

Preparation, Characterization and Crystal Structure of Lead(II) Tricyanomethanide

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The so far unknown lead tricyanomethanide, $\text{Pb}[\text{C}(\text{CN})_3]_2$, was obtained from a saturated aqueous solution of PbCl_2 and solid $\text{AgC}(\text{CN})_3$. Its IR spectrum and thermal behaviour are described. The crystal structure was determined by single-crystal X-ray diffraction (trigonal, $P31m$, $Z = 3$, $a = 1414.4(5)$, $c = 409.02(6)$ pm, $R_1 = 0.0249$, $wR_2 = 0.0527$). Two crystallographically independent ninefold coordinated Pb atoms are connected by planar tricyanomethanide ions in two distinct bridging coordination modes. The Pb–N distances range between 254 and 293 pm.

Key words: Pseudohalide, Lead, Tricyanomethanide, Crystal Structure

Introduction

The literature reveals little structural information on binary lead(II) pseudohalides. So far, crystal structures have been reported only for the thiocyanate [1], the azide [2] and more recently for the dicyanamide [3, 4]. The crystal structures of two ternary lead tricyanomethanide complexes were determined [5], while the structure of the binary lead tricyanomethanide is so far unknown. The preference of the large Pb^{2+} cation for high coordination numbers in combination with multidentate ligands gives rise to interesting network structures, as was shown in the case of $\text{Pb}\{\text{N}(\text{CN})_2\}_2$ [3, 4]. The tricyanomethanide ion is able to act in a variety of coordination modes [6, 7], similar to the dicyanamide. We supposed that the crystal structure of lead(II) tricyanomethanide should be closely related to that of lead(II) dicyanamide.

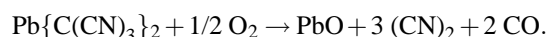
Results and Discussion

Infrared spectrum and thermal behaviour

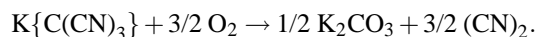
The IR spectrum of $\text{Pb}\{\text{C}(\text{CN})_3\}_2$ (nujol mull) shows the characteristic features of the tricyanomethanide ion [8]. The existence of distinct coordination modes of the $\{\text{C}(\text{CN})_3\}^-$ ions leads to a significant splitting of several vibrational frequencies. So, the $\text{C}\equiv\text{N}$ stretching mode (ν_6) is split into three com-

ponents of comparable intensity at 2207, 2172 and 2134 cm^{-1} , and the $\text{C}-\text{C}\equiv\text{N}$ out of plane deformation mode (ν_4) exhibits two components at 575 and 564 cm^{-1} .

The thermogravimetric analysis of $\text{Pb}\{\text{C}(\text{CN})_3\}_2$ in air reveals a smooth degradation from 362 to 590 °C with a maximum decomposition rate at 524 °C. The total weight loss up to 700 °C (42.3%) corresponds to the solid residue of PbO (calcd. 42.4%), which was identified by x-ray powder diffraction. We propose the decomposition reaction as



At comparable conditions the decomposition of $\text{K}\{\text{C}(\text{CN})_3\}$ occurs in a wide range from 241 to 666 °C with a maximum decomposition rate at 605 °C. In this case the total weight loss up to 700 °C (46.4%) is in accord to K_2CO_3 as solid residue (calcd. 46.5%), which was identified by IR spectroscopy. The probable decomposition reaction can be formulated as



Crystal structure

The unit cell of $\text{Pb}\{\text{C}(\text{CN})_3\}_2$ is shown in Fig. 1. As anticipated, the crystal structure is strongly related

