

CCCLII.—*The Formation and Characteristics of Crystals of Lead Azide and of Some Other Initiating Explosives.*

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No account is to be found in the literature of the crystallography of even the more usual of those explosives which detonate with sufficient energy and at high enough velocity to function as initiators to other explosives. It is the object of this paper to give this information and to detail methods by which single crystals, large enough for measurement or other experimental purposes, can be obtained, in the cases of the three substances now in most general use: lead azide, mercuric fulminate, and lead styphnate (lead trinitroresorcinoxide).

The greatest interest attaches to lead azide, for it was found in the course of the work that there are two crystalline modifications, both anhydrous. The ordinary or α -azide can be made by double decomposition without risk, although when large crystals are grown by the cooling of hot saturated solutions, unexplained explosions may occur. The less stable, or β -form, shows a greater sensitiveness to causes of accidental explosion, and during its formation by double decomposition is very liable to detonate. The long crystals which Curtius and Rissom (*Ber.*, 1891, **24**, 3346) observed to explode when lead azide was crystallised from hot aqueous solution were almost certainly of the β -variety.

Mercuric azide, which Wöhler and Krupko (*Ber.*, 1913, **46**, 2056) and Stettbacher (*Z. ges. Schiess-Sprengstoffw.*, 1920, **15**, 211) found to be very sensitive and treacherous, presents similar phenomena. In this case also, there appear to be two modifications, of which the β -variety is more unstable than its lead analogue. Mercuric azide may explode spontaneously either when dry or under water, but only when the β -form is present.

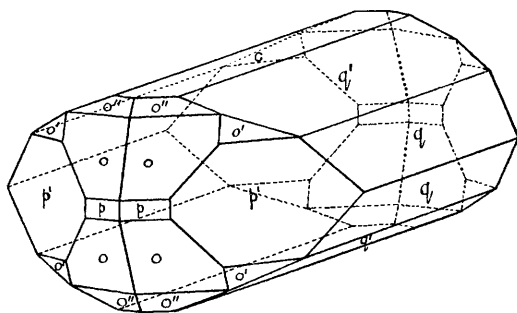
EXPERIMENTAL.

On account of the very small solubility of these compounds in water, special methods had to be adopted in all cases. It was

found very difficult to obtain satisfactory crystals. Whenever possible, the crystallographic data were derived in the following way. Angular measurements were made on a combination instrument which was at once a single-circle goniometer and an X-ray spectrometer. Sufficient X-ray diagrams of complete rotation were then made to define the unit cell unequivocally; from those taken on the three principal axes, the lengths of the three sides of the unit cell were found approximately. One of the spacings of planes parallel to two principal axes was then measured accurately on the X-ray spectrometer, filtered copper radiation being used. To do this, a face was in each case ground on the crystal parallel to the planes selected, by means of a special rotary grinding attachment. This measurement gave one axial length precisely; the others were then calculated from it and from the axial ratios previously determined. The calculated densities should be trustworthy to 1 part in 300.

Lead Azide.—Lead azide may be crystallised from solution in ammonium acetate or chloride, from Rochelle salt, or from sodium

FIG. 1.

*α-Lead azide.*

acetate. A solution containing 17 g. of sodium acetate in 100 c.c. was saturated with finely divided lead azide at 75°, and allowed to cool to about 30° during 20 hours. The best crystals were about 2 mm. long and 1 mm. wide. Numerous experiments were made, for the crystals were usually ill-developed or hollow, and often the product was lost in a violent explosion when the crystallisation was nearly complete. The material separated from the mother-liquor was never unduly sensitive, however large the crystals might be. The idea that large crystals of such explosive substances as lead azide are always excessively sensitive to shock or friction has been widely received, but in view of these facts seems to have little foundation. It is possible to grow from solution in ammonium

acetate single, rather unevenly developed crystals of lead azide which are 3 cm. or more in length, but can be crushed to powder with a spatula without explosion.

