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**ON THE CRYSTAL STRUCTURE OF PHOSGENITE
 $\text{Pb}_2\text{Cl}_2\text{CO}_3$ AND THE SYNTHETIC COMPOUNDS
 $\text{Pb}_2\text{Cl}_2\text{CO}_3$, $\text{Pb}_2\text{Br}_2\text{CO}_3$, $\text{Pb}_2(\text{Br},\text{Cl})_2\text{CO}_3$.**

BY

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With 5 figures in the text.

About 1930 I spent a considerable amount of time in trying to determine the crystal structure of phosgenite by means of Laue, powder, and oscillation photographs, the material being fragments of a large crystal from Monte Poni, Sardinia, belonging to the collections of the Mineralogisk-geologisk Museum in Oslo. The research work was done partly in Oslo, partly in the Mineralogical Laboratory in Cambridge. The arrangement of the lead ions was readily found with considerable accuracy; the other ions, however, being very light as compared with the lead ions, contribute so little to the intensities in the photographs that no definite conclusions as to their positions can be drawn from the X-ray data alone. Because of this difficulty, which does not seem surmountable (except perhaps by means of accurate quantitative intensity measurements), I did not publish the results I had arrived at. Some years later E. Onorato published a paper on the structure of phosgenite¹. Although his determination of the lead positions is in close agreement with my own it was obvious to me that the structure could not be correct in other respects. As will be seen below, the unit cell used by Onorato ($a = 8.1\text{\AA}$, $c = 4.4\text{\AA}$, containing $2 \text{ Pb}_2\text{Cl}_2\text{CO}_3$) is only a pseudo cell, the real unit cell being twice as large (at least). In addition the structure given by Onorato shows the highly improbable feature of containing no CO_3 -groups, which are otherwise characteristic of all known carbonate structures. For the above mentioned reason I am not able to prove the existence of CO_3 -groups in the phosgenite structure, but on the other hand I find it equally impossible to prove the opposite from X-ray data. Since the appearance of Onoratos,

¹ E. Onorato, La struttura della Fosgenite. Periodico Min. Roma, 5, 37, 1934.
Abstract in the Strukturbericht of the Z. Krist., Ergänzungsbd. 3, 1937.

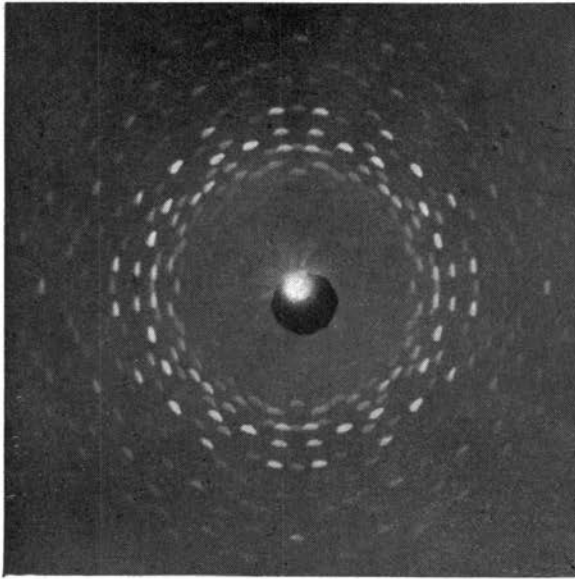


Fig. 1. Laue photograph of phosgenite, X-ray beam nearly perpendicular to 001.

paper no one seems to have published anything on the structure of phosgenite. Using my X-ray data and known ionic radii &c. I am able to propose a structure which is at least in some respects more correct and on the whole seems much more reasonable.

The complete ditetragonal symmetry of the Laue photographs of phosgenite is sufficiently known from earlier work; it is clearly demonstrated by the figures 1 and 2.

