Neutron Diffraction Study of α-Pb(N₃)₂

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The structure of the common, α form of lead azide was investigated by three-dimensional neutron diffraction techniques. The atomic positions were refined in the centrosymmetric space group, *Pcmn*, using anisotropic temperature factors. It was found that there are 4 different types of azide structures in a unit cell. The azide groups are essentially linear but they differ in degree of symmetry and also in spatial arrangement of the neighboring atoms. The symmetric and the asymmetric azides are arranged in different layers and separated by a layer of lead atoms. Each lead atom is bonded to 8 azides in a distorted tetragonal antiprismatic bond arrangement.

Introduction

Lead azide, Pb(N₃)₂, is a well known primary explosive. There are four known polymorphic forms of lead azide designated as the α-, β- γ-, and δ-forms. The first complete investigation of the α and β polymorphism in lead azide was performed by Miles (1931). Later, Pfefferkorn (1948) and Azaroff (1956) attempted to determine the space group of these two forms by X-ray investigation. In the α-lead azide study, Azaroff deduced two possible space groups, Pc2₁n and Pcmn, from the Pb atom configuration. He concluded that Pc2₁n is the probable space group because his infrared data favored an asymmetric structure for the azide group and because packing considerations of the azide groups in the Pcmn space group require at least one symmetric azide group. He determined the approximate position of the Pb atoms but could not give nitrogen atom positions because the Pb atom dominated the intensity of the X-ray scattering. Glen (1963) has recently analyzed the two-dimensional neutron diffraction data which were collected by Danner & Kay at the Brookhaven National Laboratory. He obtained approximate positions for the nitrogen atoms in the non-centrosymmetric space group Pc2₁n, but failed to investigate the details of atomic bonding because the X-coordinates were not directly determined and also because the standard deviations of the remaining parameters were rather large. In the present study, the structure of a α-lead azide was reinvestigated by a three-dimensional neutron diffraction measurement.

Experimental

A small crystal of lead azide in the form of a flat rhombic prism, 3 mm thick, 5 mm wide, and 8 mm long was used for this study. The crystal was glued in an aluminum container to prevent dissociation by white light, and mounted on the three-dimensional goniometer cradle with the crystallographic c axis parallel to the rotation axis of the goniometer. To ensure that the crystal would be immersed fully in the beam, the goniometer χ-angles were limited to less than 30 degrees, which restricted the *l*-value of (*hkl*) planes to a maximum of 4. The diffraction intensities were measured by constant speed scanning with a GE X-ray diffractometer modified for neutron diffraction. Using a 1·055 Å wavelength neutron beam, a total of 888 reflection planes were investigated of which 285 planes were too weak to detect, and about 170 more were very weak. The 0*kl* reflection data were compared with those collected previously at this laboratory by Boutin, Prask & Crimmins (1964) using a different crystal. Of the 71 earlier 0*kl* reflections, 16 are common and show excellent agreement with the data of the present investigation.

The estimated μR of this crystal ranged from about 0·1 to 0·15, and so absorption corrections were neglected because the effect is small. No secondary extinction effects were observed during the refinement procedure. The cell parameters reported by Azaroff (1956), a = 11·31 Å, b = 16·25 Å, c = 6·63 Å, were used throughout this experiment.

Refinement

The least-squares refinement was carried out with the *OR FLS* program (Busing, Martin & Levy, 1962) modified at Argonne National Laboratory for the CDC 3600 computer. The zero-intensity reflections were included for the refinement by assigning them an arbitrary observed structure factor of 3·0 with an independent scale factor. As an initial trial, Glen's structure (1963) was refined using the Pc2₁n space group. With this non-centrosymmetric space group, the R index of the least-squares refinement with isotropic temperature factors became 0·138 for all data, 0·09 excluding zero intensity reflections, and 0·081 excluding

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zero and very weak intensity reflections. The atomic arrangement of this non-centrosymmetric space group was almost the same as the result obtained by Glen. However, as the refinement progressed, the atomic positions oscillated randomly without reducing the R index. In particular, the positions of the azide groups varied in a manner which suggested that they were related by a mirror plane at $y = \frac{1}{4}$. A refinement including anisotropic thermal vibrations was attempted.

