

Short Communications

The Crystal Structure of Lead Carbonate Fluoride, $\text{Pb}_2\text{F}_2\text{CO}_3$

BENGT AURIVILLIUS

Division of Inorganic Chemistry 2,
The Lund Institute of Technology,
P.O. Box 740, S-220 07 Lund, Sweden

The crystal structure of phosgenite, $\text{Pb}_2\text{Cl}_2\text{CO}_3$, was determined by Sillén and Pettersson¹ and has later been refined by Giuseppetti and Tadini.² $\text{Pb}_2\text{Br}_2\text{CO}_3$ was found to be isotypic with $\text{Pb}_2\text{Cl}_2\text{CO}_3$.¹ In the course of a study of the system PbF_2 – $\text{Pb}(\text{SCN})_2$ by hydrothermal syntheses at 180 °C, the present author obtained a single crystal of $\text{Pb}_2\text{F}_2\text{CO}_3$ by chance. Since its crystal structure has quite another architecture than that of $\text{Pb}_2\text{Cl}_2\text{CO}_3$, the results are now reported. According to powder photographs the $\text{Pb}_2\text{F}_2\text{CO}_3$ sample is orthorhombic, $Z=4$, $a=8.0836(9)$, $b=8.309(2)$, $c=6.841(1)$ Å. Weissenberg photographs indicated space group $Pbcn$. $\text{Pb}_2\text{F}_2\text{CO}_3$ can be synthesized in the following way. Aqueous solutions of $\text{Pb}(\text{NO}_3)_2$, NaF and K_2CO_3 are mixed to give the Pb:F:CO_3 ratios 2:2:1 and the slurry is boiled for one hour and filtered. Slightly larger crystals are obtained on treating the slurry hydrothermally at 180 °C but even these were not large enough for single crystal work. The single crystal used for the structure determination was obtained together with decomposition products, among them PbS , when a $5\text{PbF}_2 \cdot \text{Pb}(\text{SCN})_2$ mixture was heated hydrothermally for 3 days at 180 °C. Because of the partial decomposition of $\text{Pb}(\text{SCN})_2$ there was an overpressure in the tube when cooled down to room temperature.

Weissenberg photographs, $\text{CuK}\alpha$ radiation, around [001], zero and first layer indicated the Laue symmetry mmm and the following conditions limited possible reflections: $0kl: k=2n$, $h0l: l=2n$, $hkl: h+k=2n$, which uniquely lead to the space group $Pbcn$. There is, however, a very weak extra reflection, 201. The single crystal had the form of a tetragonal prism with $A=B=0.082$

mm and $C=0.108$ mm. The a - and b -axes of the unit cell fall along the diagonals of the basal plane of the prism and the c -axis along the C -direction. The crystal was mounted on a Nicolet $P3m$ diffractometer and 684 independent reflections were registered by means of $\text{MoK}\alpha$ radiation in the range $5^\circ < 2\theta < 70^\circ$. 638 of the reflections had $I > 3\sigma(I)$ and were corrected for LP^{-1} and for absorption. Out of these, nine violated the systematic extinctions given above. The four strongest of them had the following hkl and $|F/\sigma(F)|$ -values: 100(19), 016(12), 014(12) and 011(6). The rest of the reflections 013, 051, 205, 401 and 405 had $|F/\sigma(F)|$ less than 5. The reflections 100, 011, 051 and 401 are not visible in the moderately exposed Weissenberg photographs and the reflection 201 visible in these photographs was not observed in the diffractometer data. The fact that different extra reflections occur in the Weissenberg photographs ($\text{CuK}\alpha$ radiation) and diffractometer data ($\text{MoK}\alpha$ radiation) is at least an indication that double reflections are present and the space group is therefore assumed to be $Pbcn$. A three-dimensional Patterson function could be interpreted assuming 8 Pb atoms to be situated at the general point position of $Pbcn$. Difference Fourier maps revealed the presence of light atoms and their positions could be rationalized as AB_3 groups with A – B distances ~ 1.2 Å and B – B distances ~ 2.2 Å and separate B atoms. No chemical analyses were performed on the single crystals, but with these distances possible formulae for the compound would be $\text{Pb}_2\text{F}_2\text{CO}_3$ or $\text{Pb}_2(\text{OH})_2\text{CO}_3$. A compound $\text{Pb}_2(\text{OH})_2\text{CO}_3$ has been described by Pannetier, Davignon and Feinstein³ but their published d -values showed no resemblance to the ones obtained from the diffractometer data. Moreover, a synthesis of $\text{Pb}_2\text{F}_2\text{CO}_3$ as described above gave powder photographs that could be completely indexed by means of the cell edges found from the diffractometer measurements. Assuming the light atoms to be F, O and C, the positions of all atoms were refined using isotropic temperature factors. Because of the nine extra reflections the restriction $0.1 < F_o/F_c < 10$ was made. The R -factor was 0.047 for 627 reflections and 0.074 for all 638 reflec-

