

Refinement of  $\alpha$ -Lead Azide by Neutron Diffraction

BY C. S. CHOI

LCWS Laboratory, Armament R &amp; D Command, Dover, NJ 07801, USA and Institute for Materials Research, National Bureau of Standards, Washington, DC 20234, USA

E. PRINCE

Institute for Materials Research, National Bureau of Standards, Washington, DC 20234, USA

AND W. L. GARRETT

LCWS Laboratory, Armament R &amp; D Command, Dover, NJ 07801, USA

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**Abstract.**  $\text{Pb}(\text{N}_3)_2$ , orthorhombic,  $Pnma$ ;  $a = 6.63$ ,  $b = 16.25$ ,  $c = 11.31$  Å,  $Z = 12$  [Azaroff (1956), *Z. Kristallogr.* **107**, 362–369]. The four independent azide groups in the structure are all asymmetric, with N–N bond distances, corrected by the riding model, ranging from 1.164 to 1.196 Å, and N–N–N bond angles as small as  $177.9^\circ$ .

**Introduction.** It is well known that the stability of azide compounds is strongly correlated with the degree of covalency of the azide bonds in crystals. The structure of  $\alpha$ - $\text{Pb}(\text{N}_3)_2$ , a well known primary explosive, was previously determined from a partial, three-dimensional, neutron diffraction data set by Choi & Boutin (1969). A recent advance (Garrett, 1972) in techniques for growing lead azide crystals has provided us with additional crystals of a size and shape suitable for neutron diffraction.

We have therefore redetermined the structure by refining a full, three-dimensional data set, in order to improve the accuracy of the structure parameters. Intensities were measured out to a limiting value of

$\sin \theta/\lambda = 0.65$  Å<sup>-1</sup> by the procedure described by Prince (1972), on a computer-controlled four-circle diffractometer at the NBS reactor. Of 1466 independent reflections within the limiting sphere, there were observable intensities for 1328. Intensities were reduced to  $F$  values, and reflections were assigned weights according to  $W = [\sigma_s^2 + (0.005F)^2]^{-1}$ , where  $\sigma_s$  is the estimated standard deviation of  $F$  due to counting statistics. The structure was refined by full-matrix least-squares methods (Finger & Prince, 1975), including an isotropic secondary extinction parameter (Zachariasen, 1968) to a weighted  $R$  of 0.043 and an unweighted  $R$  of 0.038. The extreme secondary extinction correction ( $F_{\text{corr}}/F_{\text{calc}}$ ) was 0.34 for the 004 reflection. The final least-squares atomic positional parameters are given in Table 1.\*

**Discussion.** The four crystallographically distinct azide groups, designated in the following discussion as azide I, azide II, azide III, and azide IV, are all distorted significantly from the linear, symmetric conformation found in more stable ionic azide compounds (Choi & Prince, 1976). Bond distances and angles are given in

Table 1. Final least-squares atomic positional parameters ( $\times 10^4$ ) for  $\alpha$ - $\text{Pb}(\text{N}_3)_2$ 

|       | <i>x</i>  | <i>y</i> | <i>z</i>  |
|-------|-----------|----------|-----------|
| Pb(1) | 605 (2)   | 2500 (0) | -1356 (1) |
| Pb(2) | 3387 (1)  | 890 (1)  | 1231 (1)  |
| N(1)  | 1518 (2)  | 1783 (1) | 2804 (1)  |
| N(2)  | 1526 (2)  | 2500 (0) | 2785 (1)  |
| N(3)  | 4340 (2)  | -15 (1)  | -2641 (1) |
| N(4)  | 3909 (1)  | 666 (1)  | -2375 (1) |
| N(5)  | 3514 (2)  | 1341 (1) | -2140 (1) |
| N(6)  | -71 (2)   | 1283 (1) | 55 (1)    |
| N(7)  | -1574 (2) | 905 (1)  | 14 (1)    |
| N(8)  | -3082 (2) | 536 (1)  | -32 (1)   |
| N(9)  | 3612 (2)  | 2500 (0) | 138 (1)   |
| N(10) | 5165 (2)  | 2500 (0) | -391 (1)  |
| N(11) | 6638 (2)  | 2500 (0) | -926 (2)  |