This failed because the anisotropic temperature factors of some nitrogen atoms became negative, especially for those azide ions related by the mirror plane.

In the course of the refinement with the non-centrosymmetric space group, one of the azides (designated azide I in the later sections) was symmetric in form throughout, and the overall atomic configuration showed centrosymmetry with a mirror plane at $y = \frac{1}{4}$. These facts led to the choice of the space group $Pcmn$.

Table 1. *Final least-squares parameters with estimated standard deviations*

The anisotropic temperature factor is of the form $T = \exp\left[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\right]$.

|	X	Y	Z	$\beta_{11}(\times 10^5)$	$\beta_{22}(\times 10^5)$	$\beta_{33}(\times 10^5)$	$\beta_{12}(\times 10^5)$	$\beta_{13}(\times 10^5)$	$\beta_{23}(\times 10^5)$
Pb(1)	−0·1359 (4)	0·2500 (0)	0·0595 (11)	323 (27)	170 (14)	253 (182)	0 (0)	22 (65)	0 (0)
Pb(2)	0·1236 (3)	0·0884 (2)	0·3418 (8)	288 (19)	137 (9)	146 (203)	−6 (10)	−75 (45)	−35 (27)
N(1)	0·2802 (3)	0·1784 (2)	0·1528 (10)	540 (27)	137 (9)	1585 (166)	−2 (13)	410 (65)	33 (31)
N(2)	0·2798 (4)	0·2500 (0)	0·1529 (14)	395 (32)	117 (12)	713 (351)	0 (0)	221 (74)	0 (0)
N(3)	−0·2641 (3)	−0·0015 (2)	0·4338 (9)	427 (23)	138 (9)	948 (98)	−24 (12)	−134 (54)	−2 (29)
N(4)	−0·2370 (3)	0·0664 (2)	0·3933 (7)	306 (20)	135 (9)	385 (118)	−26 (11)	−173 (45)	59 (26)
N(5)	−0·2143 (4)	0·1340 (2)	0·3485 (9)	651 (30)	184 (11)	940 (141)	−116 (15)	−120 (71)	86 (36)
N(6)	0·0059 (3)	0·1286 (2)	−0·0055 (9)	432 (23)	208 (12)	929 (130)	88 (14)	−143 (57)	−242 (36)
N(7)	0·0014 (3)	0·0904 (2)	−0·1588 (9)	268 (20)	153 (10)	683 (254)	29 (11)	−13 (45)	−4 (34)
N(8)	−0·0032 (4)	0·0536 (2)	−0·3085 (8)	546 (27)	178 (11)	603 (110)	−72 (14)	254 (60)	−219 (32)
N(9)	0·0144 (4)	0·2500 (0)	0·3587 (11)	281 (29)	231 (16)	334 (182)	0 (0)	−170 (80)	0 (0)
N(10)	−0·0396 (4)	0·2500 (0)	0·5168 (11)	357 (30)	107 (12)	472 (174)	0 (0)	−21 (87)	0 (0)
N(11)	−0·0924 (6)	0·2500 (0)	0·6645 (17)	596 (44)	263 (20)	870 (349)	0 (0)	−203 (117)	0 (0)
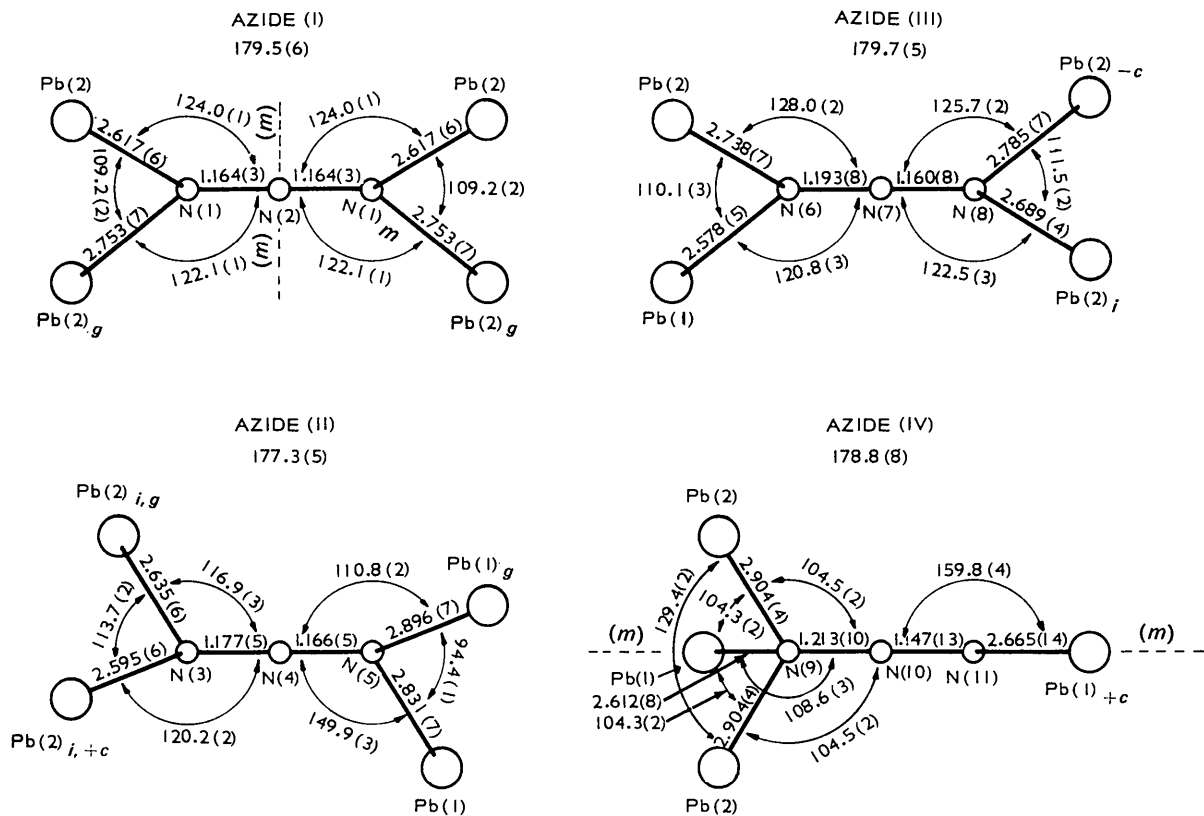
Fig. 1. Schematic illustration of the structure of the azide groups and positions of the neighboring Pb atoms. For Pb atom designations refer to Table 3.

