Crystal structure of pentapotassium dicarbodiimide monohydride, $K_5[CN_2]_2H$

R. Niewa*[I], P. Höhn[I], R. Kniep[I], A. Weiske[II] and H. Jacobs[II]

[I] Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, D-01187 Dresden, Germany
[II] Universität Dortmund, Lehrstuhl für Anorganische Chemie I, Otto-Hahn-Str. 6, D-44221 Dortmund, Germany

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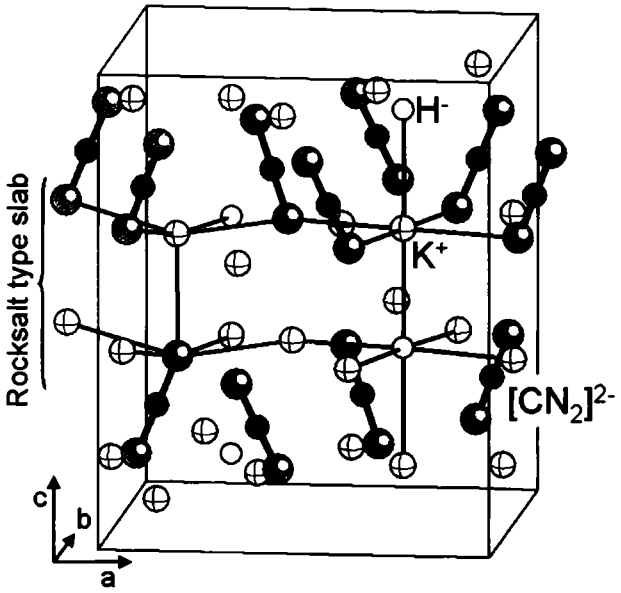

Abstract

$C_2HK_5N_4$, tetragonal, *P4/ncc* (No. 130), $a = 9.0953(3)$ Å, $c = 11.0291(6)$ Å, $V = 912.4$ Å^3, $Z = 4$, $R_{gt}(F) = 0.068$, $wR_{ref}(F^2) = 0.129$, $T = 293$ K.

Source of material

Single crystals of $K_5[CN_2]_2H$ were prepared from KNH_2 and C (molar ratio 3:1) at 923 K in an autoclave for salt melts ($V \approx 9$ cm^3, $P_{max} \approx 2$ Kbar; the autoclave is described in [1]). The major byproduct can be removed by washing with liquid ammonia. Minor byproducts could not be identified.

Experimantal details

H^- scattering factors were modeled using those of He.

Discussion

Several new carbodiimides/cyanamides were reported recently; some of these compounds additionally contain other anions like e.g. nitride N^{3-} or cyanide $[CN]^-$ [2-5]. The title compound $K_5[CN_2]_2H$ is the first carbodiimide/cyanamide hydride. In the crystal structure the linear $[CN_2]^{2-}$ ions ($\angle$N–C–N = 179.9°) are stacked within layers. Nitrogen species, hydride and potassium ions form rocksalt type slabs. These are linked at the nitrogen species by carbon in linear coordination. The rocksalt type slabs on both sides of the $[CN_2]^{2-}$ unit layers are slightly shifted and rotated by about 45° around the axis K1–H. Consequently nitrogen is in a strongly distorted octahedral surrounding of five potassium ions and the central carbon atom of the $[CN_2]^{2-}$ group. The distance d(C—N) = 1.225(4) Å is in the range of those in other carbodiimides/cyanamides. Potassium ions are coordinated by an octahedron of four nitrogen species (d(K1—N) = 2.926(5) Å) and two hydride ions or by four nitrogen species (d(K2—N) = 2.818(4) Å – 2.946(5) Å) and one hydride ion in a tetragonal pyramid with distances in the range of those found in the hydrogen cyanamide $K_5H[CN_2]_3$ [4] (d(K—N) = 2.754 Å, 2.915 Å). The hydride ion is in a nearly regular octahedron of potassium ions with distances (d(H—K) = 2.73(9) Å, 2.78(9) Å, 2.843(2) Å) close to that found for KH (d(H—K) = 2.853 Å, rocksalt structure) [6]. The resulting arrangement is very similar to the crystal structure of $Ca_4Ba[CuN]_2$ [7].

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.2 × 0.2 × 0.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	23.47 cm^{-1}
Diffractometer, scan mode:	MSC-Rigaku CCD, 840 exposures, $\Delta\omega = 0.5°$, 20 s/exposure
$2\theta_{max}$:	58.4°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9585, 580
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 575
$N(param)_{refined}$:	30
Programs:	SHELXS-97 [8], SHELXL-97 [9], DIAMOND [10]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H	4*c*	3/4	3/4	0.100(8)	0.17(4)

* Correspondence author (e-mail: niewa@cpfs.mpg.de)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K(1)	4*c*	1/4	1/4	0.1527(2)	0.0226(7)	U_{11}	0.022(1)	0	0	0
K(2)	16*g*	–0.1460(1)	0.0448(1)	0.1018(1)	0.0202(6)	0.0278(6)	0.0249(6)	0.0025(4)	0.0016(4)	–0.0019(5)
N	16*g*	0.1504(5)	–0.0560(5)	0.1535(4)	0.027(2)	0.022(2)	0.026(2)	–0.001(2)	–0.002(2)	0.003(2)
C	8*f*	0.1031(5)	–*x*	1/4	0.013(2)	U_{11}	0.019(3)	0.002(2)	–0.004(2)	U_{13}

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