Synthesis, crystal structure, vibrational spectroscopy, and thermal behaviour of lead dicyanamide $Pb[N(CN)_2]_2$

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1. Introduction

For a long time the investigation of simple inorganic C/N compounds predominantly was focused on cyanides with carbon in oxidation state +II [1]. Other simple C/N compounds are the cyanamides and dicyanamides, which may be understood as nitridocarbonates(IV). These salts contain linear $[N{=}C{=}N]^{2-}$ and bent $[N(CN)_2]^-$ anions, respectively. Only a few representatives of these nitridocarbonates(IV) have been well characterized in the past, e.g., Li_2CN_2 [2] and $Cs[N(CN)_2]$ [3].

In the last few years the interest in nitridocarbonates(IV) has increased significantly. In the ternary system M/C/N the cyanamides as well as the respective dicyanamides of the metals M = Na [4,5], K [6,7], Ag [8–10], Mg, Ca, Sr, Ba [11–13], and Zn [14–16] have been structurally characterized. Furthermore the ternary cyanamide cyanides $M_2(CN_2)(CN)_2$ with M = Sr, Ba have been obtained and they are isotypic [17]. Contrarily, in the case of the cyanamides $M^{II}CN_2$ and dicyanamides $M^{II}[N(CN)_2]_2$ the respective strontium and barium salts are not isotypic but form different structure types. The similar structural behaviour of strontium and barium compounds is explained by the similar cationic radius (Sr^{2+}: 118, Ba^{2+}: 135 pm, both values for CN 6). The radius of the Pb^{2+} ion (119 pm, CN 6) is in between that of Sr^{2+} and Ba^{2+}, thus a close relationship between the lead(II) compounds and the respective strontium and barium salts is often found (e.g., for $M^{II}CO_3$ and $M^{II}SO_4$ with M^{II} = Sr, Ba, Pb).

For the structurally characterized cyanamides [18,19] a similarity between $PbCN_2$ and $SrCN_2$ was found [20]. For lead dicyanamide $Pb[N(CN)_2]_2$ isotypic behaviour either to strontium dicyanamide or to barium dicyanamide may be possible. However, $Pb[N(CN)_2]_2$ has yet only been investigated by vibrational spectroscopy [21] and no structural data are available. In this contribution we report about the synthesis and crystal structure determination of $Pb[N(CN)_2]_2$.

2. Experimental

2.1. Synthesis

$Pb[N(CN)_2]_2$ was prepared by ion exchange in aqueous solution. A column with an ion exchange resin (Merck, Ionenaustauscher I, Art. 4765) was completely filled with a solution of $Pb(NO_3)_2$ (Merck, puriss.). An excess of lead ni-

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Table 1
Crystallographic data for $Pb[N(CN)_2]_2$

Formula	$Pb[N(CN)_2]_2$	
M_W (g mol^{-1})	339.29	
Crystal size (mm^3)	$0.397 \times 0.088 \times 0.064$	
Space group	Pnma (no. 62)	
Diffractometer	STOE STADI 4	STOE STADI P, graphite monochromator
Temperature (K)	293(2)	
Lattice constants	Single-crystal diffraction	Powder diffraction
(Radiation; λ (pm))	(Mo K_α; 71.073)	(Mo K_{α_1}; 70.926)
a (pm)	1350.45(10)	1349.8(3)
b (pm)	399.89(4)	399.80(16)
c (pm)	1199.39(11)	1199.1(3)
V ($\times 10^6$ pm^3)	647.70(9)	647.1(3)
Z	4	
ρ_{calcd} (g cm^{-3})	3.479	
$F(000)$	592	
μ (mm^{-1})	25.977	
Diffraction range (deg)	$4.54 \leqslant 2\theta \leqslant 60.00$	
Index range	$-18 \leqslant h \leqslant 18$, $-5 \leqslant k \leqslant 5$, $-16 \leqslant l \leqslant 16$ (all octants)	
Scan type	ω	
Total no. reflections	9536	
Independent reflections	1073 ($R_{\text{int}} = 0.1120$, for all reflections)	
Observed reflections	914	
Refined parameters	68	
Corrections	Lorentz, polarization, extinction, absorption	
Absorption correction	Empirical (ψ-scans)	
Min./max. transmission ratio	0.0849/0.1305	
Min./max. residual electron density (e Å^{-3})	−1.365/1.329	
Extinction coefficient χ	0.0073(4)	
G.o.f.	1.162	
R indices (for all data with $F_o^2 \geqslant 2\sigma F_o^2$)	$R_1 = 0.0275$ $wR_2 = 0.0557$ $w^{-1} = \sigma^2(F_o^2) + (0.0217P)^2$ with $P = 1/3(F_o^2 + 2F_c^2)$	