Table 2. *The observed and calculated structure factors*

Y is the scaled structure factor (observed and calculated) and *IQ* is the scale factor indicator. *IQ* for the different crystals is given in the following list.

IQ	Crystal	Reflections	Scale factor
1	A	3-dimensional	1·96967
2	B	[100] zone	2·01545
3	A & B	zero-intensity	1·79682

ZERO INTENSITY REFLECTIONS

The atoms were then reassigned to the unit cell of this new space group, Pcmn, by moving the atomic coordinates less than two standard deviations. In this space group 8 Pb and 56 N atoms were assigned to general positions (site d), and 4 Pb and 16 N atoms were assigned to special positions (site c), which gives a total of 13 atoms in the asymmetric unit. With this centrosymmetric space group, the refinement converged rapidly and the atomic positions were quickly stabilized. The R index of the refinement with isotropic temperature factors was about the same, but the standard deviations were reduced to one third of the values found by using the non-centrosymmetric space group. With anisotropic temperature factors, the R index was further reduced to $R = 0.108$, $wR = 0.102$ for all reflection data including zero intensity. The final parameters of the least-squares refinement with anisotropic temperature factors for all reflection data including zero intensity are given in Table 1. When the zero intensity and very weak intensity reflections were excluded, the R index was reduced to 0.07 but the standard deviations were somewhat increased. All observations including zero intensity reflections were given unit weight in the refinement. As fractions of the standard deviations, the maximum shift was 0.003 in the last cycle. Observed and calculated structure factors are listed in Table 2.