The powder photographs, which contain more than 50 different α -lines, lead to the above mentioned (pseudo) cell and may be completely interpreted in terms of this cell. Fig. 4 shows the indices of most of these lines and their observed intensities, by the full line in the diagram. By the powder method were also examined the synthetic compounds $\text{Pb}_2\text{Cl}_2\text{CO}_8$ and $\text{Pb}_2\text{Br}_2\text{CO}_8$. These compounds were obtained by a method described by A. de Schulten¹. The resulting preparations consisted of beautiful tabular tetragonal crystals about 0.2 mm across. As remarked by de Schulten, the Cl-compound agrees

¹ A. de Schulten, Sur la production artificielle à la température ordinaire de la phosgénite et de la phosgénite bromée. Bull. Soc. fr. de Min. 20, 191, 1897. Abstr.: Z. Krist. 31, 75, 1899.

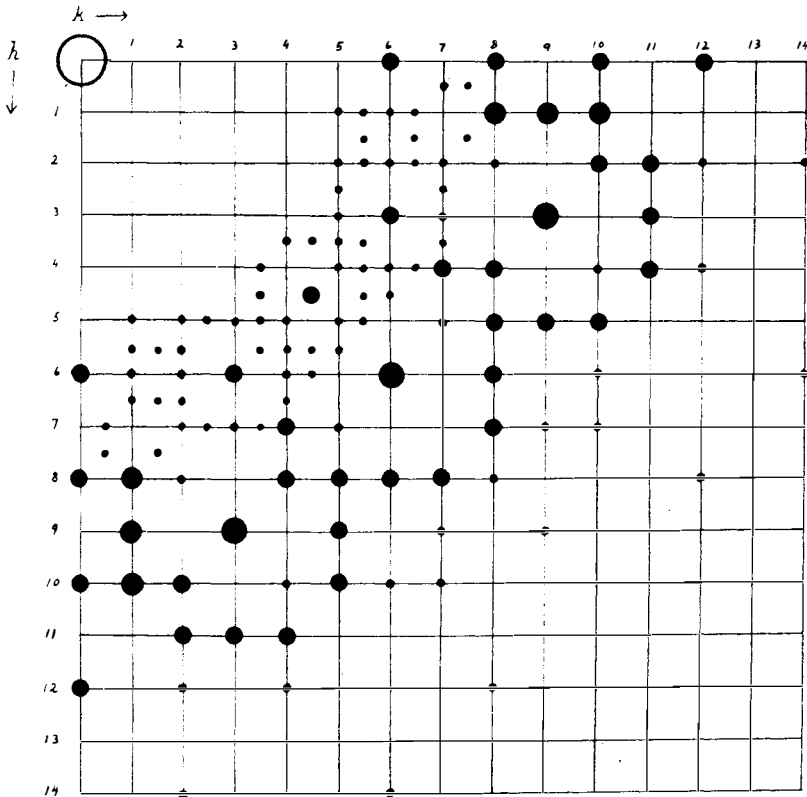


Fig. 2. Gnomonic projection of one quadrant of the Laue photograph Fig. 1.

completely with phosgenite in all its properties, and the Br-compound is very similar. The latter shows, naturally, the higher density. Optical examination shows that the Cl-compound is uniaxial positive, while the Br-compound is uniaxial negative; the birefringence is rather low in both cases. The powder photographs of natural and synthetic phosgenite are identical in all details; those of Br-phosgenite are similar apart from slight differences in spacings and intensities. It is obvious that these substances belong to the same structure type. A Laue photograph of one of the Br-phosgenite crystals, which was very faint on account of the small size of the crystal, was similar to that of natural phosgenite in symmetry and positions of the main spots (Fig. 3). It may be remarked that the intensity differences between the powder photographs of phosgenite and Br-phosgenite

