

## The Structures of Some Inorganic Cyanamides. II. The Structure of Lead Cyanamide

By M. J. COOPER\*

*Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England*

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The structure of lead cyanamide has been determined by X-ray diffraction and has been correlated with physical measurements on this compound. The structure is covalent with an asymmetric N-C-N group which is more strongly bonded to lead atoms at one end. The strong lead-nitrogen bonding forms continuous spirals with the N-C-N groups approximately perpendicular to the axis of the spirals.

### Unit cell and space group

The preparation of suitable single crystals of lead cyanamide and a preliminary investigation of the symmetry and unit cell dimensions have been described in part I (Adams, Cooper & Sole, 1964). The unit cell is orthorhombic and accurate lattice parameters were determined by Miss K. M. Adams, using the method of Farquhar & Lipson (1946), as follows:

$$\begin{aligned} a &= 5.553 \pm 0.001 \text{ \AA} \\ b &= 11.732 \pm 0.003 \\ c &= 3.867 \pm 0.002 \end{aligned}$$

The density is  $6.27 \text{ g.cm}^{-3}$  (Hang & Funke, 1954) and there are therefore 4 formula units per unit cell.

Indexing of Weissenberg and oscillation photographs indicated that the space group is  $Pna2_1$ , which was confirmed by the subsequent analysis.†

For the space group  $Pna2_1$  the fourfold positions are the general positions:

$$x, y, z; \bar{x}, \bar{y}, \frac{1}{2} + z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z; \frac{1}{2} + x, \frac{1}{2} - y, z$$

and there are no special positions. The main contribution to the scattering will be from the lead atoms which will occupy one set of general positions.

### The [001] projection

The [001] projection is centrosymmetric and the positions of the lead atoms will be:

$$\pm(x_1, y_1; \frac{1}{2} + x_1, \frac{1}{2} + y_1).$$

Prominent independent peaks will therefore occur on the [001] Patterson projection at positions  $(2x_1, 2y_1)$ ,

$(\frac{1}{2}, \frac{1}{2} - 2y_1)$  and  $(\frac{1}{2} - 2x_1, \frac{1}{2})$ , the last two of these having twice the weight of the first.

Reflexions of the form  $hk0$  were collected on a zero-layer normal-beam Weissenberg photograph with filtered  $\text{Mo } K\alpha$  radiation and a multiple-film technique. The crystal used was in the form of a needle of length  $200 \mu$  and cross-section  $40 \mu \times 10 \mu$ . An intensity scale was made from a reflexion in the [001] zone from the same crystal and intensities of reflexions out to  $\sin \theta/\lambda = 1.0 \text{ \AA}^{-1}$  were measured by visual comparison with this scale. The intensities were corrected for Lorentz and polarization factors, and for absorption by the method of Wells (1960).

The [001] Patterson projection was calculated and is shown in Fig. 1. The three independent peaks were identified as follows:  $A(2x_1, 2y_1)$ ,  $B(\frac{1}{2}, \frac{1}{2} - 2y_1)$  and  $C(\frac{1}{2} - 2x_1, \frac{1}{2})$ , and coordinates for the lead atoms were derived from the positions of these peaks as

$$x_1 = 0.106, y_1 = 0.134.$$

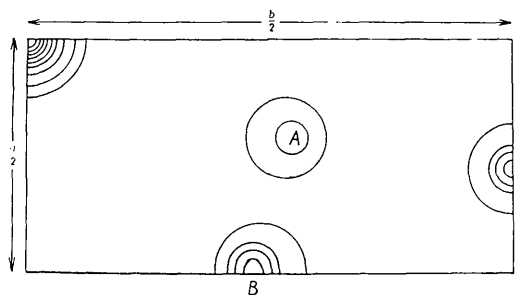


Fig. 1. The [001] Patterson projection. The contours are at equal arbitrary intervals.

Structure factors were calculated for a structure containing four lead atoms only and these were scaled in regions of  $\sin \theta/\lambda$  to the observed structure amplitudes, giving an  $R$  index of 0.125 for all measured reflexions. The atomic scattering factors used throughout this work were those given by Forsyth & Wells (1959) and a dispersion correction was made for the

\* Formerly Mullard Research Fellow, Downing College, Cambridge. Present address: Brookhaven National Laboratory, Long Island, New York, U.S.A.