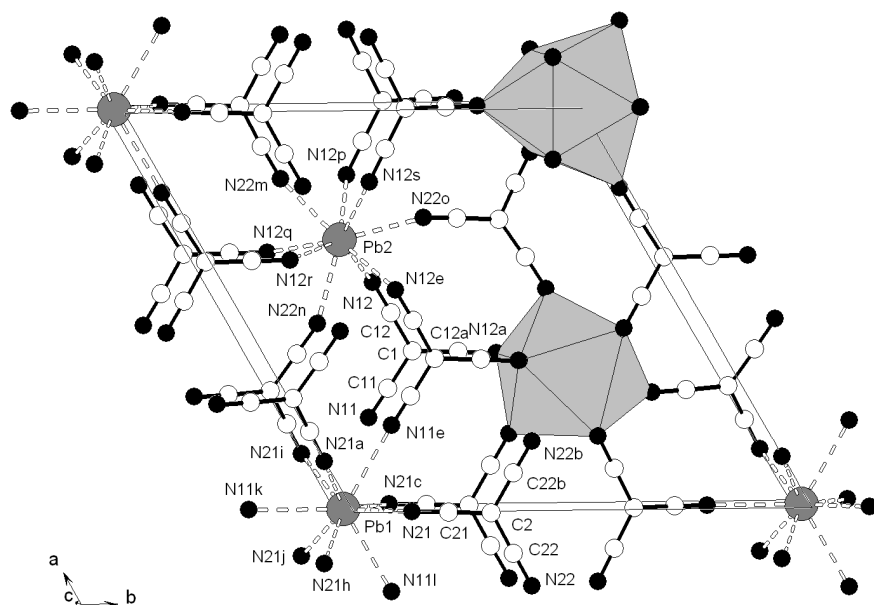


Fig. 1. View of the unit cell of $\text{Pb}\{\text{C}(\text{CN})_3\}_2$ along the c -axis (DIAMOND) [15].

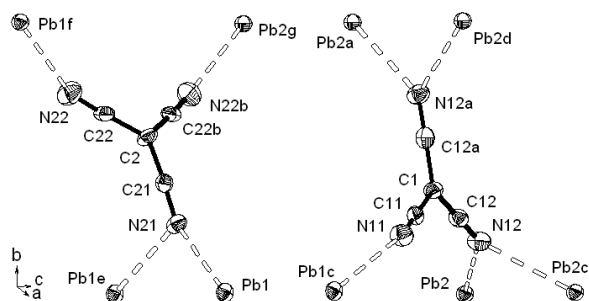


Fig. 2. Coordination modes of the two independent tricyanomethanide units (right hand side unit 1, left hand side unit 2).

to that of $\text{Pb}\{\text{N}(\text{CN})_2\}_2$ [3, 4]. Two crystallographically independent lead atoms are situated on special positions $(0, 0, z)$ and $(2/3, 1/3, z)$. Both lead atoms are ninefold coordinated by the N-atoms of the $\{\text{C}(\text{CN})_3\}^-$ ions in irregular holodirected arrangements. There is no evidence for a stereochemically active lone pair on the Pb^{2+} ion [9, 10]. The tricyanomethanide ion is found in two distinct coordination modes (Fig. 2). One of them (unit 1) exhibits one terminal coordinating and two bridging N-atoms, while the other one (unit 2) coordinates *via* one bridging and two terminal N-atoms. The bridging angles Pb-N-Pb are close to 90° . Pb atoms of two different layers are connected by the bridging N atoms of the tricyanomethanide ions. The Pb-N distances range between 254 and 293 pm and are comparable to those

Table 1. Crystallographic data and refinement parameters.