trate was removed by washing with water and subsequently a solution of $Na[N(CN)_2]$ (Fluka, ⩾ 96% (AT)) was poured onto the column. After evaporating the water at room temperature colourless crystals of $Pb[N(CN)_2]_2$ were obtained.

2.2. *Vibrational spectroscopy*

FTIR spectra of $Pb[N(CN)_2]_2$ were obtained at room temperature by using a Bruker IFS 66v/S spectrometer. The samples were thoroughly mixed with dried KBr (5 mg sample, 500 mg KBr).

2.3. *X-ray structure determination*

X-ray diffraction data of a single crystal ($0.397 \times 0.088 \times 0.064$ mm^3) were collected on a four-circle diffractometer (STOE STADI 4) using graphite monochromated Mo K_α radiation ($\lambda = 71.073$ pm). According to the observed extinction conditions of the orthorhombic lattice the space groups Pnma (no. 62) and $Pn2_1a$ (no. 33) were considered. The structure solution and refinement was only possible choosing the centrosymmetric space group Pnma. The crystal structure was solved by direct methods using SHELXTL [22] and refined with anisotropic displacement parameters for all atoms. Details of the crystal structure determination are summarized in Table 1, the atomic coordinates and anisotropic displacement factors are listed in Tables 2 and 3. All reflections detected by X-ray powder diffractometry (STOE Stadi P) of single-phase $Pb[N(CN)_2]_2$ have been indexed and their observed intensities agree well with the calculated diffraction pattern based on the single-crystal data.

Table 2
Atomic coordinates and isotropic displacement factors (in pm^2) of $Pb[N(CN)_2]_2$, all atoms in Wyckoff position 4*c*. U_{iso} is defined as one third of the trace of the U_{ij} tensor

Atom	x	y	z	U_{iso}
Pb	0.21405(2)	1/4	0.38016(2)	264(2)
C1	0.0175(7)	1/4	0.6092(6)	279(20)
C2	0.1740(6)	1/4	0.6778(9)	282(20)
C3	0.1553(6)	1/4	0.0762(7)	308(20)
C4	−0.0020(7)	1/4	0.1452(7)	344(20)
N1	−0.0668(6)	1/4	0.6118(5)	362(20)
N2	0.1125(5)	1/4	0.5946(6)	349(20)
N3	0.2364(5)	1/4	0.7440(6)	312(10)
N4	0.2162(5)	1/4	0.0080(6)	354(20)
N5	0.0949(6)	1/4	0.1593(6)	460(20)
N6	−0.0864(7)	1/4	0.1421(7)	490(20)

Table 3
Anisotropic displacement factors (in pm^2) for $\mathrm{Pb[N(CN)_2]_2}$, given as $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{13}hla^*c^*)]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb	247(2)	262(2)	283(2)	0	14(2)	0
C1	280(50)	320(30)	230(30)	0	−60(30)	0
C2	250(40)	320(40)	270(30)	0	70(30)	0
C3	280(50)	300(30)	340(40)	0	−30(40)	0
C4	290(50)	310(40)	430(50)	0	20(40)	0
N1	280(40)	450(40)	350(40)	0	−40(30)	0
N2	200(40)	590(40)	260(30)	0	0(30)	0
N3	240(30)	400(30)	290(30)	0	−10(30)	0
N4	300(40)	400(40)	370(40)	0	−10(30)	0
N5	280(40)	800(60)	310(40)	0	60(30)	0
N6	270(50)	510(40)	680(50)	0	110(40)	0

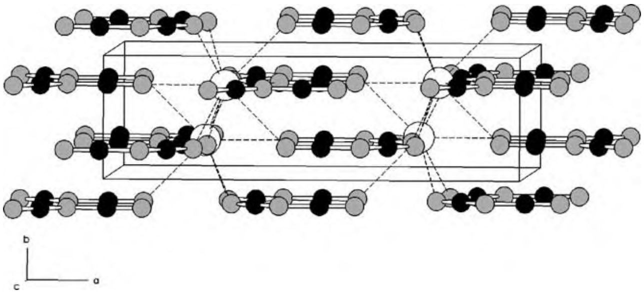

Fig. 1. Crystal structure of $\mathrm{Pb[N(CN)_2]_2}$ (view along [0 0 1]), (Pb: open circles, C: black circles, N: gray circles).

