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The Crystal Structure of Sodium Cyanide Dihydrate, NaCN·2H₂O

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The crystal structure of NaCN·2H₂O has been refined from X-ray data collected at room temperature ($22 \pm 2^\circ\text{C}$). It is monoclinic with $a = 6.622$ (3), $b = 10.561$ (4), $c = 6.064$ (3) Å, $\beta = 103.06$ (4)°, $Z = 4$, space group $P2_1/a$. Least-squares refinement of 1533 independent diffractometer data converged at a conventional R value of 0.056. The results are generally in agreement with those in a recent study at 150 K [Bats (1977). *Acta Cryst.* **B33**, 466–472] except that the CN group appears to be partially disordered at room temperature.

Introduction

Bats (1977) has reported the structure of NaCN·2H₂O using data collected at 150 K. His determination was undertaken, among other reasons, to look at the electron density in the CN ion. Prior to the report of his work we had undertaken a similar study at room temperature for the same reason. His study is more accurate than ours could possibly be since at the lower temperature there is less thermal motion, which improves the situation both directly and also indirectly by allowing meaningful data to be collected at larger Bragg angles. We did, however, find an apparent disorder in the CN group, a disorder that appears to be absent at the lower temperature. We shall discuss this aspect of our results in some detail.

Experimental

NaCN from Mallinkrodt was recrystallized from a 50% ethanol–water mixture. One of the large, thick plates so obtained was cut and ground to a sphere with a radius of 0.715 mm, which was used for data collection. It was necessary to coat the sphere with a layer of Apiezon L grease to prevent the loss of water on exposure to air.

Data were collected on a four-circle Hilger & Watts automatic diffractometer using Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). The unit-cell dimensions, determined from a least-squares fit of the Bragg angles of 12 reflections carefully measured on the diffractometer (θ between 16 and 26°) are: $a = 6.622$ (3), $b = 10.561$ (4), $c = 6.064$ (3) Å, $\beta = 103.06$ (4)° and $V = 413.1$ Å³. The space group, following Le Bihan (1958), is $P2_1/a$; for $Z = 4$ our calculated density, 1.367 g cm⁻³, agrees with her observed value, 1.361 g cm⁻³.

Intensity data for 1533 independent reflections were collected using a moving-crystal moving-counter scan with one hundred 0.01° steps in θ and ω for all reflections; step times were 1 s and background counts were 50 s at each end of the scan. Two check reflections were measured every 25 regular reflections; these check reflections increased by 10% over the course of the data collection, presumably owing to a long-term drift in the X-ray power supply; this was corrected for in the subsequent calculations. Extinction was present (see below). The calculated extinction corrections for the check reflections were 3.5% and 1.6% of the intensities. Thus, it would not appear that the variation in the check reflection intensities arose from a change in the extinction with time. To avoid coincidence losses in the counter, the high intensity reflections were measured using filters in the diffracted X-ray beam. For $0 < \theta \leq 10^\circ$, data were collected for

all four quadrants. Since equivalent reflections agreed on the average to within 1.5% only a single quadrant of data was collected for $10 < \theta \leq 33^\circ$. Collection was terminated at 33° since between 31 and 33° only 25% of the reflections had $I > 3\sigma(I)$. The data were corrected for Lorentz and polarization factors but not for absorption ($\mu = 2.21 \text{ cm}^{-1}$ for Mo $K\alpha$ radiation; $\mu r = 0.160$; the absorption correction varies by less than 1% over the complete range of data). Weights were assigned in the manner described by Corfield, Doedens & Ibers (1967); the value of 0.03 was used for p in the $\sigma(I)$ equation.

Solution and refinement

The positional parameters for Na, O, N, and C given by Le Bihan (1958) were used as the starting point for refinement. The early stages of refinement, least squares plus difference Fourier maps, indicated that the C and N positions given by Le Bihan should probably be reversed, showed that considerable secondary extinction was present, and produced the H atom positions. Correction for extinction (Stout & Jensen, 1968) was made according to

$$F_o(\text{corrected}) = F_o(1 + 2.33 \times 10^{-7} I_c).$$

Using the 1460 reflections with intensities greater than zero the CN arrangement was tested further. If CN is taken as the arrangement given in our Table 1, then the possibilities 100% CN; 87.5% CN + 12.5% NC; 75% CN + 25% NC; 100% NC (the Le Bihan arrangement) were refined and converged at $r = 0.0161, 0.0152,$

$0.0152, 0.0366$ and $R = 0.057, 0.055, 0.055, 0.077,$ respectively.* There is a broad minimum in r between 87.5% and 75% CN; the estimated value of r halfway between these values is 0.0151. If we use the \mathcal{R} factor test (Hamilton, 1965), our value of $\mathcal{R}, (0.0161/0.0152)^{1/2} = 1.029,$ should be compared to $\mathcal{R}_{1,1398,0.005} = 1.003.$ We can reject the hypothesis that the apparent improvement occurs by chance. We will describe the situation as disordered; however, see Discussion also.