Atomic arrangement

There are 12 molecules in a unit cell of α-Pb(N$_3$)$_2$. The azide ions occur as four different types as shown in Fig. 1. The azide (I) is linear and symmetric with N–N = 1.164 Å. This azide group has a mirror plane perpendicular to the azide axis through the center N atom. Consequently, the whole system including the two nearest neighbor Pb atoms at both ends show

(001) PROJECTION OF α-Pb(N₃)₂

Fig. 2. Atomic arrangement in a unit cell, as viewed along the c axis. The lead atoms are represented by the large circles and the nitrogen atoms by small circles.

mirror symmetry. There are 4 azide (I) ions in a unit cell and they are all parallel to the b axis. Each of the 2 neighboring azide (I) ions is bonded to a common Pb atom forming a continuous chain of Pb atoms alternating with terminal azide nitrogens parallel to the c axis.

The azide (II) is slightly bent (N–N–N angle = 177°) and slightly asymmetric with N'–N" = 1.177 (5) Å and N"–N"' = 1.166 (5) Å. Unlike the symmetric environment of the azide (I), the bond distances to the 2 Pb atoms at each end are quite different, 2.6 Å at one end and 2.9 Å at the other end. They also form a bond chain extending along the c axis, but the directions of the two Pb–N bonds at each end are twisted with respect to one another by an 80° rotation about the azide axis. The structure of azide (III) is also linear and shows clear asymmetry with N'–N" = 1.93 (8) Å and N"–N"' = 1.160 (8) Å. The azide (III) is also bonded to 2 Pb atoms at each end with the bond direction twisted by 80° in the same way as azide (II). This bond chain forms a two-dimensional pattern, covering the (100) plane. There are 8 azide (II) and 8 azide (III) groups in a unit cell.

Azide (IV) is essentially linear (N–N–N angle = 179°) and strongly asymmetric with N'–N" = 1.213 (10) Å and N"–N"' = 1.147 (13) Å. This azide is located in the mirror plane as are its two nearest Pb neighbors. The terminal N atom of the longer N–N bond is also weakly bonded to 2 more Pb atoms one on either side of the mirror plane. Azide (IV) groups also form a chain, parallel to the c axis with the Pb atom bonded to alternate terminal nitrogens of each azide group. There are 4 azide (IV) groups in a unit cell.

The angle between the Pb–N bond and the azide axis varies over a wide range, mostly between 105° and 128° except 150° in azide (II) and 160° in azide (IV). The interatomic distances between two terminal nitrogen atoms of azide (I), (II), (III), and (IV) are 2.327(6), 2.342(5), 2.352(7) and 2.360(12) Å respectively. It is noticed that the azide lengths increase with increasing degree of asymmetry. The closest approach between neighboring azides is 2.95 Å between N(5) of azide (II) and N(10) of azide (IV) and is 2.97 Å between N(1) of azide (I) and N(3)$_{t\ g}$ (refer to Table 3 for subscripts) of azide (II), as shown in Fig. 2. This is equivalent to the sum of the van der Waals radii of N atoms given by Pauling (1960), but definitely shorter than the anion–anion contact distances in the ionic azides (3.0–3.34 Å) reported by Pringle & Noakes (1968). Perhaps the slight bending of the azide (II) and azide (IV) groups may be caused by this packing strain.

The arrangement of the azide groups and Pb atoms in a unit cell is shown in Fig. 2. The 4 types of azide groups may be reclassified into 2 categories, namely symmetric (azide I and II) and asymmetric (azide III and IV). Then it is observed that the symmetric and asymmetric azides are arranged in different layers oriented perpendicularly to the a axis and separated by a layer of Pb atoms. Each Pb atom is bonded to 8
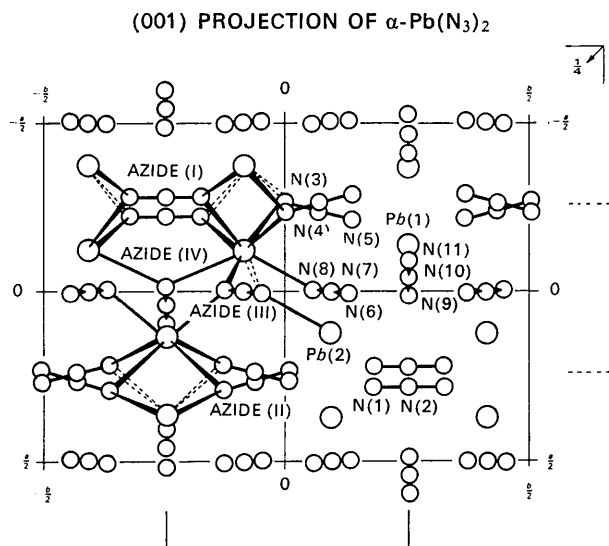
azides with bond distances ranging from 2·57 Å to 2·90 Å, and further surrounded by 4 Pb atoms at distances of 4·20, 4·36, 4·38 and 4·53 Å. The details of Pb–N bonds are summarized in Fig. 3.

