

Crystal Structure Refinement of Lead Cyanamide and the Stiffness of the Cyanamide Anion

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Dedicated to Professor Arndt Simon on the Occasion of his 60th Birthday

Abstract. The crystal structure of lead cyanamide, PbNCN, has been refined on the basis of a single crystal grown from solution. PbNCN crystallizes in space group *Pnma* ($Z = 4$) with $a = 555.66(4)$ pm, $b = 386.77(2)$ pm, and $c = 1173.50(8)$ pm. The cyanamide anion exhibits C–N bond lengths of 116 pm and 130 pm, and the N–C–N angle is 176° . Quantum-chemi-

cal DFT calculations indicate that the cyanamide unit is comparatively easy to distort.

Keywords: Crystal structure; Lead cyanamide; Electronic structure

Kristallstrukturverfeinerung von Bleicyanamid und zur „Starrheit“ des Cyanamid-Anions

Inhaltsübersicht. Die Kristallstruktur von Bleicyanamid, PbNCN, wurde anhand eines aus Lösung gezüchteten Einkristalles verfeinert. PbNCN kristallisiert in der Raumgruppe *Pnma* ($Z = 4$) mit $a = 555.66(4)$ pm, $b = 386.77(2)$ pm und $c = 1173.50(8)$ pm. Das Cyanamid-Anion weist C–N-Bin-

dungslängen von 116 pm und 130 pm auf, und der N–C–N-Winkel beträgt 176° . Quantenchemische DFT-Rechnungen zeigen, dass die Cyanamid-Einheit relativ leicht zu verzerren ist.

1 Introduction

In 1995, the growing list of synthetically available main group metal cyanamides allowed for a preliminary evaluation of their crystallographic data [1]. With the exception of lead cyanamide, PbNCN, all structural studies were consistent with the existence of a linear, symmetrical ($D_{\infty h}$) cyanamide anion in each member of the class of compounds. In addition, it became clear that a center of symmetry had been overlooked in the 1964 structure determination of PbNCN, carried out in space group *Pna2₁* [2]. Finally, important structural details such as the angle and C–N bond lengths were of limited accuracy, making the definitive answer for the true shape of PbNCN's cyanamide group difficult to obtain. Here we report on an independent refinement of the crystal structure of PbNCN and related theoretical studies.

2 Experimental

Single crystals of lead cyanamide were prepared by the reaction between aqueous solutions of molecular cyanamide and lead acetate. When adding a few drops of ammonia solution,

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Table 1 Crystallographic Data for PbNCN

Formula; molar mass:	PbNCN; 247.22 g/mol
Crystal color and form:	yellow needle
Lattice constant:	$a = 555.66(4)$ pm, $b = 386.77(2)$ pm, $c = 1173.50(8)$ pm, Stoe powder diffractometer, Cu–K α_1 , (167 reflections with $6^\circ < 2\theta < 105^\circ$)
Space group; formula units:	<i>Pnma</i> – D_{2h}^{16} (no. 62); 4
X-ray density; $F(000)$:	6.511 g/cm ³ ; 408
Diffractometer:	Enraf-Nonius CAD-4, Mo–K α , graphite monochromator, scintillation counter 293(2) K
Temperature:	2796 total, 417 unique
Number of reflections:	$-7 \leq h \leq 6$, $-5 \leq k \leq 5$, $-16 \leq l \leq 16$; 60°
Octants; max. 2θ :	
Absorption correction and crystal dimensions:	numerical, indexed faces: (100) \leftrightarrow ($\bar{1}$ 00) ± 0.0125 mm, (010) \leftrightarrow (0 $\bar{1}$ 0) ± 0.05 mm, (001) \leftrightarrow (00 $\bar{1}$) ± 0.007 mm 66.54 mm ⁻¹ ; 0.172, 0.394
Absorption coefficient; minimum and maximum transmission:	
Structure solution:	transformed parameters of PbNCN [1, 2]
Structure refinement:	Least-squares method on F^2 , full matrix
No. of intensities, variables, restraints:	417, 25, 0
Weighting scheme:	$w = 1/[\sigma(F_o^2) \times (0.0268 \times P)^2]$, $P = (\max(F_o^2, 0) + 2 \times F_c^2)/3$
Min., max. residual electron density:	$-4.56, 3.09$ e/Å ³ (proximity of Pb)
$R_1, wR_2, Goodness of fit$ (all data):	0.051, 0.094, 1.114