Further details of the crystal structure determination reported in this paper may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, by quoting the depository number CSD-412288.

Temperature-dependent in-situ X-ray diffractometry was performed on a STOE STADI P powder diffractometer (Mo K_{α_1} radiation) with a computer controlled STOE furnace. Thermoanalytical measurements were performed with a Mettler DSC 25 (heating rate: 10 °C min^{-1}) between room temperature and 500 °C.

3. Results and discussion

3.1. Crystal structure

In the solid $\mathrm{Pb[N(CN)_2]_2}$ consists of Pb^{2+} ions and two crystallographically different dicyanamide ions $[\mathrm{N(CN)_2}]^-$. All atoms are arranged on layers parallel to (0 1 0) at $y = 1/4$ and $3/4$, respectively (Fig. 1). Primarily Pb^{2+} is coordinated by each two N1, N3, and N4, respectively, which belong to the layers above and below the cation. These N are exclusively terminal ones in the anions (Fig. 2). Additionally three N atoms (N2, N5 bridging, N6 terminal) complement the coordination sphere of Pb^{2+} to a three-capped prism of nine N atoms (Fig. 3). Thus the Pb^{2+} cations are coordinated by nine different $[\mathrm{N(CN)_2}]^-$ ions, where five are N1–C1–N2–C2–N3 ions and the other four are crystallographically independent N4–C3–N5–C4–N6 ions.

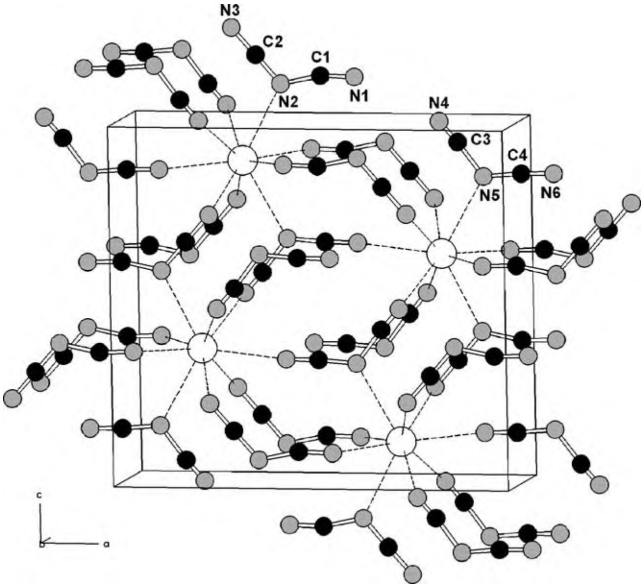

Fig. 2. Crystal structure of $\mathrm{Pb[N(CN)_2]_2}$ (view along [0 1 0]).

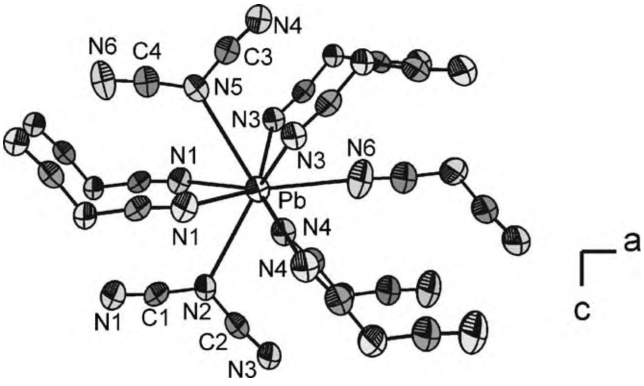

Fig. 3. Coordination sphere of the Pb^{2+} ions in $\mathrm{Pb[N(CN)_2]_2}$, displacement ellipsoids are shown at the 70% probability level.