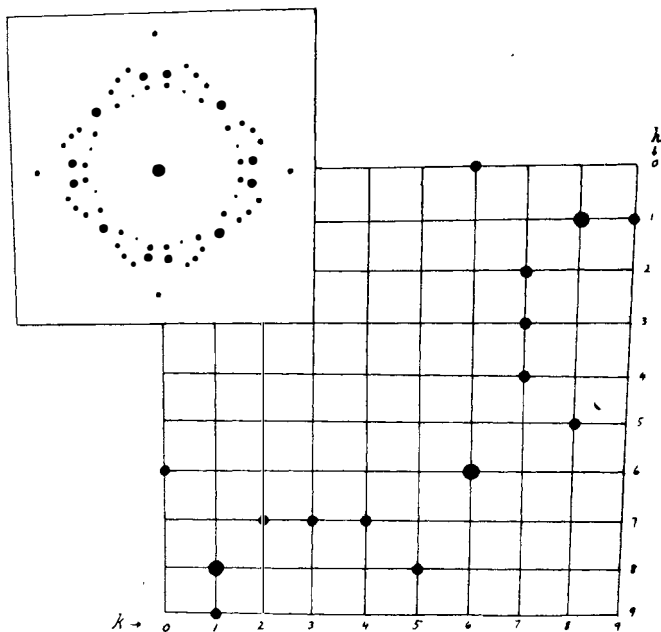


Fig. 3. Br-phosgenite. Laue photograph and gnomonic projection.
(The photograph is too faint for direct reproduction.)

are probably due to the different scattering powers of Cl and Br. It might be thought that this would help to determine the positions of the halogene ions in the structure, but unfortunately the intensity differences are too insignificant to be of any practical use. — By the method of de Schulten I also obtained similar crystals of a compound $\text{Pb}_2(\text{Br}, \text{Cl})_2\text{CO}_3$. Although I started from a solution containing equivalent quantities of Cl and Br, the resulting mixed crystals were obviously enriched in Br, as shown by the lattice constants given below. The mixed crystals were anomalously biaxial, their central parts being probably especially rich in Br.

The following quadratic forms explain — for $\text{Cu}_{K\alpha}$ -radiation — all the lines observed in the powder photographs.

Phosgenite (natural and

synthetic): $\sin^2\varphi = 0.008975 (h^2 + k^2) + 0.03015 l^2$.

Br,Cl-phosgenite: $\sin^2\varphi = 0.00860 (h^2 + k^2) + 0.0290 l^2$.

Br-phosgenite: $\sin^2\varphi = 0.00850 (h^2 + k^2) + 0.0287 l^2$.

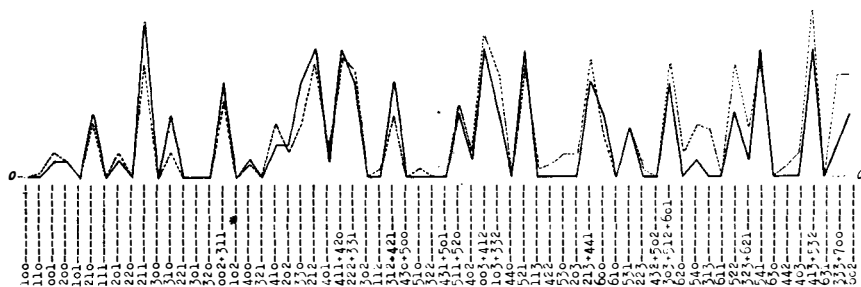


Fig. 4. Observed (full line) and calculated (dotted line) intensities for powder photographs of phosgenite, the calculated intensities being obtained from the Pb-lattice alone.

The coefficients have been fixed by means of rocksalt as a gauging substance and are thus fairly accurate. They give the following lattice dimensions.