Table 1. Final positional parameters and isotropic temperature factors for $\text{Pb}_2\text{F}_2\text{CO}_3$. Standard deviations are given within parentheses.

Atom	x	y	z	B (\AA^2)
Pb	0.18322(6)	0.15907(6)	0.04948(7)	(1.14)
F	0.6098(12)	0.6143(13)	0.1000(15)	1.53(15)
O(1)	1/2	0.1754(22)	1/4	1.76(27)
O(2)	0.1296(15)	0.4404(15)	0.1929(18)	1.56(18)
C	1/2	0.0195(28)	1/4	1.30(30)

tions. The B -value of Pb was 1.14 \AA^2 . Anisotropic temperature factors were introduced for the lead atoms and the final R -factors were 0.041 (628) and 0.045 (638). Positional and isotropic thermal parameters are given in Table 1. Lists of F_o and F_c and the anisotropic temperature factors of Pb are available on request. Selected distances are summarized in Table 2.

The crystal structure so arrived at is isotypic with that of the mineral Brenkite, $\text{Ca}_2\text{F}_2\text{CO}_3$, determined by Leufer and Tillmanns.⁴ Their structural description may be used also for $\text{Pb}_2\text{F}_2\text{CO}_3$. The building elements of the crystal structure are endless spiral chains of edge-sharing FPb_4 tetrahedra extending in the c -direction. These chains are joined by corner-sharing to a three-dimensional network of formula $(\text{PbF})_n^{n+}$. The CO_3^{2-} groups are situated in the tunnels formed by this network. The Pb atoms are nine-coordinated by 4F and 5O, cf. Table 2. The PbO_5F_4 polyhedron may be described as a very distorted three-capped trigonal prism.

The difference between the structure of $\text{Pb}_2\text{F}_2\text{CO}_3$ and $\text{Pb}_2\text{Cl}_2\text{CO}_3$ is perhaps most clearly seen when considering the F(Cl)-Pb arrangement. In $\text{Pb}_2\text{Cl}_2\text{CO}_3$ there are $[\text{Pb}, \text{Cl}(1)-\text{Cl}(2)-\text{Cl}(1)\text{Pb}]$ layers parallel to (001) and these layers are connected by CO_3^{2-}

groups. In the present structure a three-dimensional network is formed by the Pb and F atoms and the CO_3^{2-} groups are situated within the tunnels so formed.

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Table 2. Selected distances within the structure of $\text{Pb}_2\text{F}_2\text{CO}_3$. Standard deviations are given within parentheses.

Pb-F	2.42(1)	C-O(1)	1.30(3)
Pb-F	2.50(1)	C-2O(2)	1.30(2)
Pb-O(2)	2.56(1)	O(1)-2O(2)	2.26(2)
Pb-F	2.56(1)	O(2)-O(2)	2.24(3)
Pb-O(2)	2.57(1)		
Pb-F	2.72(1)		
Pb-O(1)	2.88(1)		
Pb-O(1)	2.91(0)		
Pb-O(2)	2.99(1)		