The dicyanamide ions are bent and planar (point symmetry C_s). The bond distances and angles are similar to those of other dicyanamides (Table 4). As expected the distances N–CN from the bridging N are longer (129–132 pm) than those to the terminal N atoms (114–116 pm). The

Table 4
Bond distances (in pm) and angles (in deg) in $Pb[N(CN)_2]_2$

Pb–N1	282.1(7) (2×)	Pb–N2	291.5(7)
Pb–N3	266.7(4) (2×)	Pb–N5	309.9(8)
Pb–N4	269.0(5) (2×)	Pb–N6	270.8(9)
C1–N1	114.0(12)	C3–N4	116.0(10)
C1–N2	129.5(11)	C3–N5	128.8(11)
C2–N2	129.9(10)	C4–N5	131.9(12)
C2–N3	115.7(10)	C4–N6	114.0(13)
N1–C1–N2	173.8(8)	N4–C3–N5	174.2(9)
N2–C2–N3	173.1(8)	N5–C4–N6	174.5(10)
C1–N2–C2	122.0(7)	C3–N5–C4	122.0(8)

bond angles N–C–N are almost linear (173–175°), whereas the C–N–C angle is 122°. These findings are typical for dicyanamides and they are in good agreement with single and triple bonds according to the formula $[N{\equiv}C{-}N{-}C{\equiv}N]^-$.

The distances Pb···N in $Pb[N(CN)_2]_2$ range between 267 and 310 pm, thus the smallest of these distances are significantly larger than the respective values in $PbCN_2$ (231, 262 and 343 pm [19]). Presumably this is due to the larger coordination number of Pb^{2+} in $Pb[N(CN)_2]_2$ (CN 9) as compared to $PbCN_2$ (CN 5 + 2).

Lead(II) dicyanamide $Pb[N(CN)_2]_2$ is isotypic with $Ba[N(CN)_2]_2$, while strontium dicyanamide crystallizes in a different structure type [13]. All alkaline earth dicyanamides have been obtained as fine crystalline products and thus their crystal structures only have been determined by powder diffraction [13]. Therefore the single-crystal structure determination of $Pb[N(CN)_2]_2$ also confirms the less accurate structure determination of $Ba[N(CN)_2]_2$. The crystal structure of $Ba[N(CN)_2]_2$ and $Pb[N(CN)_2]_2$ is related to that of $PbCl_2$ (cotunnite structure type) by replacing the Cl^- ions by dicyanamide ions $[N(CN)_2]^-$.

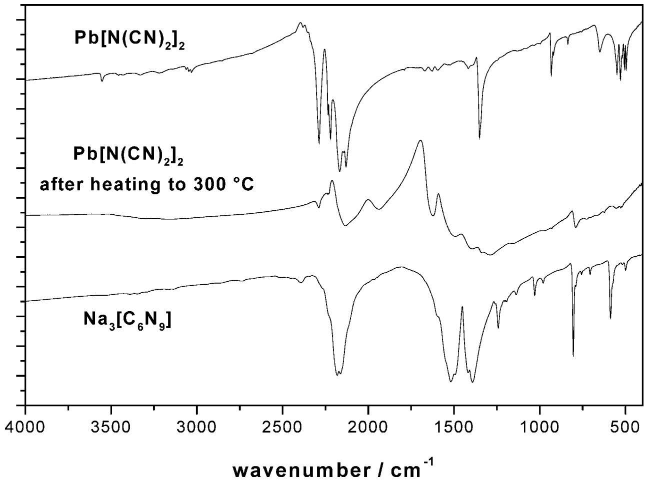

Fig. 4. FTIR spectra of $Pb[N(CN)_2]_2$ and of its thermolysis product after heating to 300 °C in comparison to the spectrum of $Na_3[C_6N_9]$.

3.2. *Spectroscopic and thermal behaviour*

For the alkali dicyanamides a thermally induced trimerization of the anions and the formation of cyclic tricyanomelaminate anions $[C_6N_9]^{3-}$ have been proved by temperature-dependent X-ray powder diffractometry, thermoanalytical and vibrational spectroscopic investigations [5,7]. In order to investigate a possible analogous behaviour of $Pb[N(CN)_2]_2$ similar experiments were carried out.

