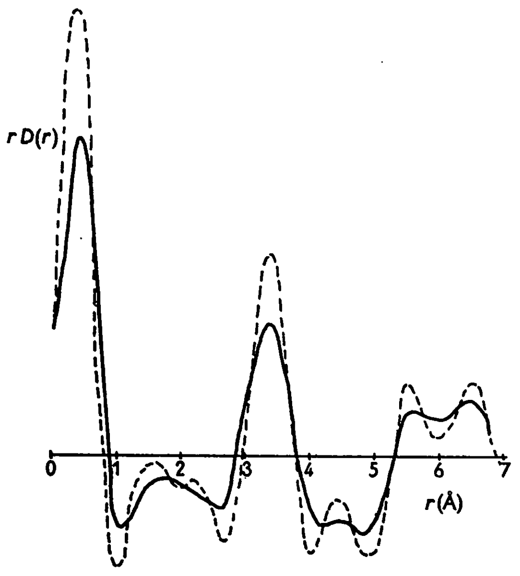

Fig. 1. Radial distribution function for Hg_2NBr.

At this stage of our study several single crystals of kleinite were sent to us through the courtesy of Dr George Switzer (National Museum, Smithsonian Institute, Washington, D.C.). Although kleinite does not have the same structure as our sample of Hg_2NBr, the similarity of the spacings, but not of intensities, led us to test the tridymite-type of structure.

The hexagonal pattern was indexed successfully on a unit cell with dimensions

$$a = 6{\cdot}65 \text{ Å} \quad \text{and} \quad c = 11{\cdot}26 \text{ Å} ,$$

where the accuracy is probably ±0·02 Å. The axial ratio $c/a = 1{\cdot}693$ is slightly greater than the ideal axial ratio of $(8/3)^{1/2} = 1{\cdot}633$ for reasons discussed below. The atomic positions

$$\begin{array}{lll} 8\,\mathrm{Hg} & \text{at} & 0, \tfrac{1}{2}, 0;\ 0, \tfrac{1}{2}, \tfrac{1}{2};\ \tfrac{1}{2}, 0, 0;\ \tfrac{1}{2}, 0, \tfrac{1}{2};\ \tfrac{1}{2}, \tfrac{1}{2}, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}; \\ & & \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{1}{4};\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{3}{4}; \\ 4\,\mathrm{N} & \text{at} & \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{1}{16};\ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{7}{16};\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{9}{16};\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{15}{16} \end{array}$$

were assumed. Two possible choices seemed most reasonable for the bromine positions, they are:

Structure *A*

$$4\,\mathrm{Br} \quad \text{at} \quad 0, 0, 0;\ 0, 0, \tfrac{1}{2};\ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{3}{4};\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{1}{4};$$

and

Structure *B*

$$4\,\mathrm{Br} \quad \text{at} \quad 0, 0, \tfrac{1}{4};\ 0, 0, \tfrac{3}{4};\ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{3}{4};\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{1}{4} .$$

Both of these possible structures, which place the Br^- in the interstices of the Hg_2N^+ framework, were tested by calculation of the intensities. The contribution of Br^- was sufficiently great to allow an unambiguous choice. The intensities of only those reflections for which $l = 2, 6, 10 \ldots$ are different for these two possible structures. The intensities for Structure *A* are listed in Table 1, and specific examples of calculated intensities for Structure *B* which disagree* with the observations are $I_{002} = 36$, $I_{102} = 40$ and $I_{202} = 213$.

Thus Structure *A*, shown in Fig. 2, is the correct one. The space group is D_{6h}^4–$C6/mmc$.

The average Hg–N bond distance is 2·06 Å, in reasonable agreement with the value of 2·07 Å found in Millon's base (Lipscomb, 1951*a*) and 2·05 Å found in $HgNH_2Cl$ (Lipscomb, 1951*b*). The Hg · · · Br distances are 3·33, 3·41 and 3·84 Å, all of which seem rather large and thus suggest that these bonds are predominantly ionic. The sum of ionic radii for Hg and Br is 3·05 Å (Pauling, 1940, p. 346) whereas the sum of covalent radii is 2·50 Å, if one obtains the Hg covalent radius by subtraction of 0·70 Å from the

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* Actually the intensities are fairly sensitive to the Br positions. About ten different Br arrangements were tested, of which Structure *A* was unquestionably the best.