Table 2 Positional parameters (all atoms on $4c$, $y \equiv 1/4$) and isotropic^{a)} as well as anisotropic^{b)} ($U_{23} \equiv U_{12} \equiv 0$) displacement parameters (pm^2) for PbNCN (standard deviations in parentheses)

atom	x	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{13}
Pb	0.3929(1)	0.63560(7)	157(3)	126(3)	187(5)	156(4)	-5(4)
N(1)	0.333(3)	0.441(2)	235(54)	121(86)	264(158)	321(112)	21(77)
N(2)	0.925(3)	0.361(2)	189(43)	125(83)	32(101)	408(106)	44(99)
C	0.114(4)	0.402(2)	245(59)	148(95)	258(178)	327(114)	25(105)

^{a)} U_{eq} is a third of the trace of the orthogonalized U_{ij} tensor

^{b)} The components U_{ij} refer to a displacement factor of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*)]$

a yellow precipitate crystallized which was filtered off, washed and dried.

A careful X-ray scan using an automated powder diffractometer and strictly monochromatized radiation allowed for the precise determination of the lattice constants, derived from a profile matching refinement of 167 reflections [3]. Selected crystals were then transferred into sealed glass capillaries and mounted on a single crystal diffractometer. A complete set of intensities was measured at room temperature and numerically corrected with respect to absorption [4]. As predicted, the structure refinement [5] was significantly more stable in the centrosymmetric space group *Pnma*. All important numerical details of the refinement may be found in Table 1. Positional and displacement parameters are listed in Table 2.¹⁾

3 Results and Discussion

Figure 1 shows a perspective view of the Pb atom's coordination in lead cyanamide. The lead atom is bonded to one close N(1) atom at 231(2) pm (solid stick), and there are four second-nearest N(1) and N(2) atoms at distances of 262(1) pm (open sticks). Two more N(2) atoms augment the coordination sphere with nonbonding distances of 343(1) pm (dashed lines). These interatomic distances are in very good agreement with the earlier study [2]. It is interesting to note that when evaluating the five nearest Pb–N distances with the tabulated bond valence parameter of 222 pm [6], the lead atom acquires a total bond order sum (empirical valence) of 2.14.

Concerning the cyanamide group itself, it is clear that the two C–N bonds differ significantly in length. While the N(2)–C bond amounts to 115.6(28) pm, the N(1)–C bond length is 129.7(29) pm; although carried out in the centrosymmetric space group, the differentiation now is even somewhat more pronounced than in the earlier study (117(8) and 125(6) pm [2]). The N–C–N angle lies at 175.6(27)°, linear within instru-

¹⁾ Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-410915, the name of the authors, and citation of the paper.

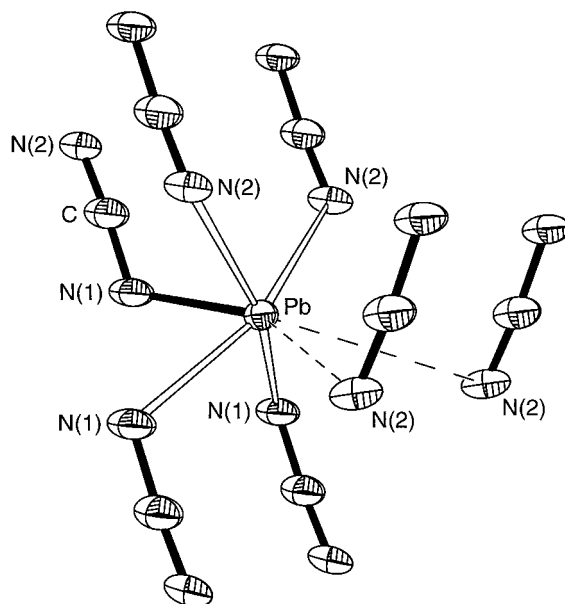


Fig. 1 Perspective view of the Pb coordination in PbNCN using 70% probability ellipsoids.

mental resolution. Nevertheless, the lowered anionic symmetry is corroborated by the complex infrared spectrum of PbNCN [7].