The IR spectrum of $Pb[N(CN)_2]_2$ (Fig. 4) shows the typical signals of the $[N(CN)_2]^-$ ion [13,23]. The observed frequencies (Table 5) agree well with previous reports of Kuhn et al. [21] for the IR spectra of $Pb[N(CN)_2]_2$ and are comparable to those found for isotypic $Ba[N(CN)_2]_2$ [13]. The existence of two crystallographically different $[N(CN)_2]^-$ ions in $M[N(CN)_2]_2$ (M = Ba, Pb) leads to a splitting of the IR signals. However, in the IR spectrum of

Table 5
Vibrational frequencies (in cm^{-1}) in $M[N(CN)_2]_2$ (M = Ba, Pb)[1]

$Ba[N(CN)_2]_2$ [13]	$Pb[N(CN)_2]_2$ [This work]	$Pb[N(CN)_2]_2$ [21]	Assignment
3556/3538(w)	3554(w)		$\nu_s C{\equiv}N + \nu_{as} N{-}C$
		3521	
3474/3451(w)	3459/3427(w)		$\nu_{as} C{\equiv}N + \nu_{as} N{-}C$
	3336(w)		
3226/3202(w)	3218(w)		$\nu_s C{\equiv}N + \nu_s N{-}C$
3078/3058(w)	3062/3047/3032(w)		$\nu_{as} C{\equiv}N + \nu_s N{-}C$
2289/2276(s)	2287(s)	2278/2254	$\nu_s C{\equiv}N$
2236/2228(s)	2236(w)/2221(s)		$\nu_{as} N{-}C + \nu_s N{-}C$
2174/2173(vs)	2170/2131(vs)		$\nu_{as} C{\equiv}N$
1340/1331(s)	1350(s)	1351/1327	$\nu_{as} N{-}C$
940/928(m)	933(m)	933/914	$\nu_s N{-}C$
664(m)	650(m)		$\delta_s N{-}C{\equiv}N$
547/541(m)	550(m)	548	$\gamma_s N{-}C{\equiv}N$
518(m)	529(m)	528	$\gamma_{as} N{-}C{\equiv}N$
508/501(m)	505/496(m)	507/496	$\delta_{as} N{-}C{\equiv}N$

[1] vs: very strong, s: strong, m: medium, w: weak.

$Ba[N(CN)_2]_2$ this splitting is more significant as compared to $Pb[N(CN)_2]_2$.

According to the temperature-dependent X-ray powder diffractometry neither a phase transition of $Pb[N(CN)_2]_2$ nor a transformation to another crystalline product could be detected at higher temperature. Above 230 °C the samples became X-ray amorphous.

During heating a broad exothermic effect occurs in the DSC between 235 and 270 °C. Previous investigations of the alkaline earth dicyanamides $M[N(CN)_2]_2$ (M = Mg, Ca, Sr, Ba) showed a similar behaviour at higher temperature. For example, $Ba[N(CN)_2]_2$ becomes X-ray amorphous above 360 °C [13]. Single-crystalline needles of $Pb[N(CN)_2]_2$ were heated in alumina crucibles under an atmosphere of argon to 300, 400, and 500 °C, respectively. After cooling to room temperature yellow (300 and 400 °C) and brown needles (500 °C) remained. It is conspicuous that the habit of the starting material kept unchanged after heating.

After heating the products were characterized by IR spectroscopy. In Fig. 4 the FTIR spectra of $Pb[N(CN)_2]_2$, of its X-ray amorphous thermolysis product ($T_{\max} = 300\,^\circ\mathrm{C}$) and of $Na_3[C_6N_9]$ are compared. The FTIR spectrum of the thermolysis product neither shows the typical signal pattern which belongs to the $[N(CN)_2]^-$ ion nor that of the cyclic $[C_6N_9]^{3-}$ ion [23]. Apparently $Pb[N(CN)_2]_2$ behaves similarly to the alkaline earth dicyanamides but it shows a lower thermal stability. Equally broad signals have been observed in the IR spectra after thermolysis, which may be attributed to conjugated cyclic C=N (1623, 1492 cm^{-1}) and N=C=N (2134 cm^{-1}) groups. The observed signal at 790 cm^{-1} may be indicative for a deformation vibration ($\delta_s >$ C–N–C) of a CNC group with one C belonging to a triazine ring [23]. A similar vibration is also observed in the spectrum of $Na_3[C_6N_9]$ (803 cm^{-1}). This may be indicative for the formation of triazine rings during heating of $Pb[N(CN)_2]_2$. Presumably a further polymerization occurs leading to species of hitherto unknown structure.

Acknowledgements

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