

The Structure of $\text{Pb}(\text{NH}_4)_2(\text{SO}_4)_2$ and Related Compounds

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Double salts of the type $\text{PbMe}_2(\text{SO}_4)_2$, where Me represents K or NH_4 , have been described in the literature¹, and it is now found that those with Me = Rb or Tl may also be prepared. Although the structure of the potassium compound has been determined by X-ray methods by Bellanca², the structure of the other double salts, where the monovalent ion has a somewhat larger ionic radius (about 1.49 Å as against 1.32 Å), need not necessarily be the same. Hence it was thought worthwhile to investigate these double salts by X-ray methods and compare the results with Bellanca's. However, the Rb- and Tl-salts have been investigated by the powder method only because it so far has not been possible to obtain crystals large enough for single crystal work in these cases.

PREPARATION

All the above mentioned double salts were prepared in the microcrystalline state by stirring a precipitate of lead sulphate with a sufficiently concentrated solution of the sulphate of the monovalent ion, filtering, and washing with dilute alcohol. In the case of $\text{Pb}(\text{NH}_4)_2(\text{SO}_4)_2$ rather large single crystals were prepared in the following way. Freshly precipitated lead sulphate was boiled with a strong solution of ammonium acetate and ammonium sulphate; upon filtering the hot solution, to get rid of excess of lead sulphate, and leaving the filtrate to cool slowly, nice crystals with dimensions up to about 1/2 mm precipitated. They were filtered off, washed with dilute alcohol, and dried at room temperature. The usual qualitative tests for NH_4^+ , SO_4^{--} and Pb^{++} were all positive, and on heating to about 450° C there was a loss in weight of 30.1 % (the literature¹ gives 30.3 %).

OPTICAL AND OTHER TESTS

Under the polarizing microscope the crystals of $\text{Pb}(\text{NH}_4)_2(\text{SO}_4)_2$ appeared to be hexagonal prisms, uniaxial negative and strongly birefringent. The refractive indices for sodium light were determined by observing the behaviour of 'Becke's line' for the crystals embedded in mixtures of α -monobromo-

naphthalene with paraffin oil or methylene iodide, the refractive indices being measured with a Pulfrich refractometer:

$$n_{\omega} = 1.721 \quad n_{\varepsilon} = 1.642$$

The density was determined with a small-scale pycnometer using absolute alcohol as reference substance:

$$d = 3.69 \pm 0.03 \text{ g/cm}^3$$

No piezoelectric effect could be detected by the electrostatic method with a very sensitive Lindemann electrometer³.

X-RAY INVESTIGATION

Rotation and Weissenberg photographs of single crystals of the ammonium compound were taken in a 57.3 mm camera using unfiltered Cu-radiation. From the diagrams the space group and approximate values of the axes were derived. More exact values were obtained from powder photographs of the same substance in a 19 cm Bradley camera using $\text{CoK}\alpha$ -radiation ($\lambda(K\alpha) = 1.7889 \text{ \AA}$). Assuming next that the K-, Rb- and Tl-compounds also are hexagonal with axes not very different from those of the NH_4 -salt, powder photographs of these in the same camera could be indexed and hence the space group and crystal axes determined. In all cases the crystals turned out to be hexagonal; as the Weissenberg and rotation diagrams indicated a diad axis or a plane of symmetry, and reflections (hkl) were present only for $h-k+l=3n$ where n is a whole number, the space group can be either $R32$, $R3m$ or $R\bar{3}m$, the last being most probable since the single crystals of the K- or NH_4 -compound show no piezoelectric effect². The axes of the hexagonal unit cells are given in Table 1. The uncertainty is estimated to be $\pm 0.01 \text{ \AA}$ on the a -axes and $\pm 0.05 \text{ \AA}$ on the c -axes.

From the density and volume of the unit cell the number of molecules per unit cell is calculated to be 3.00 for the NH_4 -compound and it seems reasonable to assume that it is 3 for the Rb- and Tl-salts also.