Although the carbon–nitrogen double bond in neutral organic molecules can be expected to lie around 130 pm [8], the literature data on all of the $D_{\infty h}$ cyanamide anions show C–N bond lengths between 119 and 125 pm, and the average value is 122 pm, coinciding with the one in the most common cyanamide, CaNCN. Using these 122 pm as the standard length of the cyanamide double bond, the bond orders for the shorter and longer C–N bonds in PbNCN are 2.38 and 1.62, perfectly summing up to two double bonds (4.00). Thus, C–N bonding seems to be nicely adjusted in this asymmetrical cyanamide species.

The symmetry reduction of the cyanamide anion obviously goes back to the one short Pb–N(1) bond which most certainly is polar covalent in nature. In the spirit of Pearson's acid-base language, the comparatively soft lead atom (absolute hardness: 8.46 eV) is much better suited for such bond formation than the respective alkali or alkaline-earth metals (twice as hard or harder) [9], which interact more ionically. Thus the cyanamide bonding situation in PbNCN very much resembles the situation of the singly protonated cyanamide anion in KHNCN [10], which has C–N bond lengths of 117 and 129 pm and an N–C–N angle of 174°.

To investigate the stiffness of the cyanamide anion in more detail, *ab initio* (DFT) quantum-chemical calculations on the NCN^{2-} unit were performed assuming N–C bond lengths of 122 pm and a linear geometry at the very beginning. The local-density approximation (VWN parametrization) [11] together with the BLYP

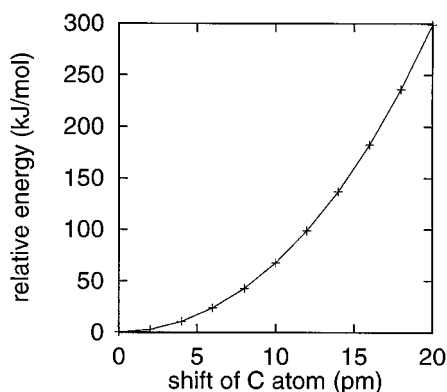


Fig. 2 Theoretical course of the energy of a linear cyanamide anion upon shifting the central carbon atom away from the anionic center.

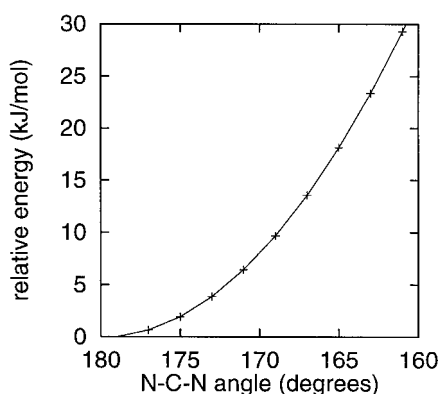


Fig. 3 Theoretical course of the energy of the experimentally observed cyanamide anion upon varying the central N-C-N angle.

gradient correction [12] was used, and the basis set was of triple- ζ (+2 polarization functions) quality [13], with a 1s frozen core orbital (program ADF [14]). Figure 2 surprisingly reveals that a local symmetry lowering introduced by a small shift of the C atom away from the center of the anion is uncritical. In fact, the observed bond length asymmetry (about 7 pm) in the cyanamide unit only costs about 30 kJ/mol. This energy loss must be more than counterbalanced by the buildup of the one short Pb-N bond.

Changes in the N-C-N bond angle are even less important. In Figure 3 we show how the total energy of the experimentally observed cyanamide geometry, with N-C bond lengths of 116 and 130 pm, is affected by varying the N-C-N angle. Less than 2.5 kJ/mol (the room temperature thermal energy) is needed to bend the linear unit to 175°. The small deviation away from linearity observed experimentally, if taken seriously, is unlikely to be caused by electronic structural effects.

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