The Pb–N bonds of each Pb atom in α-lead azide form a distorted tetragonal antiprismatic arrangement. The bond directions extend from the body centered Pb atom toward the 8 corners of 2 opposing distorted tetragons, and form two distorted tetragonal pyramids with a common apex. The tetragonal bases of the antiprism differ in distortion; one is rectangular and the other is rhombic as shown in Fig. 3. Around the Pb(1) atoms the rectangular pyramidal bonds are much longer than rhombic bonds. The 4 nitrogen atoms forming the base of the rectangular pyramid are coplanar but those of the rhombic pyramid are out of the best fit plane as shown in Table 3. For the Pb(2) atom, the pyramidal bases have irregular form but they may be best approximated as a rectangle and a rhombus. The rectangular pyramidal bonds from the Pb(2) atom are also longer than the rhombic bonds. The 4 atoms forming the rectangular base are also essentially coplanar but those of the rhombic base are considerably out of the plane. The rectangular bonds of Pb(1) and the rhombic bonds of Pb(2) are directed to the azide (I) and (II) in the symmetric layer. The rectangular bonds of Pb(2) and the rhombic bonds of Pb(1) are directed to the azides (III) and (IV) in the asymmetric layer.

Discussion

The N–N distances in azide (I) (1·164 Å) and (II) (1·177 and 1·166 Å) in the symmetric azide layer agree with those found in the ionic azides. The N–N distances of the monovalent azide ion are reported as 1·16 or 1·17 Å for α-NaN$_3$, β-NaN$_3$, LiN$_3$, and Sr(N$_3$)$_2$, by Pringle & Noakes (1968); for AgN$_3$ by Hair & Robinson (1960); for CuN$_3$ by Levine & Fernelius (1954), and for NH$_4$N$_3$ by Frevel (1936). The N–N distances of the asymmetric azide (III) (1·193 and 1·160 Å) and (IV) (1·213 and 1·147 Å) are similar to those found in the covalent azide of N$_3$Co(NH$_3$)$_5$(N$_3$)$_2$ by Palenik (1964) (1·208 and 1·145 Å) but more symmetrical than those found in CH$_3$N$_3$ by Livingston & Rao (1960) (1·24 and 1·12 Å) and in HN$_3$ by Amble & Dailey(1950) (1·240 and 1·134 Å). From this comparison, it is believed that the azide (I) and (II) in the symmetric layer are mainly ionic in character. It is also the author's belief that the bonds of the azide (III) and (IV) in the asymmetric layer have more covalent character, forming 4 covalent bonds lying to one side of the Pb atom as the case of tetragonal PbO (Moore & Pauling, 1941) and orthorhombic PbO (Kay. 1961).
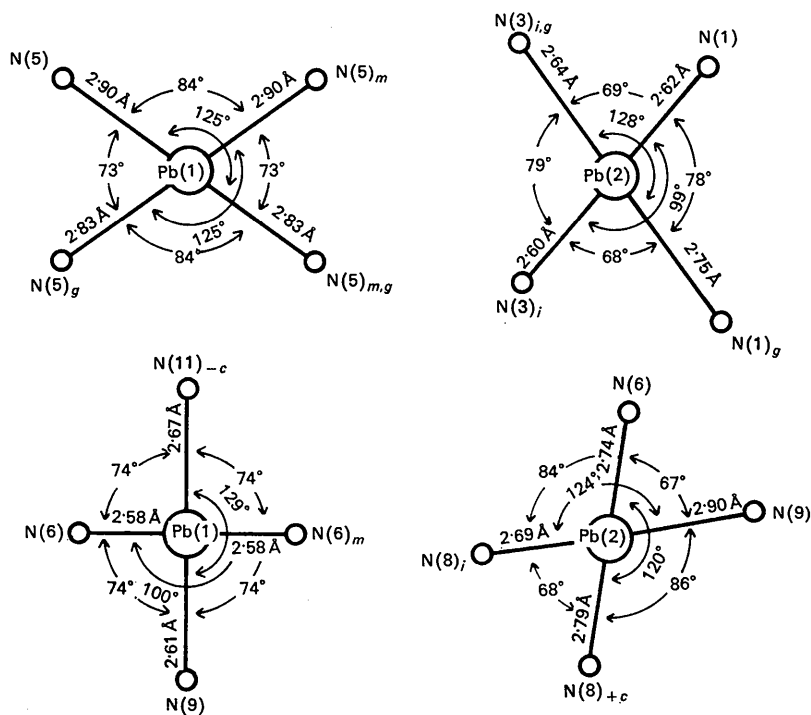
Fig. 3. Diagram to illustrate the bond arrangements of Pb(1) and Pb(2) atoms in α-Pb(N$_3$)$_2$. The two distorted tetragonal pyramid arrangements of each Pb atom are viewed down from the common apex (Pb atom). For nitrogen atom designations, refer to Table 3.