Taking Weissenberg diagrams about the a -axis and applying a multiple film technique the relative intensities of reflections with indices ($h0\bar{h}l$) could be roughly estimated by visual comparison with a calibrated scale. However, for small $\sin \vartheta$ -values the absorption was so strong that in certain cases only a narrow edge of the reflection was recorded on the films. As it seemed rather hopeless to correct for the absorption, the maximum intensity, and not the

Table 1. Unit cell dimensions.

| Compound | a -axis | c -axis | Volume of unit cell |
|---|-------------------|--------------------|---------------------|
| $\text{PbK}_2(\text{SO}_4)_2$ | 5.49 \AA | 20.83 \AA | 544 \AA^3 |
| $\text{Pb}(\text{NH}_4)_2(\text{SO}_4)_2$ | 5.58 \AA | 21.84 \AA | 589 \AA^3 |
| $\text{PbRb}_2(\text{SO}_4)_2$ | 5.60 \AA | 21.58 \AA | 585 \AA^3 |
| $\text{PbTl}_2(\text{SO}_4)_2$ | 5.59 \AA | 22.12 \AA | 598 \AA^3 |

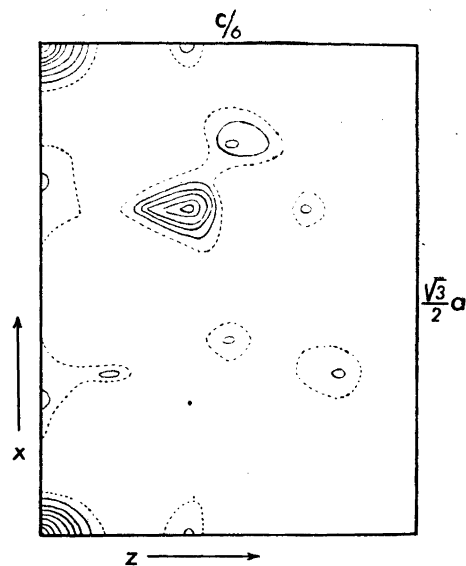


Fig. 1. Electron projection on the $(1\bar{2}10)$ -plane. Contour lines are drawn at intervals of roughly $2.5 e/\text{\AA}^2$ except for the Pb-atoms at the origin where the intervals are roughly $10 e/\text{\AA}^2$. The broken line is at ca. $2 e/\text{\AA}^2$.

integrated intensity, has been used for Fourier calculations, the absorption being neglected. These intensities were corrected for the Lorentz and polarization effects. From the $F(h0\bar{h}l)$ -values finally obtained an electron projection on the $(1\bar{2}10)$ -plane was calculated. The space group $R\bar{3}m$ requires that the Pb-atoms are located in centres of symmetry⁴, either $(0\ 0\ 0)$, $(\frac{1}{3}\ \frac{2}{3}\ \frac{1}{3})$, $(\frac{2}{3}\ \frac{1}{3}\ \frac{2}{3})$ or in $(0\ 0\ \frac{1}{2})$, $(\frac{1}{3}\ \frac{2}{3}\ \frac{5}{6})$ and $(\frac{2}{3}\ \frac{1}{3}\ \frac{1}{6})$. Assuming the first set to be appropriate all the $F(h0\bar{h}l)$ must be positive because the atomic scattering factor of Pb far outweighs the sum of those of the other atoms. Also, due to the symmetry of the space group, it is sufficient to calculate the projection for x running from 0 to $\sqrt{3} a/2$ and z running from 0 to $c/6$.

On the projection the maxima at $(0.66_7; 0.06_7)$ and $(0.81_0; 0.08_3)$ may easily be identified as due to an S-atom, and two O-atoms projected on top of one another respectively. To fit into this picture the maximum at $(0.39_0; 0.08_3)$ then has to be interpreted as an oxygen maximum. The x - and z -coordinates so obtained comply excellently with the space group requirements (see Table 2). The space group symmetry further requires the remaining oxygen atom of the sulphate group, and the nitrogen, to be located on the triad axes through the S-atoms (i.e. $x = 0; \frac{1}{3}$ or $\frac{2}{3}$). Of the three maxima $(0.00_0; 0.06_7)$, $(0.66_7; 0.11_7)$ and $(0.33_3; 0.13_3)$ the first two are much too close to either the S-maximum or the Pb-maximum to be consistent with the ionic radius of NH_4^+ (1.43—1.49 \AA) so that it seems reasonable to identify the last one as an N-maximum.