Analysis of the selected crystals gave Pb, 70.8, 71.0 (calc. for PbN_6 : Pb, 71.1%). For the determination of density, finely granular azide was prepared under conditions which ensured homogeneous crystals and the absence of basic material, and was dried in a vacuum. Redistilled benzene was employed as immersion liquid and air was removed from the crystals by boiling the benzene under reduced pressure. The density found in benzene was 4.71 at 25°.

Crystal system : orthorhombic. Class : holohedral.

Axial ratios : $a : b : c = 0.586 : 1 : 1.433$.

Forms observed : $c\{001\}$, $p\{110\}$, $p'\{120\}$, $q\{011\}$, $q'\{013\}$, $o\{111\}$, $o'\{121\}$, $o''\{112\}$, (o' , o'' , and p always very small).

The angles co and ap' (70° 34' and 49° 31' respectively) were selected for calculation of the axial ratios. Other calculated angles agreed with the observed values within 13', but in the principal zone (100) the divergencies were 35' or less.

Unit cell : $a = 6.64 \text{ \AA}$.	}	Cell volume = 1223.7 \AA^3 .
$b = 11.34$,,		Contains 12 molecules.
$c = 16.25$,,		$d(040) = 2.835 \text{ \AA}$.

Twelve molecules in the cell is an abnormal number for an orthorhombic crystal, and indicates that the molecules or ions must be arranged about the elements of symmetry in equivalent groups of three. The calculated density (the mass of the hydrogen atom being taken as 1.662×10^{-24} g.) is 4.71 (observed 4.71).

The optic axial plane is (100). The acute bisectrix is the b axis. The axes emerge from the $\{011\}$ faces at an angle (in air) of 74.5° with each other. The optical sign is negative. By using Madan's solution of phosphorus in methylene iodide, α_D was found by the Becke method to be 1.860 ± 0.005 . Neither of the other indices was determined, but both were observed to be higher than 2.05.

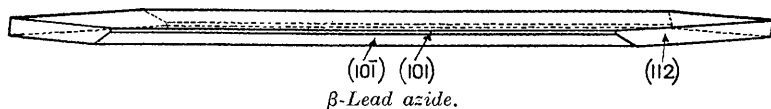
β -Lead Azide.—The β -form was discovered in the attempt to grow the ordinary crystals by a diffusion method. To avoid explosion, it was found best to fill a capsule of 1¼" diameter with sodium azide solution (7 g./100 c.c.), and to place it in the centre of a 4-inch crystallising dish containing lead nitrate (4 g./100 c.c.) to the depth of ½ inch. Water was then run in very slowly until the level was ½ inch above the rim of the capsule. After about 16 hours, the dish was almost filled with radiating clusters of thin needles showing brilliant reflex on their broader faces, some being

4 cm. long. Under certain conditions, the β -modification resulted from simple mixing of the two solutions. Sodium azide solution (3.4%) was added to lead nitrate solution (4%) until a marked blue opalescence, followed by a distinct turbidity, was seen. After an hour, the colloidal material had disappeared and β -crystals were present. If the conditions vary slightly from those given, α -material only may result, for the $\beta \rightarrow \alpha$ transition may be very rapid (Found for a sample of material made by the first method, and freed as far as possible from the α -crystals which are always present: Pb, 71.0, 71.2; N, 29.1, 28.9. Calc. for PbN_6 : Pb, 71.1; N, 28.9%. Lead was determined as sulphate; nitrogen by measuring the gas produced by oxidation with cerium ammonium nitrate).

The determination of density could not be made in any of the ordinary ways, for the crops of crystals always contained α -material and were for the most part so fine and defective that not more than about a centigram of clear transparent needles could be collected at once. This amount of the best crystals was weighed in a small glass bowl hanging by a single fibre of viscose silk from the arm of an assay balance sensitive to less than 10^{-5} g. The weighing was done first in air, then in ethylene dibromide. Air was removed by suspending the loaded pan in the dibromide under a bell-jar and exhausting the air above the liquid. The mean of three experiments gave $D^{20^\circ} = 4.93$. The less stable form has therefore a higher density than the stable one.