Empirical formula	$\text{C}_8\text{N}_6\text{Pb}$
M_w [g mol^{-1}]	387.33
Crystal size [mm]	$0.35 \times 0.05 \times 0.05$
Diffractometer	Enraf Nonius CAD4
Radiation; λ [pm]	$\text{Mo-K}\alpha$; 71.073
Temperature [K]	208(2)
Crystal system	trigonal
Space group	$P31m$
Lattice constants	
a [pm]	1414.4(5)
c [pm]	409.02(6)
Volume [$\times 10^6 \text{ pm}^3$]	708.7(4)
Z	3
ρ Calcd. [g cm^{-3}]	2.723
Abs. Coefficient [mm^{-1}]	17.827
$F(000)$	516
Diffraction range (deg)	$3.33 \leq 2\theta \leq 31.00$
Index range	$-1 \leq h \leq 20,$ $-20 \leq k \leq 18,$ $-5 \leq l \leq 5$
Scan type	ω scans
Collected reflections	4946
Independent reflections	1591 ($R_{\text{int}} = 0.0414$)
Observed reflections	1445 [$I > 2\sigma(I)$]
Refined parameters	79
Absorption correction	DELABS
Min./max. transmission	0.88276/0.96106
Structure solution	SHELXS-97 [13]
Structure refinement	SHELXL-97 [14]
Molecular graphics	DIAMOND [15]
Refinement method	full-matrix least-squares on F^2
Absolute structure parameter	$-0.005(14)$
Goodness-of-fit on F^2	1.029
R Indices [$I > 2\sigma(I)$]	$R_1 = 0.0249, wR_2 = 0.0527$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) for $\text{Pb}\{\text{C}(\text{CN})_3\}_2$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	W.-symbol	x	y	z	$U(\text{eq})$
Pb(1)	1a	0	0	0.4638(2)	22(1)
Pb(2)	2b	2/3	1/3	0.6241(1)	20(1)
C(1)	3c	0.3761(7)	x	1.2230(20)	25(2)
C(11)	3c	0.2812(7)	x	1.3490(20)	26(2)
N(11)	3c	0.2071(6)	x	1.4490(20)	34(2)
C(12)	6d	0.4731(5)	0.3741(5)	1.1560(14)	26(1)
N(12)	6d	0.5517(5)	0.3710(5)	1.1048(15)	32(1)
C(2)	3c	0	0.2893(7)	-0.2380(30)	26(2)
C(21)	3c	0	0.2028(6)	-0.0850(20)	23(2)
N(21)	3c	0	0.1272(6)	0.0265(19)	28(2)
C(22)	6d	-0.0998(5)	0.2824(5)	-0.3242(15)	26(1)
N(22)	6d	-0.1786(5)	0.2801(6)	-0.4004(16)	41(1)

Table 3. Selected bond lengths [pm] and angles [deg] for $\text{Pb}\{\text{C}(\text{CN})_3\}_2$.

C(1)–C(11)	143.9(14)	Pb(1)–N(21)	253.7(8)
C(1)–C(12)	141.3(8)	Pb(1)–N(21) ^b	253.7(8)
C(1)–C(12) ^a	141.3(8)	Pb(1)–N(21) ^a	253.7(8)
C(11)–N(11)	112.4(13)	Pb(1)–N(21) ^j	292.2(9)
C(12)–N(12)	115.3(9)	Pb(1)–N(21) ^c	292.2(9)
C(2)–C(21)	137.4(12)	Pb(1)–N(21) ^j	292.2(9)
C(2)–C(22)	141.1(7)	Pb(1)–N(11) ^e	293.0(9)
C(2)–C(22) ^b	141.1(7)	Pb(1)–N(11) ^k	293.0(9)
C(21)–N(21)	116.2(12)	Pb(1)–N(11) ^l	293.0(9)
C(22)–N(22)	114.2(9)	Pb(2)–N(12)	276.8(6)
C(11)–C(1)–C(12)	120.9(4)	Pb(2)–N(22) ^m	264.8(6)
C(12)–C(1)–C(12) ^a	118.3(8)	Pb(2)–N(22) ⁿ	264.8(6)
C(21)–C(2)–C(22)	119.9(4)	Pb(2)–N(22) ^p	264.8(6)
C(22)–C(2)–C(22) ^b	120.1(8)	Pb(2)–N(12) ^p	276.8(6)
C(1)–C(11)–N(11)	179.8(14)	Pb(2)–N(12) ^q	276.8(6)
C(1)–C(12)–N(12)	178.9(7)	Pb(2)–N(12) ^r	288.2(6)
C(2)–C(21)–N(21)	176.1(10)	Pb(2)–N(12) ^s	288.2(6)
C(2)–C(22)–N(22)	177.6(8)	Pb(2)–N(12) ^s	288.2(6)