Table 3. *Planarity of the four nitrogen atoms forming the base of a pyramid*

The nitrogen atoms in a symmetric unit are specified with subscripts which indicate symmetry operations: m = mirror ($\pm b/2 \mp y$), g = glide mirror ($\pm a/2 \mp x$, $z \pm c/2$), i = inversion ($-x, -y, -z$), c = unit cell translation along c-axis.

Apex	Base shape	Best fit plane	Departures from planarity (Å)
Pb(1)	Rectangle	$x - 0.2436z = -2.9866$	N(5) = 0, N(5)$_m$ = 0, N(5)$_g$ = 0, N(5)$_m$ $_g$ = 0
Pb(1)	Rhombus	$x - 0.3629z = -0.1948$	N(9) = -0.48, N(11)$_{-c}$ = -0.04, N(6) = 0.26, N(6)$_m$ = 0.26
Pb(2)	Rhombus	$x - 0.9448y + 0.4727z = 3.8159$	N(1) = -0.42, N(1)$_g$ = 0.42, N(3)$_i$ = 0.85, N(3)$_i$ $_g$ = -0.85
Pb(2)	Rectangle	$x - 0.04151y - 0.005375z = -0.01862$	N(6) = -0.001, N(8)$_{+c}$ = -0.006, N(8)$_i$ = 0.007, N(9) = 0.000

References

AMBLE, E. & DAILEY, B. P. (1950). *J. Chem. Phys.* **18**, 1422.

AZAROFF, L. V. (1956). *Z. Kristallogr.* **107**, 362.

BOUTIN, H. P., PRASK, H. J. & CRIMMINS, D. (1964). Unpublished.

BUSING, W. R., MARTIN, K. O. & LEVY, H. L. (1962). ORNL–TM 305, and 306. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

DANNER, H. R. & KAY, M. I. Private communication.

FREVEL, L. K. (1936). *J. Amer. Chem. Soc.* **58**, 779.

GLEN, G. L. (1963). *J. Amer. Chem. Soc.* **85**, 3892.

HAIR, M. L. & ROBINSON, P. L. (1960). *J. Chem. Soc.* p. 2775.

KAY, M. I. (1961). *Acta Cryst.* **14**, 80.

LEVINE, R. & FERNELIUS, W. C. (1954). *Chem. Rev.* **54**, 452.

LIVINGSTON, R. L. & RAO, C. N. R. (1960). *J. Phys. Chem.* **64**, 756.

MILES, F. D. (1931). *J. Chem. Soc.*, p. 2532.

MOORE, W. J. & PAULING, L. (1941). *J. Amer. Chem. Soc.* **63**, 1392.

PALENIK, T. J. (1964). *Acta Cryst.* **17**, 360.

PAULING, L. (1960). *The Nature of the Chemical Bond*, p. 260. Ithaca: Cornell Univ. Press.

PFEFFERKORN, G. (1948). *Z. Naturf.* **3**, 364.

PRINGLE, G. E. & NOAKES, D. E. (1968). *Acta Cryst.* B**24**, 262.