The best crystals available for measurement were from 1.0 to 1.5 mm. long, about 0.5 mm. wide and 0.2 mm. thick. Fig. 2 shows the typical habit.

FIG. 2.



Crystal system: monoclinic. Class: holohedral.

Axial ratios: $a : b : c = 0.578 : 1 : 1.993$, $\beta = 90^\circ 49'$.

Forms observed: $c\{001\}$, predominant; $\{10\bar{1}\}$; $\{101\}$ very narrow; $\{10\bar{3}\}$ replaces $\{10\bar{1}\}$ in crystals grown at $50-60^\circ$.

In this instance, the angular measurements, although useful to identify the forms, were useless for calculation, and X-ray methods alone were employed. Two axial lengths (a and c) were obtained by measuring the spacings (200) and (0014); the third (b) by calculation from a rotation diagram taken on $[010]$ at 4 cm. distance with a very narrow beam. The results were:—

$$a = 5.10 \text{ \AA.}; \quad b = 8.83 \text{ \AA.}; \quad c = 17.60 \text{ \AA.}$$

The angle β was determined by a special method. From oscillation diagrams, it had been found that the planes (2014 and 20 $\bar{1}$ 4) could both reflect from the same (001) face, the crystal being rotated on the [010] axis. Both reflexions were received on the same film, and β was calculated from the angular distance of each from the beam, and from the quantities a and c .

The unit cell so defined contains the substance of eight (8.13) molecules, accounts for all the reflexions observed on rotation diagrams, and is the smallest that will do so.

The plane of the optic axes is (010). The acute bisectrix lies in the obtuse angle between the a and c axes at very approximately 56° with the c axis. One optic axis emerges through (001); the other through (101).

When dry and protected from light, the crystals of the β -azide remain unchanged for years. They may be heated in a vacuum at 200° for short periods without obvious change, but in water, or more rapidly in a solution of a lead salt, they pass into the α -form by a process of solution and recrystallisation. Comparison by means of the fall hammer showed that the sensitiveness of the β was markedly higher than that of the α -azide. The tests were carried out on powders made by crushing crystals of each variety to about the same grain.

Mercuric Azides.— α -Mercuric azide was prepared by mixing a saturated solution of mercuric chloride with an equivalent one of sodium azide made slightly acid with hydrazoic acid. Crystals slowly appeared in thin, evenly developed prisms 2—4 mm. in length (Fig. 3c). The prisms were optically biaxial and negative in sign. Since they showed straight extinction in all three principal sections, this variety of mercuric azide is almost certainly orthorhombic (Found: Hg, 70.4. Calc. for HgN_6 : Hg, 70.45%). The solubility in water was found to be 0.257 g. in 100 g. of solution at 20° .

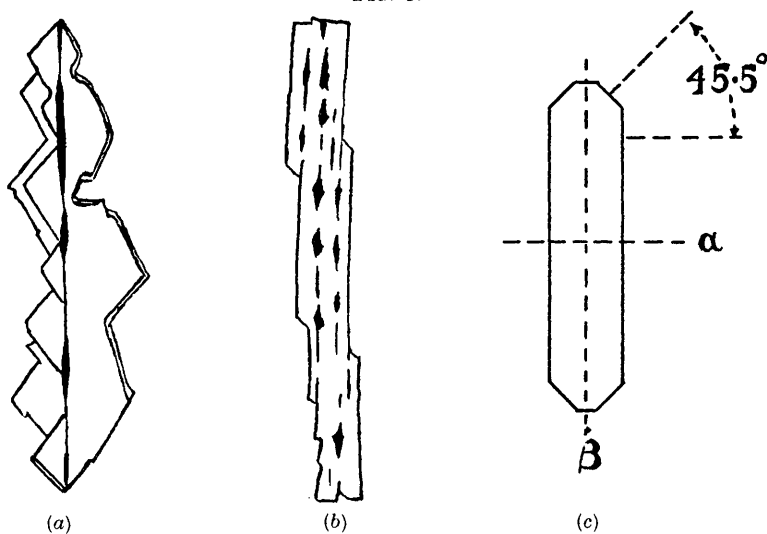
α -Mercuric azide is not abnormally sensitive, for no explosion occurred during these tests, and the substance was many times dried and coarsely powdered without mishap.

