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Olaf Reckeweg* and Francis J. DiSalvo

Synthesis and single-crystal structure of the pseudo-ternary compounds LiA[N(CN)$_2$]$_2$ (A = K or Rb)

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Abstract: Crystals of LiA[N(CN)$_2$]$_2$ were obtained from the reaction of LiCl and ACl (A = K or Rb) with Ag[N(CN)$_2$] in water and subsequent evaporation of the filtered solution at 80 °C under normal atmospheric conditions. Crystals of the title compound form thin rectangular plates that are transparent, colorless, and very fragile. Single-crystal structure analyses have shown that both compounds are isotypic and adopt the tetragonal space group $I4/mcm$ (no. 140, $Z = 4$) with the cell parameters $a = 701.53(12)$ and $c = 1413.7(5)$ pm for LiK[N(CN)$_2$]$_2$ and $a = 730.34(10)$ and $c = 1414.4(4)$ pm for LiRb[N(CN)$_2$]$_2$. The crystal structure is described and compared to that of the pseudo-binary alkali metal dicyanamides.

Keywords: dicyanamides; lithium; potassium; rubidium; structure elucidation.

1 Introduction

Recently, we determined the single-crystal structure and the vibrational spectra of Li[N(CN)$_2$] [1]. With this compound, all pseudo-binary alkali metal dicyanamides were structurally characterized [2–4]. Therefore, it seemed logical to explore the pseudo-ternary alkali metal dicyanamides containing lithium and a second cation because no such compound has been structurally characterized as yet. We report here the synthesis and single-crystal structure determinations of the new compounds LiA[N(CN)$_2$] (A = K or Rb).

2 Experimental section

2.1 Synthesis

Ag[N(CN)$_2$] was synthesized by blending an aqueous solution containing 200 mg (2.25 mmol) Na[N(CN)$_2$] (96 %, powder; Alfa Aesar, Ward Hill, MA, USA) with a second solution containing 400 mg (2.35 mmol) of AgNO$_3$ (≥99 %, Sigma-Aldrich, St. Louis, MO, USA), respectively. The gray precipitate was washed with deionized water and dried using an aspirator. The precipitate was mixed with 50 mg (1.2 mmol) LiCl and 90 mg (1.2 mmol) KCl (2.35 mmol) or 50 mg (1.2 mmol) LiCl and 145 mg (1.2 mmol) RbCl (all alkali metal chlorides: ≥99 %; Sigma-Aldrich) in 5 mL of deionized water. After stirring this mixture for 6 h, the resulting solution was filtered to remove the precipitated AgCl and allowed to evaporate at atmospheric conditions. In both cases, colorless, transparent, very thin, and fragile rectangular crystals were observed after a few days.

2.2 Crystallographic studies

Samples of the respective crystallized product were taken directly out of the Petri dish used for the evaporation and immersed in dried polybutene oil (M_n ~ 320, isobutylene > 90 %; Aldrich). Single-crystal selection took place with the help of a polarization microscope. A suitable crystal was mounted in a drop of polybutene sustained in a plastic loop and placed onto the goniometer. A cold stream of nitrogen [T = 223(2) K] froze the polybutene oil, thus keeping the crystal stationary and protected from oxygen and moisture in the air. Intensity data were collected with a Bruker X8 Apex II diffractometer equipped with a 4-K CCD detector and graphite-monochromatized MoK_α radiation (λ = 71.073 pm). The intensity data were manipulated with the program package [5] that came with the diffractometer. An empirical absorption correction

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***Corresponding author: Olaf Reckeweg,** Baker Laboratory, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853-1301, USA, Fax: +1-607-255-4137, E-mail: olaf.reykjavik@gmx.de
Francis J. DiSalvo: Baker Laboratory, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853-1301, USA

Table 1: Details of the X-ray single-crystal structure determinations on LiK[N(CN)$_2$]$_2$ and LiRb[N(CN)$_2$]$_2$.

Compound	**LiK[N(CN)$_2$]$_2$**	**LiRb[N(CN)$_2$]$_2$**
M_r	178.14	224.51
Crystal color	Transparent colorless	Transparent colorless
Crystal shape	Thin rectangular plate	Thin rectangular plate
Crystal size, mm^3	0.05 × 0.04 × 0.01	0.11 × 0.07 × 0.02
Crystal system	Tetragonal	Tetragonal
Space group (no.)	$I4/mcm$ (140)	$I4/mcm$ (140)
Z	4	4
Lattice parameters		
a, pm	701.53(12)	730.34(10)
c, pm	1413.7(5)	1414.4(4)
V, Å^3	695.7(3)	754.4(2)
D_{calcd}, g/cm^3	1.70	1.98
F(000); e	352	424
μ, mm^{-1}	0.7	6.5
Diffractometer	Bruker X8 Apex II equipped with a 4-K CCD	
Radiation/λ, pm/monochromator	MoK_α/71.073/graphite	
T, K	223(2)	
Scan mode	ϕ and ω scans	
$2\,\theta_{max}$, deg	61.23	66.29
hkl range	$-7 \rightarrow 10$	$-11 \rightarrow 11$
	$-5 \rightarrow 10$	$-5 \rightarrow 11$
	$-20 \rightarrow 15$	$-21 \rightarrow 16$
Data correction	Lp, SADABS [8]	
Transmission: min/max	0.5485/0.7461	0.5424/0.7465
Reflections: measured/unique	2040/315	2510/412
Unique reflections with $F_o > 4\,\sigma(F_o)$	208	332
R_{int}/R_σ	0.0929/0.0619	0.0335/0.0248
Refined parameters	21	22
$R1^a/wR2^b$/GoF^c (all refl.)	0.0792/0.0853/1.067	0.0312/0.0590/1.107
Factors x/y (weighting scheme)^b	0.019/0.73	0.028/0.34
Max shift/esd in last refinement cycle	<0.0001	<0.00005
$\Delta\rho_{fin}$ (max, min), e/Å^3	0.34 (0 pm to K)	0.52 (193 pm to C1)
	−0.46 (64 pm to K)	−0.42 (80 pm to Rb)
CSD number	430275	430276