† The space group  $Pnam$  ( $=Pnma$ ) is also possible. However, the fourfold positions for this space group are included in the general positions for  $Pna2_1$ , and the additional symmetry would be apparent from the final atomic positions.

lead atoms, the value of  $\Delta f'$  given by Dauben & Templeton (1955) being used.

$F_o - F_c$  syntheses were used to refine the positions of the lead atoms in this projection and the  $R$  index for a structure containing lead atoms only was reduced to 0.098. An isotropic temperature factor of  $B = 1.0 \text{ \AA}^2$  was applied to the lead atoms and the scaling factor was then approximately constant for all regions with  $\sin \theta/\lambda > 0.4 \text{ \AA}^{-1}$ , for which the contributions from the light atoms are very small.

Throughout this refinement of the lead positions the  $F_o - F_c$  syntheses exhibited a positive region in the area where the cyanamide group was expected to lie. This positive region included three peaks in a straight line with approximately equal separations of about  $1.2 \text{ \AA}$ . The light atoms were therefore identified with these peaks and initial coordinates were chosen as follows:

C	$x_2 = 0.610$	$y_2 = 0.100$
N(1)	$x_3 = 0.830$	$y_3 = 0.060$
N(2)	$x_4 = 0.420$	$y_4 = 0.145$

Structure factors were calculated for a structure including atoms at these positions, with an arbitrary temperature factor of  $B = 2.0 \text{ \AA}^2$  applied to all the light atoms. Scaling of these structure factors to the observed structure amplitudes gave an  $R$  index of 0.080. Only the structure factors for reflexions in the regions with  $\sin \theta/\lambda < 0.4 \text{ \AA}^{-1}$  were affected appreciably by the inclusion of the light atoms and the  $R$  index for these regions was reduced from 0.149

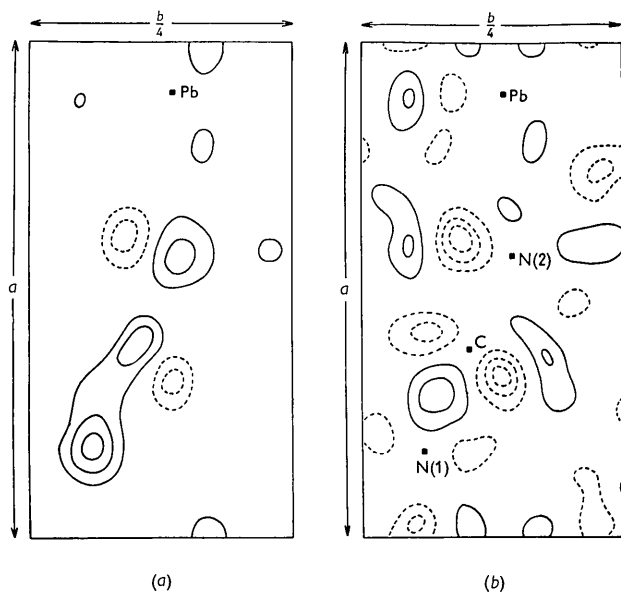


Fig. 2. The final  $F_o - F_c$  [001] Fourier syntheses. (a) For a structure containing lead atoms only; the contours are at intervals of  $5.2 \text{ e. \AA}^{-2}$ . (b) For a structure containing all atoms; the contours are at intervals of  $2.6 \text{ e. \AA}^{-2}$  (the standard deviation of the electron density). Zero contours have been omitted. Squares represent atomic sites.

to 0.092. Comparison of  $F_o$  and  $F_c$  for these regions indicated that the nine reflexions of highest intensity suffered from extinction. An empirical correction for secondary extinction gave an approximately constant scaling factor for regions with  $\sin \theta/\lambda < 0.4 \text{ \AA}^{-1}$  and further reduced the  $R$  index for these regions to 0.057 (0.085 for lead only). The final refinement was carried out by scaling in two regions of  $\sin \theta/\lambda$  only ( $0.0\text{--}0.4$  and  $0.4\text{--}0.8 \text{ \AA}^{-1}$ ), thus allowing for resolution of the  $\alpha_1\text{--}\alpha_2$  doublet, and the final  $R$  index was 0.053 (0.082 for lead only). The final  $F_o - F_c$  syntheses are shown in Fig. 2, for structures containing (a) lead atoms only and (b) all atoms.