	<i>a</i>	<i>c</i>	<i>ca</i>	<i>d</i>
Phosgenite	8.125 Å	4.430 Å	0.5453	6.19
(Br, Cl)-phosgenite	8.299 Å	4.519 Å	0.5445	
Br-phosgenite	8.347 Å	4.541 Å	0.5441	6.62

These figures are uncertain only by a few units in the last place. *d* is the calculated density for $Z=2$. de Schulten (l. c.) determined directly the densities of his synthetic crystals and found 6.134 for Cl-phosgenite and 6.550 for Br-phosgenite. (The agreement is very good, but, as in many other cases, the directly measured densities are systematically a little lower than those calculated from X-ray measurements, possibly because of invisible cracks or cavities in the crystals.)

The interpretation of the powder photographs leads uniquely to the following arrangement of the Pb ions, in terms of the (pseudo) cells given above.

$$uu0; \bar{u}\bar{u}0; u + \frac{1}{2}, \frac{1}{2} - u, 0; \frac{1}{2} - u, u + \frac{1}{2}, 0, \quad u \text{ being close to } 1/6.$$

This Pb-lattice gives calculated intensities which on the whole agree well with the observed ones (Fig. 4), showing, as might be foreseen, that the other ions contribute relatively little to the intensities. Taking into account the halogene ions, placed in positions

$$\nu\nu\frac{1}{2}; \bar{\nu}\bar{\nu}\frac{1}{2}; \nu + \frac{1}{2}, \frac{1}{2} - \nu, \frac{1}{2}; \frac{1}{2} - \nu, \nu + \frac{1}{2}, \frac{1}{2} \quad (\text{forming layers midway between the basal Pb-layers})$$

and with a suitable value for ν , the agreement is considerably improved; however, we now proceed

to consider the oscillation photographs, which yield more complete data. The oscillation photographs were taken with a Bernal X-ray photogoniometer¹, using a copper anticathode. Axes of rotation were the crystallographic axes c and a . Only natural phosgenite could be examined by this method. These photographs give the following dimensions of the unit cell: c about 8.8Å, a about 8.1Å. The c -axis used above has thus to be doubled, and more accurately the cell dimensions come out:

$$c=8.860 \text{ \AA} \quad a=8.125 \text{ \AA} \quad c/a=1.091.$$

This cell naturally contains 4 $\text{Pb}_2\text{Cl}_2\text{CO}_3$. Its axial ratio agrees closely with the value given for phosgenite in mineralogical textbooks, which is 1.0876. — The interpretation of the oscillation photographs was done by the graphical method worked out by J. D. Bernal². The result, with observed intensities, is shown in Table 1. It is seen at once that the pseudo cell is highly pronounced, the indices with l odd being represented by relatively very weak spots only. This is a consequence of the Pb-arrangement, which can — at least very approximately — be described in terms of the pseudo cell as above. Of abnormal spacings we have the following: $h0l$ is halved if h is odd. This is also seen from the Laue photograph, fig. 2. This applies to the space groups D_{2d}^7 — $P4b2$, C_{4v}^2 — $P4bm$, D_{4h}^5 — $P4/mbm$, which are also in accordance with the Laue symmetry of phosgenite. If phosgenite is piezoelectric, as stated by Onorato (l. c.), this is in favour of the two former space groups, which belong to the tetragonal scalenohedral and the ditetragonal pyramidal class respectively. From observations of the crystal faces the holohedral and the trapezohedral classes have been proposed. (Onorato arrived at the trapezohedral space group D_4^2 — $P42_1$, but this is not in accordance with my X-ray data, even when the above pseudo cell is used.) The question as to the correct space group can hardly be decided with certainty. In view of the relatively very few and weak observed spots with index l odd also the space groups with no abnormal spacings (D_{2d}^1 , D_{2d}^5 , C_{4v}^1 , D_4^1 , D_{4h}^1) — and even still larger unit cells — strictly have to be considered. However, as the observed distribution of intensities definitely points to the above three space groups we may assume

¹ J. D. Bernal, J. Sc. Instr. 4, No. 9, 1927: 5, Nos. 8/9, 1928: 6, Nos. 10 and 11, 1929.