$^a R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, where $P = [(F_o^2) + 2F_c^2]/3$ and x and y are constants adjusted by the program. ^{c}GoF(S) $= [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, with n being the number of reflections and p being the number of refined parameters.

Table 2: Atomic coordinates and anisotropic^a and equivalent isotropic displacement parameters^b (pm^2) of LiK[N(CN)$_2$]$_2$ and LiRb[N(CN)$_2$]$_2$.

	Site	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
K	$4a$	0	0	¼	266(5)	U_{11}	325(8)	0	0	0	286(4)
Li	$4c$	0	0	0	338(35)	U_{11}	218(48)	0	0	0	293(23)
N0	$8h$	0.2371(4)	0.2629(4)	½	448(16)	U_{11}	203(17)	0	0	183(20)	366(10)
N1	$16l$	0.3434(3)	0.1566(3)	0.34345(16)	313(9)	U_{11}	226(13)	23(9)	−23(9)	15(9)	284(7)
C1	$16l$	0.3002(3)	0.1998(3)	0.4195(2)	256(10)	U_{11}	265(10)	55(10)	−55(10)	−11(13)	259(7)
Rb	$4a$	0	0	¼	210(2)	U_{11}	352(3)	0	0	0	257(2)
Li	$4c$	0	0	0	238(20)	U_{11}	206(31)	0	0	0	227(14)
N0	$8h$	0.2371(4)	0.2629(4)	½	470(12)	U_{11}	177(12)	0	0	207(14)	372(8)
N1	$16l$	0.3434(3)	0.1566(3)	0.34345(16)	318(6)	U_{11}	210(8)	10(8)	−10(5)	18(7)	282(4)
C1	$16l$	0.3002(3)	0.1998(3)	0.4195(2)	263(6)	U_{11}	210(9)	19(6)	−19(6)	17(8)	245(4)

^{a}The anisotropic displacement factor takes the form $U_{ij} = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.
$^b U_{eq}$ is defined as a third of the orthogonalized U_{ij} tensors.

Table 3: Selected bond lengths (pm) and angles (deg) of LiA[N(CN)$_2$]$_2$ (A = K or Rb) and ionic radii sum of Li$^+$, K$^+$, and Rb$^+$ (in italics) with their respective coordination number coordinated by N^{3-} according to Shannon [11].

K–	N1	8×	295.1(1)	Rb–	N1	8×	308.1(1)
K–	*N*	*8×*	*297*	*Rb–*	*N*	*8×*	*307*
Li–	N1	4×	203.9(3)	Li–	N1	4×	204.9(2)
Li–	*N*	*4×*	*205*	*Li–*	*N*	*4×*	*205*
N0–	C1	2×	129.9(4)	N0–	C1	2×	129.7(3)
C1–	N1	1×	115.7(3)	C1–	N1	1×	115.8(3)
∡(N0–C1–N1)		2×	173.0(3)	∡(N0–C1–N1)		2×	173.1(2)
∡(C1–N0–C1)		1×	122.4(4)	∡(C1–N0–C1)		1×	121.6(3)