### The [100] projection

The [100] projection is centred but is not centrosymmetric and the origin of the unit cell can be chosen at any arbitrary position along the  $c$  axis. The origin was therefore chosen so that  $z_1 = 0$  for the lead atoms. Only the  $z$  coordinates of the light atoms therefore remained to be determined from this projection.

Reflexions of the form  $0kl$  were collected on a zero-layer normal-beam Weissenberg photograph with filtered Cu  $K\alpha$  radiation and a multiple-film technique. The crystal used was  $200 \mu$  long and had a cross section of  $50 \mu \times 50 \mu$ . An intensity scale was made as before and intensities were measured out to  $\sin \theta/\lambda = 0.6 \text{ \AA}^{-1}$  and corrected for Lorentz and polarization factors and for absorption.

Structure factors were calculated for a structure with lead atoms only and these were scaled to the observed structure amplitudes in regions of  $\sin \theta/\lambda$ , giving an  $R$  index of 0.089. An  $F_o - F_c$  synthesis indicated that the lead atoms were in their correct positions and showed a positive region at  $z = \frac{1}{2}$  between two lead atoms at  $z = 0$  and  $z = 1$ . This synthesis is shown in Fig. 3, in which the  $y$  coordinates of the light atoms have been indicated at  $z = \frac{1}{2}$ . Since the arrangement of the lead atoms is centrosymmetric in this projection the difference synthesis will also be centrosymmetric. Hence the occurrence of this peak at  $z = \frac{1}{2}$  only indicates that the light atoms are near this position, since the positions of the light atoms will be duplicated by a reflexion across the plane  $z = \frac{1}{2}$  arising from the centrosymmetry. The  $R$  index for a structure with all the light atoms at  $z = \frac{1}{2}$  was 0.086. Since this structure is centrosymmetric a difference synthesis may not indicate clearly any small deviation from centrosymmetry in the positions of the light atoms.

The approximate Pb-N distances calculated for this centrosymmetric structure were:

Pb-N(1)	$2.32 \text{ \AA}$
Pb-N(1)	$2.62 \text{ \AA}$ (two N(1) neighbours)
Pb-N(2)	$2.64 \text{ \AA}$ (two N(2) neighbours).

The shortest bond is between lead and nitrogen atoms

Table 1. *The final atomic coordinates for lead cyanamide*

Pb	$x_1 = 0.1071 \pm 0.0002$	$y_1 = 0.1359 \pm 0.0001$	$z_1 = 0.0000$
C	$x_2 = 0.620 \pm 0.008$	$y_2 = 0.102 \pm 0.003$	$z_2 = 0.460 \pm 0.020$
N(1)	$x_3 = 0.826 \pm 0.008$	$y_3 = 0.059 \pm 0.003$	$z_3 = 0.450 \pm 0.020$
N(2)	$x_4 = 0.430 \pm 0.013$	$y_4 = 0.144 \pm 0.005$	$z_4 = 0.475 \pm 0.025$

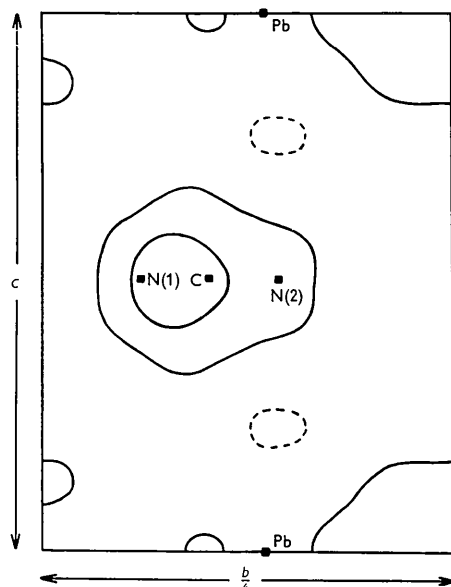


Fig. 3. The initial  $F_o - F_c$  [100] Fourier synthesis for a structure containing lead atoms only (centrosymmetric). The contours are at intervals of  $5.2 \text{ e.}\text{\AA}^{-2}$ . Squares represent atomic sites, with  $z_2 = z_3 = z_4 = \frac{1}{2}$ .