Table 1. *Crystal Data for* Hg_2NBr

hkl	I_c	$(\sin\theta/\lambda)_o$	I_o
100	138	0·086	139
002	105	0·089	104
101	33	0·097	38
102	1	—	< 2
110	20	0·150	21
103	6	0·159	6
200	97	0·174	240
112	100		
004	102	0·178	133
201	8		
202	335	0·195	432
104	33	0·198	45
203	3	0·219	5
210	24	0·230	22
114	8	0·234	19
211	8		
105	4	0·239	5
212	0	0·248	77
204	76		
300	4	0·260	3
006	5	0·266	6
213	3		
302	30	0·275	26
106	0	—	< 2
205	3	0·282	5
214	21	0·290	21
220	66	0·301	62
116	23	0·306	32
310	9	0·314	34
222	21		
304	3	0·316	3
311	3		
206	77	0·318	69
215	3	—	< 2
107	1	—	< 2
313	2	0·340	2
400	12	0·347	10
224	78	0·349	64
401	1		
216	0	—	< 2
008	12	0·356	13
207	1		
402	50	0·359	51
314	10		
108	5	0·366	6
403	1	—	< 2
306	11	0·373	10
320	5	0·379	4
321	2	0·382	3
315	2	0·384	2
118	1	—	< 2
217	1	—	< 2
404	17	0·390	14
208	17	0·396	11
410	2	0·398	2
323	1	0·402	8
226	8		
412	15	0·408	16
109	1		
405	1	—	< 2
324	6	0·418	5
218	6	0·424	6
414	2	—	< 2
406	27	0·438	18
325	1	—	< 2
308	1	—	< 2
317	1	—	< 2
0,0,10	1	—	< 2
420	10	0·460	16
332	5		
421	1	—	< 2
219	1		
228	31	0·466	19
422	46	0·468	20
1,1,10	6	0·469	13
504	2		
318	4	0·474	5
2,0,10	23	0·477	8
423	1	0·479	11
416	11		
510	2	—	< 2
334	1	—	< 2
511	1	—	< 2
505	1	—	< 2
327	1	—	< 2
424	19	0·493	11
1,0,11	1	0·498	8
408	10		

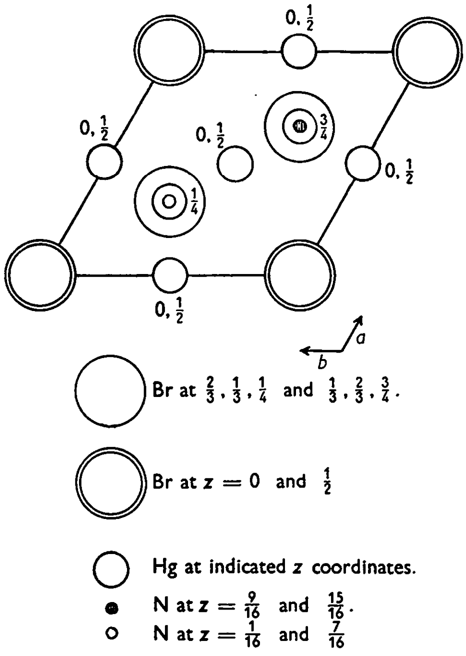

Fig. 2. The unit cell of hexagonal Hg_2NBr.

Hg–N distance, and assumes a covalent radius of 1·14 Å for Br (Pauling, 1940, p. 164).

The Br · · · N distance is 3·52 Å, which is very close to the sum of van der Waals radii of 1·5 Å for N and 1·95 Å for Br (Pauling, 1940, p. 189). It seems very likely that this contact, along the *c* axis, is mainly responsible for the expansion resulting in an axial ratio of $c/a = 1·693$ instead of 1·633. A comparison of this hexagonal form of Hg_2NBr with the cubic Hg_2NCl suggests that the relatively large Br^- ion renders the cubic Hg_2NBr less stable by requiring this non-ideal axial ratio, and hence hexagonal Hg_2NBr forms more readily in ordinary chemical reactions involving either Hg(I) or Hg(II) salts. Thus the only method by which we have prepared cubic Hg_2NBr

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 & Lipscomb, 1952*b*). 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

$$a = 5{\cdot}52,\ b = 4{\cdot}56 \quad \text{and} \quad c = 6{\cdot}87\ \text{Å}\,.$$

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, $a_0 = 10{\cdot}98$, $c_0 = 8{\cdot}13$ 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, $M_2(SO_4)_3.9\,H_2O$, and chlorides, $MCl_3.7\,H_2O$, are known for the rare earths, lanthanum through praseodymium, while the heavier rare earths form the compounds $M_2(SO_4)_3.8\,H_2O$ and $MCl_3.6\,H_2O$ 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

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