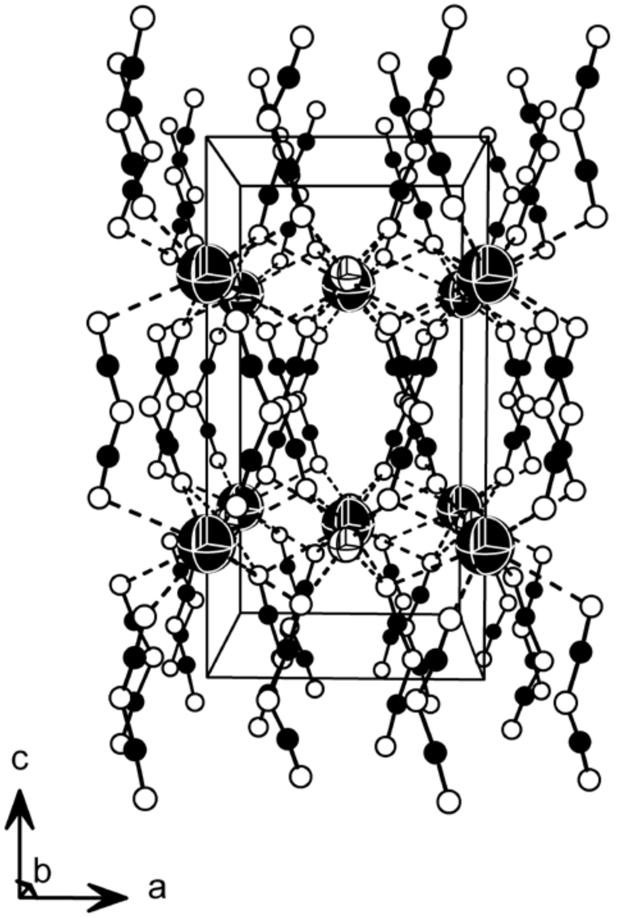

Fig. 1: Unit cell of LiA[N(CN)$_2$]$_2$ as seen along the crystallographic *b* axis. Li$^+$ and A$^+$ are shown as displacement ellipsoids with white (Li$^+$) or black octands (A^+). Displacement ellipsoids are displayed at the 90 % probability level. Carbon atoms are displayed as black; nitrogen atoms as white spheres with fixed atomic radii.

was applied using Sadabs [6]. The intensity data were evaluated, and the input files for solving and refining the crystal structure were prepared by Xprep [7]. The program Shelxs-97 [8, 9], with the help of Direct Methods techniques, easily found the positions of potassium or rubidium. C, N, and Li positions were apparent from the positions of the highest electron density on the difference Fourier maps resulting from the first refinement cycles by full-matrix least-squares calculations on F^2 in Shelxl-97 [9, 10]. Doing further refinement cycles, the refinement converged and resulted in a stable model for the crystal structures. Additional crystallographic details are described in Table 1. Atomic coordinates and equivalent isotropic displacement coefficients are shown in Table 2. Table 3 displays selected interatomic distances and angles of the title compounds and their alkali metal thiocyanate analogue.

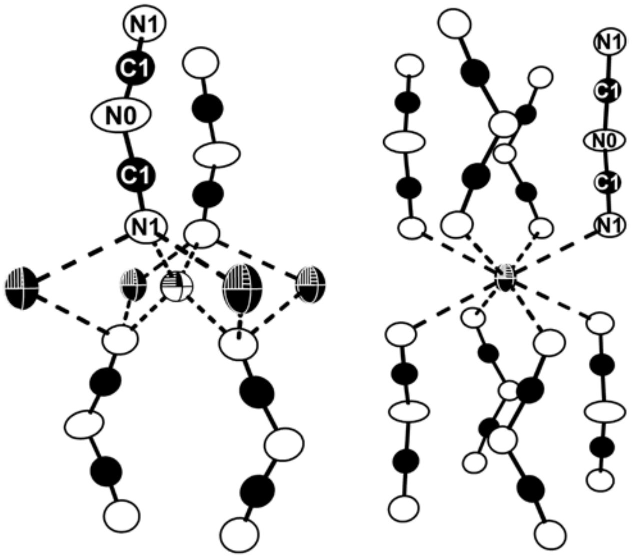

Fig. 2: Coordination of Li$^+$ (left) and A^+ cations (right), shown as displacement ellipsoids with white (Li$^+$) or black octands (A^+), by [N(CN)$_2$]$^-$ anions. Carbon atoms are displayed as black, nitrogen atoms as white spheres with fixed atomic radii.

Further details of the crystal structure investigations may be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, on quoting the deposition number CSD-430275 for LiK[N(CN)$_2$]$_2$ and CSD-430275 for LiRb[N(CN)$_2$]$_2$.

3 Results and discussion

3.1 Crystal structure

The crystal structure of LiA[N(CN)$_2$]$_2$ is built from layers consisting of Li$^+$ and A^+ (A = K or Rb) ions and the dicyanamide anions connecting these cationic layers (Fig. 1). The [N(CN)$_2$] anions coordinate Li$^+$ cations in a tetrahedral fashion (Fig. 2a), whereas A^+ cations are surrounded by squashed square antiprisms formed by the very same anions (Fig. 2b). The coordination geometries (angles and bond lengths) are nearly ideal when using the radii given by Shannon [11] (Table 3). The layered structure is reflected in the plate-like habit of the crystals.

4 Conclusion

With Li*A*$[N(CN)_2]_2$, the first two pseudo-ternary, lithium-containing dicyanamide compounds are presented showing the bond lengths and angles typical for $[N(CN)_2]^-$ anions. The habits of the crystals of the title compounds reflect their layered structure. Owing to the complementary coordination required of Li^+ and A^+ cations (A = K or Rb), nearly ideal coordination environments are found for the respective cation. Nevertheless, similar experiments to replace K^+ or Rb^+ with Na^+ or Cs^+, respectively, have not been successful, perhaps indicating narrow stability limits for this structure type.

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