at the same height ( $z$ ), whereas all other distances are between atoms at different heights in such a way that moving the nitrogen atom concerned off the  $z = \frac{1}{2}$  plane will shorten one distance and lengthen the other. It was to be expected that one nitrogen atom would be strongly bonded to two lead atoms and this was seen to be so if the N(1) atom was moved to about  $z = 0.4$  (or  $0.6$ ). The Pb-N(1) distances then become about  $2.36, 2.36$  and  $2.65 \text{ \AA}$ . A trial structure was therefore chosen with the following  $z$  coordinates:

$$z_2 = 0.450, z_3 = 0.400, z_4 = 0.500.$$

The  $R$  index for this trial structure was  $0.068$  and the difference synthesis indicated small movements in the positions of the light atoms. Comparison of  $F_o$  with  $F_c$  indicated that the three reflexions of highest intensity suffered from extinction. Further refinement was carried out scaling in two regions of  $\sin \theta/\lambda$  only ( $0.0-0.4$  and  $0.4-0.6 \text{ \AA}^{-1}$ ) and the final  $R$  index was  $0.055$ . The final  $F_o - F_c$  syntheses are shown in Fig. 4 for structures containing (a) lead atoms only, but using correct phases, and (b) all atoms. The final atomic coordinates with their standard deviations are given in Table 1. The standard deviations have been calculated from the final  $F_o - F_c$  syntheses by the method suggested by Lipson &

Cochran (1953). Tabulated values of  $F_o$  and  $F_c$  are available.

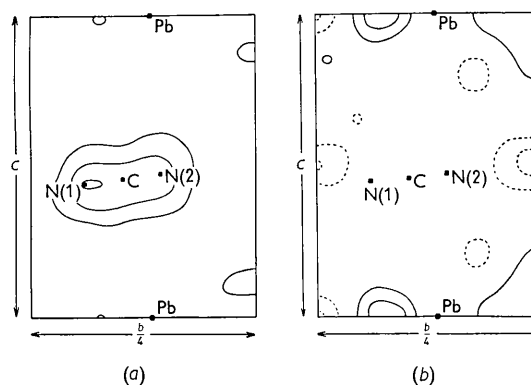


Fig. 4. The final  $F_o - F_c$  [100] Fourier syntheses. (a) For a structure containing lead atoms only, but assigning phases to  $F_o$  as calculated for  $F_c$  for a structure containing all atoms; the contours are at intervals of  $2.6 \text{ e.}\text{\AA}^{-2}$ . (b) For a structure containing all atoms; the contours are at intervals of  $1.7 \text{ e.}\text{\AA}^{-2}$  (one half the standard deviation of the electron density). Zero contours have been omitted. Squares represent atomic sites.

### Discussion of the structure

All interatomic distances less than  $3.0 \text{ \AA}$  are listed in Table 2, together with the interbond angles (the standard deviations of the angles are of the order of  $2$  to  $4^\circ$ ). A projection of the structure down the  $c$  axis is shown in Fig. 5(a). The shortest Pb-N bonds ( $2.33, 2.51 \text{ \AA}$ ) are indicated in the projection, showing how these form continuous -Pb-N(1)-Pb-N(1)- spirals parallel to the  $c$  axis. The N-C-N groups, which are slightly asymmetric, project from the spirals and are almost perpendicular to the  $c$  axis. Identical spirals pack closely together along the  $a$  axis, being linked by the weaker Pb-N(2) bonds ( $2.57, 2.71 \text{ \AA}$ ), and so form closely packed sheets perpendicular to the  $b$  axis. Fig. 5(b) shows a side view of a single spiral with one group of an adjacent spiral outlined to show how these packs in front of the first spiral. The closely packed sheets alternate with sheets containing spirals of the opposite hand, with only weak bonding between the sheets, the closest distances of approach being the Pb-N(2) distances of  $3.32$  and  $3.43 \text{ \AA}$ .