Small amounts of azide were also made by distilling hydrazoic acid into a suspension of mercuric oxide in water according to the method of Stettbacher (*loc. cit.*). A mass of interlacing needles crystallised as the reaction liquid cooled, and frequently detonated either during the crystallisation or when the contents of the vessel were moved. It was found possible, however, by careful work, to separate and dry some of the crystals. The dry material was unusually sensitive to friction—much more so than β -lead azide—and sometimes detonated spontaneously during drying. Micro-

scopic examination revealed that there were two kinds of material clearly distinguishable by their appearance and by their double refraction, which was positive in the direction of elongation for the α (Fig. 3a) and negative for the β -variety (Fig. 3b), although the latter was rather variable in its optical properties. The diffusion method gave the same result and a mixture of both kinds of crystal was always obtained when the α -azide was recrystallised from water or from acetone. In every case when the β -crystals were present the material was sensitive to touch and was liable to explode spontaneously.

The β -crystals could not be collected for analysis, but in a speci-

FIG. 3.



Mercuric azides.

men obtained by recrystallisation and containing as high a proportion of them as possible the estimation of mercury as sulphide gave Hg, 70.4, 70.4%. The identity of the aggregates illustrated in Fig. 3a and the insensitive α -prisms (Fig. 3c) was established by optical tests and measurement of the terminal angles of the prisms. In water, or more rapidly in mercuric nitrate solution, the β was found to be unstable and to be replaced by the α -type, just as in the parallel case of lead azide.

The Explosions during the Formation of β -Lead Azide.—No satisfactory explanation has been found for the apparently spontaneous detonations which occur during crystal growth. The case of the β -azide of lead is important, and some observations may be re-

corded which seem to indicate the direction in which an explanation may be sought.

By trial with variations of the diffusion method already described, it was found that explosions still occurred when lead nitrate was replaced by lead acetate, and sodium azide by calcium azide, when the surrounding water was slightly acid or alkaline, or when very dilute solutions of the reacting salts were used. It is unlikely, therefore, that any subsidiary chemical reaction was the cause. Silver and mercurous azides may be made in this way without explosion. Neither has been found in a β -modification.

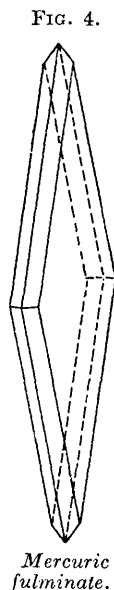
The instability of the β -azide cannot itself be the cause in the case of the lead salt, for the sensitiveness of this substance, once isolated, is too low. Garner and Gomm (this vol., p. 2123) have studied the thermal decomposition of the lead azides and have found that the heat of activation of the slow thermal change is 38,750 calories for the β -substance, whereas for the α -azide it is 47,600 calories. These figures are too close to one another to support the idea that the structure of the β -azide might be very easily broken down.

No trace of a third modification of lead azide could be detected even on the occasion when the crystallisation was examined under the microscope just before an explosion occurred.