Unfortunately the oxygen maximum to be expected on the triad axes is very badly blurred by an extra maximum — presumably due to diffraction effects accompanying the Pb-maximum — and is in fact displaced a little away from the expected x -coordinate. But there seems no reason to doubt that $x = \frac{1}{3}$ is correct, and using $x = 0$ with $z = 0.330$ as a starting point for this

particular atom, all the parameters obtained from the Fourier projection have been finally adjusted by trial and error. The three extra maxima occurring in the projection are all likely to be due to diffraction effects and neglect of the absorption. The following also supports this conclusion: From the atomic parameters obtained above relative $F(hkil)$ -values have been calculated and compared with the experimental $F(hkil)$, still neglecting absorption. The quotient $F(hkil)_{\text{calc}} / F(hkil)_{\text{obs}}$ for high $\sin \theta$ -values is nearly one and shows only relatively small variations, whereas for small $\sin \theta$ -values and strong reflections it can amount to about two. This effect is probably due to absorption because the reflections of low scattering angle are most influenced by absorption. In the worst cases (marked with an asterisk in Table 3) the F_{obs} 's have been corrected so as to give the same quotient as for high scattering angles and a correction to the first Fourier projection calculated on this basis. It then turns out that apart from the two blurred-out maxima which are practically unaffected, the extra maxima are reduced 20–30 % while the oxygen maxima are increased by a similar amount. The Pb- and S-maxima are also increased a little but the N-maximum is slightly reduced. The positions of the maxima, however, are not affected.

Although as explained above the quotient $F_{\text{calc}}/F_{\text{obs}}$ is larger for small scattering angles than for higher ones, the calculated relative F -values show a variation very similar to that of the observed F 's so that the parameters given in Table 2 may be considered fairly reliable.

Table 2. Atomic positions in $Pb(NH_4)_2(SO_4)_2$.

| Atomic positions according to space group $R\bar{3}m$: | Values obtained for parameters |
|---|-----------------------------------|
| $(0, 0, 0; \frac{1}{2} \frac{2}{3} \frac{1}{3}; \frac{2}{3} \frac{1}{3} \frac{2}{3}) \pm$ | |
| 3 Pb in $0, 0, 0$ | |
| 6 S in $0, 0, z_1$ | $z_1 = 0.394$ |
| 6 N in $0, 0, z_2$ | $z_2 = 0.200$ |
| 6 O' in $0, 0, z_3$ | $z_3 = 0.325$ |
| 18 O'' in $x, \bar{x}, z; x, 2x, z; 2x, x, z$ | $x = 0.820; z = 0.083$ |

DESCRIPTION OF THE STRUCTURE

The main feature of the structure is that the lead atoms are arranged in planes perpendicular to the c -axis of the crystal; between successive planes of Pb-atoms there is a 'double layer' of sulphate ions kept together by the positive ammonium ions. This explains the rather strong birefringence.

The lead atoms are coordinated by 6 sulphate groups forming a regular octahedron about the lead. The nearest neighbours of the lead atoms are 6 oxygen atoms, the Pb-O distances being 2.5_2 Å.

The NH_4 -ions are irregularly coordinated by 7 sulphate groups and have as nearest neighbours 10 oxygen atoms. Of these, the one lying on the same triad axis as the N-atom seems to be nearer than the others: 2.7_4 Å as against 3.0_5 Å, the latter being somewhat above the sum of the ionic radii: 2.8_0 Å.

Table 3. Calculated and observed relative $F(hkil)$ -values.