² J. D. Bernal, On the Interpretation of X-ray, Single Crystal, Rotation Photographs. Proc. Roy. Soc. (A) 113, 117, 1927.

Table 1.

Estimated intensities from oscillation photographs.

<i>hkl</i>	Int.	<i>hkl</i>	Int.	<i>hkl</i>	Int.	<i>hkl</i>	Int.	<i>hkl</i>	Int.
100	-	101	-	102	-	103	-	104	-
110	8	111	-	112	10	113	-	114	?
200	6	201	-	202	8	203	4	204	15
210	30	211	-	212	30	213	6	214	20
220	8	221	-	222	15	223	4	224	6
300	-	301	-	302	-	303	-	304	-
310	30	311	-	312	20	313	-	314	20
320	2	321	-	322	2	323	2	324	-
330	30	331	6	332	30	333	4	334	30
400	15	401	-	402	15(?)	403	2(?)	404	15(?)
410	30	411	-	412	30(?)	413	6	414	20
420	15	421	4	422	20	423	-	424	15
430	6	431	-	432	2	433	-	434	-
440	20	441	-	442	10	443	2	444	10
500	-	501	-	502	-	503	-	504	-
510	2	511	-	512	2	513	2(?)	514	6
520	30	521	-	522	30	523	6	524	20
530	15	531	-	532	25	533	6	534	20
540	30	541	-	542	30	543	6	544	20
550	2	551	-	552	?	553	-	554	4
600	25(?)	601	-	602	20(?)	603	-	604	30(?)
610	2(?)	611	-	612	2	613	-	614	?
620	15	621	-	622	15	623	2	624	15
630	?	631	-	632	-	633	-	634	-
640	20	641	2	642	15	643	-	644	15
650	6	651	-	652	-	653	2	654	-
660	30	661	-	662	30	663	4(?)	664	30
700	?	701	-	702	?	703	-	704	?
710	2	711	-	712	?	713	-	714	4(?)
720	30	721	-	722	25	723	2	724	20
730	25	731	4	732	20	733	-	734	20
740	25	741	-	742	25	743	4	744	20
750	6	751	-	752	6	753	?	754	10
760	4	761	-	762	4	763	-		
770	6								
800	15	801	-	802	15	803	6	804	15
810	30	811	-	812	30	813	4	814	20
820	4	821	-	822	8	823	4	824	15
830	?	831	-	832	-	833	2	834	-
840	10	841	-	842	15	843	4	844	15
850	30(?)	851	-	852	30(?)	853	8		
860	15	861	-	862	15	863	-		
900	?	901	-	902	?	903	-	904	?
910	30	911	-	912	20(?)	913	2		
920	2	921	-	922	-	923	4		
930	30	931	4	932	30	933	6		
940	2	941	-	942	6				
950	30								
001	-	002	30	003	1	004	30	005	6

that the structure is built on one of these. Further, as the point coordinates in the space group P4/mbm may be built up of suitable sets of point coordinates in each of the space groups P4bm and P4b2, the structure may probably be approximately described by means of the former (holohedral) space group, even if the correct space group should be one of the latter ones. We therefore try to build the structure on the space group P4/mbm; if necessary we can afterwards displace the points in accordance with P4bm or P4b2.

The Pb-arrangement found from the powder photographs is now expressed as follows.

$$8\text{Pb in (k): } u, \frac{1}{2}-u, \nu; u+\frac{1}{2}, u, \nu; \frac{1}{2}-u, \bar{u}, \nu; \bar{u}, u+\frac{1}{2}, \nu; \\ \bar{u}, u+\frac{1}{2}, \bar{\nu}; \frac{1}{2}-u, \bar{u}, \bar{\nu}; u+\frac{1}{2}, u, \bar{\nu}; u, \frac{1}{2}-u, \bar{\nu}, \\ u \text{ being close to } 1/6 \text{ and } \nu=1/4.$$