The explosions happened not only at the ordinary temperature, but also when the whole experiment was carried out at 0° or at 60° . The crystals formed at the high temperature were in one respect different from the others. When immersed in warm lead nitrate solution, they dissolved only very slowly and evenly, triangular etch-figures consistent with the symmetry being developed regularly all over the principal faces. The material made at room temperature, still more so that grown at 0° , dissolved very rapidly and irregularly. The α -prisms were seen to eat their way into the β -crystal at certain places and finally to divide it, whilst portions of it remained unattached. The crystals of the low-temperature crops, moreover, showed considerable differences among themselves. By using a Leitz dark-ground condenser with a 100 c.p. Pointolite lamp, it was seen that in dilute nitric acid (1%), solution was often very uneven; fragments of the crystal were detached from the edges and dissolved in the surrounding liquid. Occasionally the fragments formed a brilliant cloud round the crystal. The phenomena strongly recalled those observed by Traube during the solution of mercuric chloride and other salts (*Z. physikal. Chem.*, 1928, **138**, 85), but the particles were by no means all ultra-microscopic. Many were distinctly acicular and about 2μ in length. In other cases, solution was quite even, with no breaking-up into particles visible in the dark-ground illumination.

These differences which can be seen in recoverable crystals are possibly significant of greater differences of the same kind in crystals too unstable for recovery. According to modern views, especially those held by Smekal (*Physikal. Z.*, 1926, **27**, 837), distortions of the crystal structure are often sufficiently marked to determine many of the physical properties. At the places in a crystal where such distortion occurs, the energy of the structure will be higher than normal. One possible process by which apparently spontaneous detonation might occur would involve the delivery to an element of the crystal of an increment of energy sufficient to initiate detonation. If the crystal structure were distorted, the increment necessary at certain points of the crystal might be very low and a detonation which would spread throughout the crystal might be set up from no readily apparent cause.

Mercuric Fulminate.—The best crystals were obtained from ammoniacal solution. A mixture of equal volumes of concentrated aqueous ammonia (d 0.88), water, and alcohol was saturated with the technical fulminate. The solution was filtered and allowed to stand, and in order to prevent too rapid evaporation of ammonia the surface of the liquid was covered with a sheet of filter-paper which was prevented from sinking by means of glass floats. After some days, pyramidal crystals 1–2 mm. long were found attached to the under side of the paper by their more pointed ends (Fig. 4). The development of these crystals was the same as that of the fulminate which had not been recrystallised. By a modification of the thiosulphate method of titration (Philip, *Z. ges. Schiess.-Sprengstoffw.*, 1912, **7**, 181) they were found to contain 99.4% of anhydrous fulminate.



Crystal system : orthorhombic. Class : probably holohedral.

Axial ratios : $a : b : c = 0.712 : 1 : 1.353$.

Forms observed : $\{111\}$; $\{010\}$; $\{001\}$ (only on crystals from aqueous ammonia).

Observed angles : (010) ; $(111) - 57^\circ 48'$; (100) ; $(111) - 41^\circ 30'$.

Unit cell : $a = 5.48 \text{ \AA}$. } Cell volume = 440.7 \AA^3 .

$b = 7.71 \text{ ,,}$ } Contains 4 molecules.

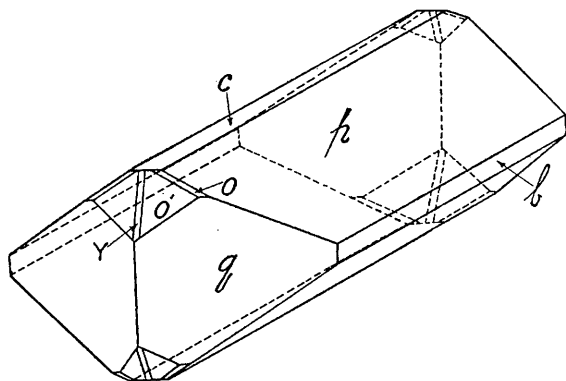
$c = 10.43 \text{ ,,}$ } $d(040) = 1.927 \text{ \AA}$.

The calculated density is 4.26. For the direct determination technical fulminate was twice dissolved in aqueous ammonia and reprecipitated by acetic acid, and was then dried in a vacuum. The

purity of the material was given by the thiosulphate method of estimation as 99.9%. The density was determined in α -bromonaphthalene at 20° with the precautions necessary for a powder and found to be 4.307. Mercury fulminate is very liable to be impure and it is not surprising that the two values given in the literature are both higher. Berthelot (*Compt. rend.*, 1880, **90**, 946) gave the figure 4.42 for technical material; Solonina (*Z. ges. Schiess.-Sprengstoffw.*, 1910, **5**, 69) found 4.39 for fulminate purified by solution in potassium cyanide.

