Synthesis and Characterization of $Na_5H(CN_2)_3$†

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Single phase $Na_5H(CN_2)_3$ was obtained by thermal decomposition of Na(HNCN) and structurally characterized by Rietveld refinement of X-ray powder diffraction data; $Na_5H(CN_2)_3$ was found to be isostructural to $K_5H(CN_2)_3$, and identical to a phase that was previously reported as '$Na_4H_2(CN)_3$'.

Up to now two sodium salts of cyanamide, Na(HNCN) and $Na_2(NCN)$,[1] have been identified and structurally characterized. Both substances are highly sensitive to the atmosphere. Another sodium salt of cyanamide, '$Na_4H_2(CN_2)_3$' was reported in 1989.[2] However, the powder diffractogram calculated for the proposed structure shows significant deviations from the experimental one, and a reinvestigation seemed worthwhile.

Results

The title compound was synthesized using the procedure previously reported for '$Na_4H_2(CN_2)_3$'.[2] A crystal structure determination by Rietveld's profile fitting method based on X-ray powder data revealed the true composition to be $Na_5H(CN_2)_3$. The crystal data and atomic parameters are given in Table 1. On comparing the experimental X-ray powder diffractograms it became quite clear that the previously published '$Na_4H_2(CN_2)_3$' and $Na_5H(CN_2)_3$ are identical. Using the right composition and structural model, the significant discrepancies between the calculated and observed X-ray powder diffractograms disappear (*cf.* Fig. 1). Furthermore, empty octahedral voids, an unreasonable feature of the previous structural model, are now occupied by sodium with interatomic distances as one would expect. $Na_5H(CN_2)_3$ is isostructural to $K_5H(CN_2)_3$.[3]

Discussion

The structure of $Na_5H(CN_2)_3$ consists of two interpenetrating ReO_3-analogous sublattices with the compositions $Na(CN_2)_3$ which are shifted with respect to each

Table 1 Crystallographic parameters for $Na_5H(CN_2)_3$, average deviation in brackets

	$Na_5H(CN_2)_3$		
(*a*) Crystal data			
Symmetry	cubic		
Space group	$Im\bar{3}m$		
a/pm	724.49(9)		
(*b*) Atomic co-ordinates: *x, y, z*			
Na(1)	0	0	0
Na(2)	0.25	0.25	0.25
C	0.5	0	0
N	0.339(1)	0	0
(*c*) Interatomic distances [pm]			
r[Na(1)–N]	266.6(2)		
r[Na(2)–N]	255.0(71)		
r[Na(1)–Na(2)]	313.71		
r[C ··· N]	107.2(71)		
(*d*) interatomic angles [°]			
N–C–N	180		
Na(1)–N–C	180		
N–Na(1)–N (12 times)	90		
N–Na(1)–N (3 times)	180		
N–Na(2)–N (6 times)	94.87(217)		
N–Na(2)–N (6 times)	85.13(217)		
N–Na(2)–N (3 times)	180		
Na(2)–N–C	106.09(147)		

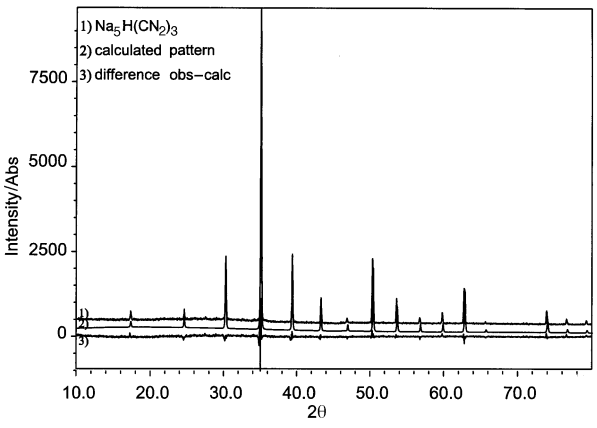

Fig. 1 X-Ray powder pattern and difference plot after Rietveld refinement of $Na_5H(CN_2)_3$

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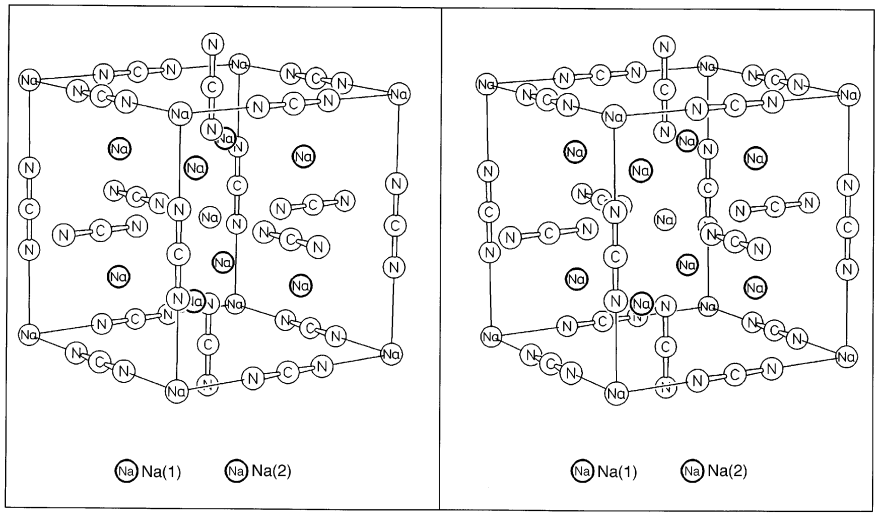

Fig. 2 Unit cell of $Na_5H(CN_2)_3$

other by the vector (0.5/0.5/0.5). Each resulting octahedral hole is occupied by sodium. Thus $Na(1)^+$ is found in a regular, octahedral coordination sphere formed by CN_2^{2-} ligands [$r(Na(1)^+–N)$ = 266.6 pm; $Na(1)^+–N–C$ = 180 °] (Fig. 2).

$Na(2)^+$ shows a slight deviation from a regular octahedral coordination [$r(Na(2)^+–N)$ = 255.0 pm; $Na(2)^+–N–C$ = 106.09 °]. Pertinent crystallographic data, including interatomic distances and angles, are collected in Table 1. The protons in $Na_5H(CN_2)_3$ are disordered. At the level of significance of the present structure determination, no deviations in the geometry of $(N–C–N)^{2-}$, which might be caused by attached hydrogen atoms, are found.

Experimental

The monosodium salt of cyanamide was synthesized from a solution of the free acid in rigorously dried ethanol using sodium ethoxide as a base. $Na_5H(CN_2)_3$ was obtained as the residue remaining after thermal treatment of Na(HNCN) under vacuum (275 K; 0.1 Nm^{-2}; 12 h).[2] The samples obtained were colourless, polycrystalline and, according to X-ray powder diffraction, free of alien phases. The experimental data were collected on a Stoe Stadi P diffractometer using a Germanium monochromator with CuK_α radiation (λ = 1.54051 Å). The structure refinement was carried out by Rietveld methods[4,5] out of 15 reflections with 2 θ in the range 10 to 80 °. The residual value for the refinement converged to $R(p)$ = 0.095 and $R(i)$ = 0.082.

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