| Indices | F_{calc} | F_{obs} | Indices | F_{calc} | F_{obs} |
|--------------------------|-------------------|------------------|-------------------------------------|-------------------|------------------|
| 0 0 0 3 | 38 | (17) * | 4 0 $\bar{4}$ 20 | 23 | 21 |
| 0 0 0 6 | 8 | 9 | 4 0 $\bar{4}$ 17 | 12 | 13 |
| 0 0 0 9 | 24 | 26 | 4 0 $\bar{4}$ 14 | 7 | 5 |
| 0 0 0 12 | 35 | 35 | 4 0 $\bar{4}$ 11 | 14 | 11 |
| 0 0 0 15 | 26 | 34 | 4 0 $\bar{4}$ 8 | 24 | 23 |
| 0 0 0 18 | 20 | 21 | 4 0 $\bar{4}$ 5 | 24 | 31 |
| | | | 4 0 $\bar{4}$ 2 | 12 | 15 |
| 1 0 $\bar{1}$ 20 | 20 | 21 | 4 0 $\bar{4}$ 1 | 14 | 14 |
| 1 0 $\bar{1}$ 17 | 15 | 18 | 4 0 $\bar{4}$ $\bar{4}$ | 19 | 18 |
| 1 0 $\bar{1}$ 14 | 15 | 15 | 4 0 $\bar{4}$ 7 | 17 | 16 |
| 1 0 $\bar{1}$ 11 | 16 | 12 | 4 0 $\bar{4}$ $\bar{10}$ | 20 | 20 |
| 1 0 $\bar{1}$ 8 | 19 | 11 * | 4 0 $\bar{4}$ 13 | 20 | 17 |
| 1 0 $\bar{1}$ 5 | 38 | 24 * | 4 0 $\bar{4}$ $\bar{16}$ | 20 | 16 |
| 1 0 $\bar{1}$ 2 | 29 | 18 * | | | |
| 1 0 $\bar{1}$ $\bar{1}$ | 18 | 11 * | 5 0 $\bar{5}$ 13 | 21 | 17 |
| 1 0 $\bar{1}$ $\bar{4}$ | 14 | 8 * | 5 0 $\bar{5}$ 10 | 24 | 23 |
| 1 0 $\bar{1}$ $\bar{7}$ | 24 | 15 * | 5 0 $\bar{5}$ 7 | 13 | 9 |
| 1 0 $\bar{1}$ $\bar{10}$ | 37 | 20 * | 5 0 $\bar{5}$ 4 | 9 | 5 |
| 1 0 $\bar{1}$ $\bar{13}$ | 24 | 17 | 5 0 $\bar{5}$ 1 | 15 | 14 |
| 1 0 $\bar{1}$ $\bar{16}$ | 17 | 15 | 5 0 $\bar{5}$ $\bar{2}$ | 18 | 17 |
| 1 0 1 $\bar{19}$ | 15 | 14 | 5 0 $\bar{5}$ 5 | 19 | 18 |
| | | | | | |
| 2 0 $\bar{2}$ $\bar{20}$ | 25 | 19 | 1 1 $\bar{2}$ 0 | 38 | > 18 |
| 2 0 $\bar{2}$ $\bar{17}$ | 13 | 14 | 2 2 $\bar{4}$ 0 | 39 | 31 |
| 2 0 $\bar{2}$ $\bar{14}$ | 6 | 3 | 3 0 $\bar{3}$ 0 | 31 | 22 |
| 2 0 $\bar{2}$ $\bar{11}$ | 17 | 8 * | 6 0 $\bar{6}$ 0 | 25 | 18 |
| 2 0 $\bar{2}$ $\bar{8}$ | 32 | 20 * | 5 $\bar{1}$ $\bar{4}$ 0 | 24 | 17 |
| 2 0 $\bar{2}$ $\bar{5}$ | 32 | 27 | 6 $\bar{3}$ $\bar{3}$ 0 | 22 | 23 |
| 2 0 $\bar{2}$ $\bar{2}$ | 11 | 12 | | | |
| 2 0 $\bar{2}$ 1 | 18 | 11 * | Intensities from powder photograph: | | |
| 2 0 $\bar{2}$ 4 | 29 | 20 | Indices | I_{calc} | I_{obs} |
| 2 0 $\bar{2}$ 7 | 22 | 16 | 2 1 $\bar{3}$ 2 | 26 | <i>m-w</i> |
| 2 0 $\bar{2}$ 10 | 22 | 21 | 2 1 $\bar{3}$ 4 | 8 | 0 |
| 2 0 $\bar{2}$ 13 | 24 | 20 | 2 1 $\bar{3}$ 5 | 30 | <i>m-w</i> |
| 2 0 $\bar{2}$ 16 | 24 | 19 | 2 1 $\bar{3}$ 8 | 11 | <i>m</i> |
| 2 0 $\bar{2}$ 19 | 12 | 8 | 2 1 $\bar{3}$ $\bar{10}$ | 26 | <i>m-w</i> |
| | | | 2 2 $\bar{4}$ 3 | 8 | <i>vw</i> |
| 3 0 $\bar{3}$ 18 | 23 | 20 | 2 2 $\bar{4}$ 6 | 3 | 0 |
| 3 0 $\bar{3}$ 15 | 24 | 23 | 3 1 $\bar{4}$ $\bar{2}$ | 6 | <i>vw</i> |
| 3 0 $\bar{3}$ 12 | 17 | 16 | 3 1 $\bar{4}$ $\bar{5}$ | 15 | <i>w</i> |
| 3 0 $\bar{3}$ 9 | 20 | 18 | 3 1 $\bar{4}$ $\bar{10}$ | 17 | <i>w</i> |
| 3 0 $\bar{3}$ 6 | 22 | 18 | 3 2 $\bar{5}$ 1 | 3 | <i>vw?</i> |
| 3 0 $\bar{3}$ 3 | 23 | 17 | | | |
| 3 0 $\bar{3}$ 0 | 31 | 33 | | | |
| 3 0 $\bar{3}$ $\bar{3}$ | 28 | 35 | | | |
| 3 0 $\bar{3}$ $\bar{6}$ | 23 | 22 | | | |
| 3 0 $\bar{3}$ $\bar{9}$ | 15 | 10 | | | |
| 3 0 $\bar{3}$ $\bar{12}$ | 17 | 18 | | | |
| 3 0 $\bar{3}$ $\bar{15}$ | 27 | 23 | | | |
| 3 0 $\bar{3}$ 18 | 23 | 19 | | | |