The details of the structure indicate that the bonding is covalent. The N-C-N group is linear within experimental error, and the Pb-N(1)-C bond angles for the two shortest Pb-N bonds are both close to  $120^\circ$  ( $122^\circ 45'$  and  $116^\circ 30'$ ). The weaker bonding between Pb and N(2) atoms involves larger Pb-N-C bond

Table 2. Bond lengths and inter-bond angles in lead cyanamide

Atom	Neighbour	Distance	Standard deviations	Bonds	Angle
Pb	N(1)(A)	2.33 Å	0.04 Å	N(1)(A)-Pb-N(1)(B)	78° 45'
	N(1)(B)	2.51	0.06	N(1)(A)-Pb-N(2)(C)	89°
	N(2)(C)	2.57	0.09	N(1)(A)-Pb-N(2)(D)	82° 15'
	N(2)(D)	2.71	0.09	N(1)(A)-Pb-N(1)(E)	74° 15'
	N(1)(E)	2.79	0.06	N(1)(B)-Pb-N(2)(C)	87° 15'
				N(2)(C)-Pb-N(2)(D)	94°
C	N(1)	1.25	0.06	N(2)(D)-Pb-N(1)(E)	79°
	N(2)	1.17	0.08	N(1)(E)-Pb-N(1)(B)	93°
N(1)	N(2)	2.42	0.08	N(1)-C-N(2)	177° 30'
	3 Pb			Pb-N(1)-Pb	109° 20'
N(2)	C			Pb-N(1)(A)-C	122° 45'
				Pb-N(1)(B)-C	116° 30'
	N(1)			Pb-N(1)(E)-C	101°
				Pb-N(2)-Pb	94°
				Pb-N(2)(C)-C	130° 30'
				Pb-N(2)(D)-C	128° 30'

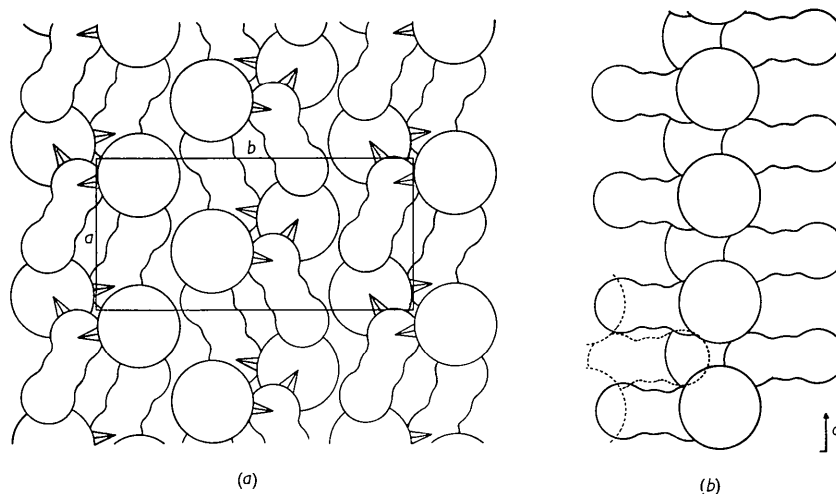


Fig. 5. (a) A projection of the structure down the *c* axis. (b) Side view of a single spiral (see text). Large circles represent lead atoms. Triple units represent N-C-N groups.

angles of about 130°. The C-N(2) distance is shorter than the C-N(1) distance, which is consistent with the stronger bonding between Pb and N(1). The two shortest bonds from each lead atom, to N(1)(A) and N(1)(B), are at an angle of 78° 45' to each other and the slightly weaker Pb-N(2)(C) bond is almost perpendicular to both of these (89° and 87° 25' respectively). The weaker Pb-N(2)(D) and Pb-N(1)(E) bonds are almost opposite the Pb-N(1)(B) and Pb-N(2)(C) bonds respectively.