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32798 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Bond lengths and angles of the azide groups

| Type | Bond        | Length (Å) |        | N–N–N angle (°) |
|------|-------------|------------|--------|-----------------|
|      |             | Raw        | Riding |                 |
| I    | N(1)–N(2)   | 1.166 (1)  | 1.179  | 177.9 (2)       |
|      | N(3)–N(4)   | 1.181 (2)  | 1.186  | 178.2 (1)       |
| III  | N(5)–N(4)   | 1.160 (2)  | 1.173  |                 |
|      | N(6)–N(7)   | 1.172 (2)  | 1.181  | 179.2 (1)       |
| IV   | N(8)–N(7)   | 1.167 (2)  | 1.176  |                 |
|      | N(9)–N(10)  | 1.191 (2)  | 1.196  | 178.3 (2)       |
|      | N(11)–N(10) | 1.149 (2)  | 1.164  |                 |

Table 2, Fig. 1 and Fig. 2. Azide I crosses a mirror plane, so the bond distances must be equal, but the group is slightly bent. The other azide groups, in addition to being slightly bent, all have significantly different lengths for the two N–N bonds. Azide II is more asymmetric than azide III, in disagreement with the earlier findings of Choi & Boutin (1969). Azide IV, with bond lengths, as corrected by the riding model, of 1.164 and 1.196 Å, is the most asymmetric.

The distortions of the azide groups are also reflected in differences in the distances from the end N atoms to the neighboring Pb atoms, with the long N–N bonds being associated with short Pb–N bonds, and *vice versa*. This is to be expected, in the light of the electronic structures of covalently bonded azides

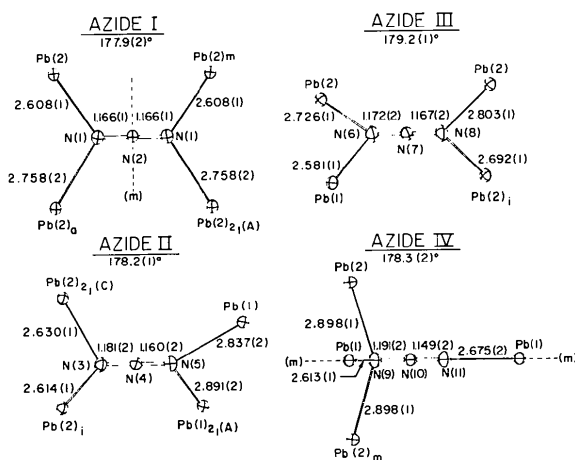


Fig. 1. ORTEP drawing (Johnson, 1965) of the four azide groups and their neighboring lead atoms. The subscripts of atom designators, e.g. *n*, *i*,  $2_1(A)$ , etc., indicate the symmetry operations for corresponding atoms.

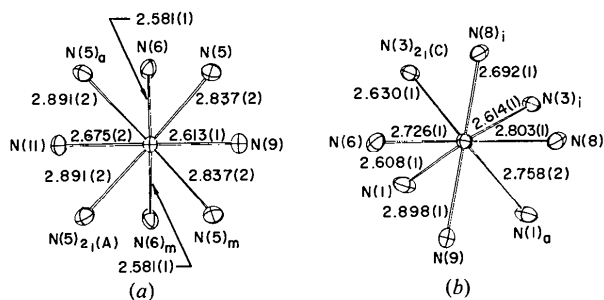


Fig. 2. Pb atoms and their neighboring N atoms, (a) for Pb(1) and (b) for Pb(2).

(Pauling, 1960). This uneven Pb–N bonding for azide groups II, III, and IV accentuates the distortion of the observed N–N bond length because of the asymmetric librational motion of the azide group. Hence, it is reasonable to find that the corrected N–N bond lengths are less different than the uncorrected ones.

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## The Potassium Thiocyanate Complex of 2,3-Naphtho-20-crown-6

BY DONALD L. WARD, HOUSTON S. BROWN AND LYNN R. SOUSA

*Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, USA*

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**Abstract.**  $C_{23}H_{30}KNO_6S$ ,  $M_r = 487.66$ , monoclinic,  $C2/c$ ,  $a = 15.698(6)$ ,  $b = 20.543(6)$ ,  $c = 8.274(2)$  Å,  $\beta = 109.98(2)^\circ$ ,  $24^\circ\text{C}$ ,  $Z = 4$ ,  $D_x = 1.292$  g cm $^{-3}$ ; crystallized from ethyl acetate. Full-matrix least-squares refinement [1383 data,  $I \geq 2\sigma(I)$ ] led to  $R = 0.056$ . A twofold axis, passing through the  $K^+$  ion,

relates the two halves of the ligand; the  $SCN^-$  ion is disordered. The six O atoms lie within  $\pm 0.35$  Å of their mean plane, the naphthalene C atoms within  $\pm 0.004$  Å of their mean plane; both planes contain the  $K^+$  ion and are twisted  $51^\circ$  about the twofold axis from each other. The  $K^+$  ion is 6.97 Å from the center of the