The sulphate groups are all in pairs lying on triad axes; the plane ($\bar{1}210$) bisects the O—S—O angle and passes through the other two O-atoms belonging to the same group. The O—S—O angle can therefore be measured directly on the Fourier projection as the angle between the triad axis through the S-atom

and the S—O" line; it is found to be $110^\circ \pm 3^\circ$. Within the limits of uncertainty the S—O distances are all the same: 1.5₅ Å.

A list of interatomic distances is given below together with the distances expected from ionic radii or bond lengths⁵; the uncertainty is estimated to be ± 0.10 Å or less.

Table 4. List of interatomic distances.

| Distance | From this investigation | From ionic radii or bond lengths |
|----------|-------------------------|----------------------------------|
| S—O | 1.55 Å | 1.51 Å |
| Pb—S | 3.49 Å | |
| Pb—O | 2.52 Å | 2.64 Å |
| O—O | 2.55 Å | 2.6 Å |
| N—O' | 2.74 Å | 2.8 Å |
| N—O" | 3.05 Å | |

The double salts containing Rb⁺ or Tl⁺ instead of NH₄⁺ are likely to have the same structure as the NH₄-compound because the ionic radii are nearly identical although the much higher polarizability of the Tl⁺-ion may be of some importance in this connection. The structure of PbK₂(SO₄)₂ as proposed by Bellanca differs from the one found here for the corresponding NH₄-compound only in the arrangement of the K⁺- and SO₄²⁻-ions along the *c*-axis, *i. e.*, the order of these ions on lines through the Pb-atoms and parallel to the *c*-axis is changed. However, the arguments on which Bellanca has based his structure seem not completely convincing, and above all an electron projection on the (1210)-plane seems highly desirable to supplement the information obtained from the Patterson projection. Considering the structural similarities of these double salt crystals one would feel inclined to assume the same atomic arrangement in case of PbK₂(SO₄)₂ also, though it must be admitted that the ionic radius of K⁺ is smaller than the radii of the other monovalent ions mentioned above.

COMPARISON OF MOLECULAR VOLUMES

Let us finally compare the molecular volumes of the PbMe₂(SO₄)₂-compounds obtained from our crystal analysis with the values given in the literature⁶ for the single compounds PbSO₄ and Me₂SO₄. Although these values are rather old they are supposed to be accurate to ± 1 Å³ except in the case of Tl₂SO₄ where the uncertainty presumably is larger.

Table 5. Comparison of crystal molecular volumes.

| Me | Vol. of Me ₂ SO ₄ V ₁ | Vol. of PbSO ₄ V ₂ | Vol. of PbMe ₂ (SO ₄) ₂ V ₃ | $\Delta V =$ V ₁ + V ₂ - V ₃ |
|-----------------|---|---|---|--|
| K | 108 Å ³ | 79 Å ³ | 181 Å ³ | 6 Å ³ |
| NH ₄ | 123 Å ³ | 79 Å ³ | 196 Å ³ | 6 Å ³ |
| Rb | 122 Å ³ | 79 Å ³ | 195 Å ³ | 6 Å ³ |
| Tl | 125 Å ³ | 79 Å ³ | 199 Å ³ | 5 Å ³ |

From Table 5 it is seen that in all four cases of double salt formation there is a significant decrease in volume. This shows that the ions are more densely packed in the double salt crystals than in the pure Me₂SO₄ and PbSO₄ separa-

tely and also gives the clue as to why these solid double salts are formed: The closer packing of the ions gives less electrostatic energy and hence greater stability.

SUMMARY

The unit cell dimensions and space group of some double salts of the type $\text{PbMe}_2(\text{SO}_4)_2$ have been determined by X-ray methods. In case of $\text{Me} = \text{NH}_4$ atomic parameters and interatomic distances have been obtained. It is shown that on formation of these double salts from the single compounds there is a decrease in molecular volumes.

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