Symmetry operations used to generate equivalent atoms: ^a (y, x, z); ^b (–x, –x + y, z); ^c (x, y, 1 + z); ^d (y, x, 1 + z); ^e (x, y, –1 + z); ^f (–1 + x, y, –1 + z); ^g (y, x, –1 + z); ^h (–y, x – y, z); ⁱ (y, x, 1 + z); ^j (–y, x – y, 1 + z); ^k (–x + y, –x, –1 + z); ^l (–y, x – y, –1 + z); ^m (1 + x, y, 1 + z); ⁿ (–x + y, –x, 1 + z); ^o (1 – y, 1 + x – y, 1 + z); ^p (1 – x + y, 1 – y, z); ^q (1 – y, x – y, z); ^r (1 – y, x – y, –1 + z); ^s (1 – x + y, 1 – x, –1 + z).

found for (C≡N)–Pb in $\text{Pb}[\text{N}(\text{CN})_2]_2$ (269–282 pm) in which the Pb atoms exhibit a similar coordination sphere (c. n. 9) [3, 4]. The $\{\text{C}(\text{CN})_3\}^-$ ions have almost ideal planar D_{3h} geometry with mean deviations from planarity of 0.38 pm for unit 1 and 3.23 pm for unit 2. The two symmetry independent tricyanomethanide groups are inclined to each other by $24.3(2)^\circ$ and are stacked in columns parallel to the crystallographic *c* axis. Bond lengths and angles within the $\{\text{C}(\text{CN})_3\}^-$ ion (Table 3) are similar to those found in other tricyanomethanides [7].

Crystallographic data for $\text{Pb}\{\text{C}(\text{CN})_3\}_2$ have been deposited with the Cambridge Crystallographic Data Centre (CCDC 267368). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Experimental Section

Reagents were used as purchased without further purification. IR spectra were recorded on a BOMEM model 100 FT-IR spectrometer in the range $4000\text{--}400\text{ cm}^{-1}$ from Nujol mulls. The thermogravimetric analyses were performed on a Shimadzu Thermogravimetric Analyzer TGA-50 in alumina crucibles at a heating rate of $5^\circ\text{C}/\text{min}$ in air.

Synthesis

$\text{Ag}\{\text{C}(\text{CN})_3\}$. Silver tricyanomethanide was prepared according to Trofimenko [11].

$\text{Pb}\{\text{C}(\text{CN})_3\}_2$. A solution of 0.278 g PbCl_2 (1 mmol) in 40 ml H_2O was stirred with 0.594 g $\text{Ag}\{\text{C}(\text{CN})_3\}$ (3 mmol) for 24 h on a water bath. The solution was filtered from insoluble silver salts and the filtrate evaporated to dryness, yielding 350 mg crude $\text{Pb}\{\text{C}(\text{CN})_3\}_2$ (90%). Colorless crystal needles. Solubility in water 100 g/l at 25°C . IR (Nujol mull): $\tilde{\nu} = 2207\text{ s}, 2172\text{ vs}, 2134\text{ s}, 1269\text{ vw}, 1243\text{ w}, 1233\text{ vw}, 685\text{ vw}, 660\text{ vw}, 607\text{ w}, 575\text{ m}, 564\text{ m}, 493\text{ vw cm}^{-1}$.

X-ray structure determination

Colorless needles were obtained by recrystallization of the title compound from H_2O . The cell constants were calculated from 25 reflections measured under a wide range of 2θ . The intensity data were collected by the ω scan technique, on an Enraf Nonius CAD4 diffractometer at 208 K with graphite-monochromated $\text{Mo-K}\alpha$ radiation. Orientation was monitored every 300 measurements and intensity was checked every hour with 3 standard reflections. Intensity fluctuations remained within 3.3%. The program HELENA (PLATON) was used for the data reduction [12]. The Laue symmetry and the systematic absences were consistent with the trigonal space groups $P312$ (acentric), $P31m$ (acentric) and $P31m$ (centric), with much lower probability for the last one [12]. The structure could be successfully solved in the acentric space group $P31m$ by direct methods [13]. All atoms were refined with anisotropic displacement parameters [14], with final indices $R_1 = 0.0249$ and $wR_2 = 0.0527$ for $I > 2\sigma(I)$, and the absolute structure was confirmed by a Flack parameter of $-0.005(14)$. A DELABS (PLATON) empirical absorption correction was performed [12]. More detailed information related to the crystallographic data and the structure refinement is given in Table 1.

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