Naturally this Pb-lattice alone gives calculated intensities which agree roughly with the observed ones, but it does not explain the spots for which index l is odd. Such spots would occur if ν had a value differing a little from $1/4$; this possibility will be discussed later; in any case the deviation from $1/4$ must be exceedingly small, as otherwise some of the spots with index l odd would have to be much stronger than they actually are. We therefore for the present assume that ν is exactly $1/4$. As mentioned above the agreement between calculated and observed intensities is improved by taking into account the Cl-ions placed in layers midway between the basal Pb-layers, that is 4Cl in (g) and 4Cl in (h), with suitable u -values. However, a consideration of this Pb-Cl-arrangement shows that it hardly leaves spaces where the C and O can be placed; moreover it does not necessarily explain the spots with index l odd. Now it is possible to exchange one of the Cl-layers, e. g. (h), against a layer of CO_8 -groups; the 4 CO_8 -groups can be placed lying wholly in one plane and still in full accordance with the known ionic distances. This arrangement is possible in the real unit cell only, and thus helps to explain the occurrence of spots with index l odd. It still remains to put 4 Cl into the structure. These may be placed in the centres of the Pb-squares in the Pb-layers themselves (positions (e) with $u=1/4$). With suitable parameter values the whole arrangement can be brought in accordance with the known ionic radii. The structure is then expressed as follows, including the above Pb-positions.

Fig. 5. Proposed structure of phosgenite. A unit cell projected on the basal plane. 8 Pb in heights $1/4 c$ and $3/4 c$; 4 Cl' in heights $1/4 c$ and $3/4 c$; 4 Cl'' in height 0; 4 CO₃ in height $1/2 c$. Thin full lines connect neighbouring O-ions.

4 Cl in (g): $u, u + \frac{1}{2}, 0; \frac{1}{2} - u, u, 0; u + \frac{1}{2}, \bar{u}, 0; \bar{u}, \frac{1}{2} - u, 0, u \sim 1/6$.

4 Cl in (e): $00u; 00\bar{u}; \frac{1}{2}\frac{1}{2}\bar{u}; \frac{1}{2}\frac{1}{2}u, u = 1/4$.

4 C in (h): $u, u + \frac{1}{2}, \frac{1}{2}; \frac{1}{2} - u, u, \frac{1}{2}; u + \frac{1}{2}, \bar{u}, \frac{1}{2}; \bar{u}, \frac{1}{2} - u, \frac{1}{2}, u \lesseqgtr 1/4$.

4 O in (h) with $u \sim 1/8$.

8 O in (j): $uv\frac{1}{2}; v\bar{u}\frac{1}{2}; v + \frac{1}{2}, u + \frac{1}{2}, \frac{1}{2}; u + \frac{1}{2}, \frac{1}{2} - v, \frac{1}{2}; \bar{u}v\frac{1}{2}; \bar{v}u\frac{1}{2}; \frac{1}{2} - v, \frac{1}{2} - u, \frac{1}{2}; \frac{1}{2} - u, v + \frac{1}{2}, \frac{1}{2}, u \gtrless 1/8, v \sim 1/6$.