The plane of the optic axes is (010). The acute bisectrix is the c axis and the optical sign is positive. α_D was found to be 1.530 ± 0.005 and β_D to be 1.56 ± 0.005 . γ is very high. The axial angle in air ($2E$) [measured on crystals developed on (001)] is 66.4° .

FIG. 5.

*Lead styphnate.*

When the recrystallisation was carried out by the method given, but from a mixture of equal volumes of aqueous ammonia (25% NH_3) and water, the alcohol being omitted, the fulminate was recovered in thin plates developed on (001) and of irregular outline. The purity of this material was low (98.3%). It was found from the examination of rotation and powder diagrams that in spite of the surprising differences in habit these plates were essentially identical with the ordinary crystals.

Lead Styphnate.—The diffusion method in the form employed for β -lead azide was the only one which gave measurable crystals. Lead nitrate solution (10 g./100 c.c.) was placed in the inner dish, and a dilute solution of magnesium styphnate in the outer one. In a fortnight, a fringe of crystals formed round the rim of the inner dish. Many were hollow, and only one complete at both ends was obtained.

The analysis gave results in accordance with the accepted formula for lead styphnate, $C_6H(NO_2)_3(OH)_2PbO$. The molecule of water is firmly retained even at 100° , but it can be driven out by heating at 120° in a vacuum. This dehydration causes no change in the shape or clarity of the crystal.

Crystal system : monoclinic. Class : holohedral.

Axial ratios : $a : b : c = 0.799 : 1 : 0.638$, $\beta = 92^\circ 51'$.

Forms observed : $p\{011\}$, $q\{110\}$; $r\{201\}$, $o\{211\}$, very variable; $b\{010\}$, $c\{001\}$, $o'\{111\}$, small; $r\{20\bar{1}\}$, $o\{2\bar{1}1\}$, $o'\{1\bar{1}\bar{1}\}$ very small.

The angles pq ($68^\circ 24'$), bq ($51^\circ 24'$), and bp ($57^\circ 30'$) were selected for calculation. Five out of six calculated angles agreed with the observed values within $5'$.

Unit cell : $a = 10.02 \text{ \AA}$. } Cell volume = 1003.9 \AA^3 .
 $b = 12.54 \text{ ,,}$ } Contains 4 molecules.
 $c = 8.00 \text{ ,,}$ } $d(400) = 2.503 \text{ \AA}$.

The density determined in benzene at 20° was 3.085. The value calculated from the cell dimensions is 3.077.

The b axis is the obtuse bisectrix. The acute bisectrix axis lies in the acute angle between the a and c axes, making an angle of 50° with the former. The sign is negative. α_D is 1.550 ± 0.005 . Both β and γ appeared to be over 1.8, but could not be measured.

Lead Styphnate Hydrate.—From the jelly which is always formed when solutions of a lead salt and of a soluble styphnate are mixed in the cold, a hydrate is deposited if the salts are pure and the solution dilute. A solution of pure magnesium styphnate containing 6 g. of combined and 0.5 g. of free styphnic acid in 100 c.c. was mixed with the same volume of equivalent lead nitrate solution diluted with four times its volume of water. After standing for 36 hours at 10° , the jelly first formed had given place to fibrous masses of fine needles with a few large crystals of the ordinary salt. The needles were unstable in contact with water, and when stirred rapidly became dehydrated. They were removed quickly by filtration on a Buchner funnel, washed with alcohol and ether, and dried in a desiccator [Found : PbO , 45.8; loss in a high vacuum at 120° , 7.6. Calc. for $C_6H(NO_2)_3(OH)_2PbO, H_2O$: PbO , 45.9; H_2O , 7.4%].

When dry the substance is comparatively stable, although it eventually loses a molecule of water at the ordinary temperature.

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ARDEER.

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