There are few other structure analyses available with which to compare the details of the N-C-N group in lead cyanamide. Figures have been reported for calcium cyanamide (Yamamoto, Kinoshita, Tamura & Yamanaka, 1958) and for cyanamide, H<sub>2</sub>N-C≡N (Zvonkova & Khvatkina, 1961). In both cases the N-C-N group is linear. In calcium cyanamide both C-N distances are 1.25 Å indicating two double bonds in the symmetrical -N=C=N<sup>-</sup> ion. In cyanamide the C-N distances are C-N(1), 1.31 Å and C=N(2),

1.15 Å; the single  $\sigma$  bond (C-N(1)) being shortened from the expected value (1.39 Å) by an additional  $\pi$  bonding. Values of these distances obtained from infrared spectra have been given as C-N(1), 1.32 ± 0.03 Å and C=N(2), 1.172 ± 0.006 Å (Sukhorukov & Finkel'shtein, 1959). The values of 1.25 and 1.17 Å obtained for lead cyanamide in the present analysis are similar to those in cyanamide, although the C-N(1) distance has been shortened further.

### Physical properties

The details of the structure can now be correlated with the physical measurements (Sole, 1963; Sole & Yoffe, 1964).

(1) The physical measurements indicate that the structure is covalent. Infrared measurements give a value of 1.21 Å for the mean C-N distance, in excellent agreement with the X-ray value.

(2) The crystals form as needles parallel to the  $c$  axis, which is the direction of the Pb-N spirals.

(3) The needles form as thin plates perpendicular to the  $b$  axis, consistent with the weak bonding between the sheets of spirals.

(4) The needles are easily deformed and show plastic behaviour. This arises from flexibility of the spirals and many crystals were observed in which the direction of the  $c$  axis was not constant. In one case a Weissenberg photograph for oscillation about the  $a$  axis showed that the  $c$  axis direction varied continuously over a range of about  $10^\circ$  within the length of the crystal (about  $200 \mu$ ).

(5) Optical absorption is greatest for the direction of the  $a$  axis which is the direction towards which all the N-C-N groups are aligned.

(6) Thermal decomposition results in the evolution of cyanogen, but the powder pattern of the material is not appreciably altered. This corresponds to bond fission between the Pb and N(2) atoms and between the N(1) and C atoms so that C-N(2) units from adjacent groups form cyanogen and the -Pb-N-spirals remain unchanged. The Pb-N(2) and the N(1)-C bonds are the weakest in the structure.

I am most grateful to Dr M. J. Sole for valuable discussions about the correlation between the structure and physical properties. I am also grateful to Miss K. M. Adams for assistance with crystal selection

and setting and for the determination of the accurate lattice parameters.

It is a pleasure to thank Prof. Sir Nevill Mott, F.R.S. and Dr W. H. Taylor for provision of facilities and for their interest and encouragement. I am also indebted to Dr M. V. Wilkes and Mr E. N. Mutch for providing time on the EDSAC.

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## A Direct Analysis of Atomic Displacement in Disordered Alloys from X-ray Diffuse Scattering

By K. Doi\*

*Service de Physique des Solides, Faculté des Sciences Paris-Orsay, Orsay (S. et O.), France*

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The displacements of lattice points around a Cu atom in perfectly disordered AuCu<sub>3</sub> are derived by means of a Fourier transformation of diffuse scattering *amplitude*, without making any assumptions as to the nature of the distortion field.

The results show that the displacement  $\delta_{mn}$  of lattice point  $n$  at the position  $\mathbf{r}_{mn}$  with respect to the distortion centre  $m$  is expressed by

$$\delta_{mn} = c_A(\mathbf{r}_{mn}/|\mathbf{r}_{mn}|^3) - \mathbf{K}$$

where  $c_A$  is a constant and  $\mathbf{K}$  is an additive term which may be identified with the image term as discussed by Eshelby (*J. Appl. Phys.* (1954) **25**, 255).

The possibility of deriving the Zernike parameter of the order-disorder phenomena, when they are accompanied by size effect lattice distortions, is suggested.

The present author has suggested (Doi, 1960*b*, 1961) that with a Fourier transformation of diffuse scattering *amplitude* distribution the order-disorder phenomena

\* On leave of absence from Japan Atomic Energy Research Institute, Tokai-mura, Japan.

of binary alloys can be discussed from a new point of view, *i.e.* that of the propagation of order (Zernike, 1940), which may open a way accessible to the 'exact solution' in the sense of Onsager (1944) as pointed out by Ashkin & Lamb (1943).