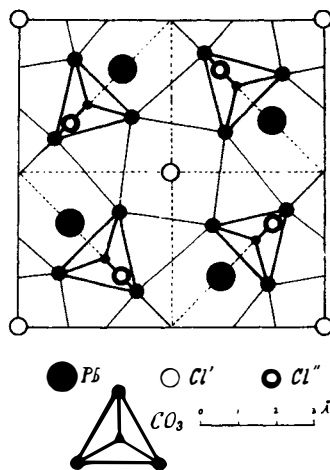


Fig. 5 shows a unit cell of this structure, projected on 001. The CO₃-groups have been assumed to have the usual shape of equilateral triangles with side lengths about 2.2Å. They form a plane sheet, the shortest distance O-O between neighbouring CO₃-groups being about 2.6Å, which is the value to be expected from the ionic radius of O²⁻; each O has 3 neighbours in this distance, but as to the arrangement of these there are 2 kinds of O, corresponding to the above division of the O-positions into 4+8 equivalent positions. This CO₃-sheet looks very plausible. If it really occurs in the phosgenite structure we should expect the phosgenite to be strongly optically negative, while it is actually weakly positive. It is possible, therefore, that the planes of the CO₃-groups themselves are inclined or even perpendicular to the plane of the sheet. Perpendicular positions can be effected in the same space group, but it seems difficult then to arrange for sufficient distances to the Pb and Cl ions. Inclined positions are possible in the two other space groups, P4bm and P4b2, which have no center of symmetry. However, the optical character of phosgenite may be due to other things than the CO₃-groups; as mentioned the substitution of Br for Cl in phosgenite changes the optical sign. Thus speculations as to the exact positions of the CO₃-groups are obviously futile. — Each Pb is surrounded by 5 Cl in the distances 3.0 Å, 2.9Å, 3.3Å (calculated from the ionic radii: 3.13Å) and 2 O distant 2.5Å (calculated 2.64Å), further 3 O about 3.1Å distant. The shortest distance Cl-Cl is about 3.7Å (calculated 3.62Å) and Cl-O about 2.8Å (calculated 3.13Å). Thus

the structure is in accordance with the ionic radii involved. As emphasized above it is not possible to check this arrangement of the lighter ions by means of the X-ray data, the fixed Pb-arrangement in combination with any arrangement of the other ions giving calculated intensities which agree fairly well with the observed intensities. This difficulty is further increased by the following fact. It is seen from the intensity table that there is a distinct increase of intensities in the series 001, 003, 005, and on the whole that the spots $hk3$ are on the average much stronger than $hk1$. Such a feature points to small deviations in the c -direction from the positions given by the pseudo cell (half cell), and the rather high intensity of 005 makes it probable that also the Pb ions are involved in these deviations. This would mean that the parameter ν in the Pb-positions is not exactly $1/4$; in fact a value about 0.24 or 0.26 gives good agreement for the basal reflections. This small uncertainty in the Pb-positions naturally makes it still more difficult to trace the intensity contributions of the lighter ions.

Summary.

Natural and synthetic phosgenite, $\text{Pb}_2\text{Cl}_2\text{CO}_3$, as well as the synthetic compound $\text{Pb}_2\text{Br}_2\text{CO}_3$ (Br-phosgenite) and a mixed crystal of these two components, belong to the same tetragonal structure type. The lattice constants and calculated densities are as follows.

	c	a	c/a	d
Phosgenite	8.860 Å	8.125 Å	1.091	6.19
Br-phosgenite	9.082 Å	8.347 Å	1.088	6.62

For the mixed crystal were found values intermediate between these. The unit cells contain 4 "molecules"; this is in full agreement with the observed densities. The following arrangement of the ions in the phosgenite cell is proposed. See Fig. 5.

Space group: $P4/mbm$. Coordinate notation after Wyckoff:

- | | |
|--|---|
| 8 Pb in (k) with $u \sim 1/6$ and $\nu \sim 1/4$. | 4 C in (h) with $u \sim 1/4$. |
| 4 Cl in (g) with $u \sim 1/6$. | 4 O in (h) with $u \sim 1/8$. |
| 4 Cl in (e) with $u = 1/4$. | 8 O in (j) with $u \sim 1/8$ and $\nu \sim 1/6$. |

The Pb-positions have been determined from the X-ray data, the positions of the other ions mainly from considerations of the ionic radii. The above space group has not been proved to be the correct one; $P4bm$ and $P4b2$ are equally possible, or perhaps even more probable as they would explain the piezoelectricity which is said to have been observed in phosgenite. The above structure is a kind of ideal arrangement, especially as to the position of the CO_3 -groups. In the real structure these may be inclined to the basal plane.

Oslo, Mineralogisk-geologisk museum,
November 1944.