The final refinement was made using all 1533 independent data items; anisotropic thermal parameters were used for the non-hydrogen atoms, isotropic thermal parameters for the H atoms; the disorder was taken as 75% CN, 25% NC. The refinement converged at $r = 0.0129, R = 0.056.$ The final parameters are given in Table 1.†

* $r = \sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^4; R = \sum ||F_o| - |F_c|| / \sum |F_o|.$ The numerator of r was the function minimized. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Scattering factors for neutral atoms were used in all cases. No corrections were made for anomalous dispersion.

† A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33474 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional and thermal (\AA^2) parameters for $\text{NaCN} \cdot 2\text{H}_2\text{O}$

Positional parameters are multiplied by 10^4 . The anisotropic thermal parameters are of the form

$$\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + \dots + 2B_{12}hka^*b^* + \dots)].$$

Estimated standard deviations for the final significant figures are given in parentheses.

	x	y	z	B
Na	9429 (1)	1700 (1)	78 (1)	3.23
O(1)	6852 (2)	3010 (1)	7546 (2)	3.80
O(2)	6936 (2)	4833 (1)	2003 (2)	3.36
N	6286 (2)	1548 (1)	2383 (3)	4.80
C	7028 (2)	702 (2)	3185 (3)	4.63
H(11)	7090 (30)	3707 (23)	7354 (33)	3.6 (5)
H(12)	6311 (47)	2614 (30)	6390 (50)	6.3 (7)
H(21)	8043 (30)	4599 (20)	1984 (30)	3.5 (4)
H(22)	7029 (36)	4983 (22)	3194 (48)	5.3 (7)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Na	3.25 (2)	2.56 (2)	3.76 (2)	-0.16 (1)	0.50 (2)	-0.33 (1)
O(1)	4.49 (5)	2.94 (4)	3.90 (4)	0.02 (3)	0.80 (4)	0.03 (3)
O(2)	3.27 (4)	3.38 (4)	3.16 (4)	0.52 (3)	0.14 (2)	-0.19 (3)
N	4.58 (6)	3.97 (6)	5.80 (7)	0.50 (5)	1.07 (5)	1.17 (5)
C	4.88 (6)	4.40 (7)	4.73 (7)	0.52 (5)	1.32 (5)	1.15 (5)

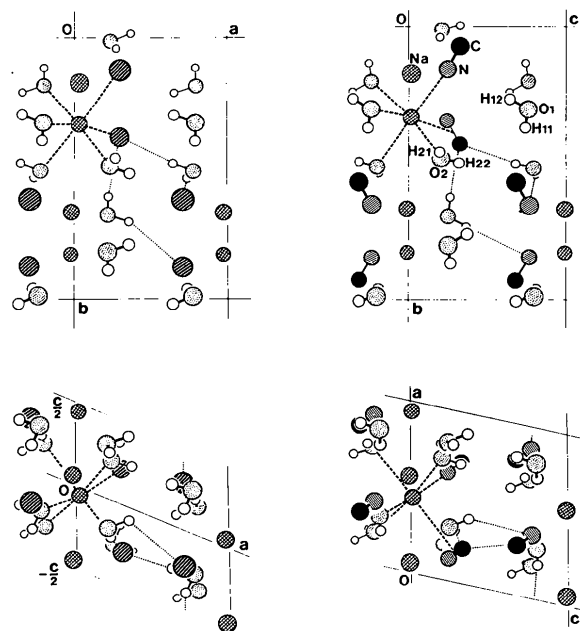


Fig. 1. The structures of $\text{NaCN} \cdot 2\text{H}_2\text{O}$ and $\text{NaCl} \cdot 2\text{H}_2\text{O}$ (Klewe & Pedersen, 1974). Top left: view of $\text{NaCl} \cdot 2\text{H}_2\text{O}$ structure along c . Bottom left: view of $\text{NaCl} \cdot 2\text{H}_2\text{O}$ structure along b . Right: corresponding views of $\text{NaCN} \cdot 2\text{H}_2\text{O}$ structure. The coordination octahedron around sodium is shown with dashed lines in each case. The hydrogen bonds are shown with dotted lines.

Table 2. Distances in the sodium coordination sphere

The distances are those shown in Fig. 1. The Na atom is at $x - \frac{1}{2}, \frac{1}{2} - y, z$ relative to that in Table 1. The displacements of the other atoms relative to the positions in Table 1 are given below. The corresponding distances in the NaCl.2H₂O structure are also given.

		NaCN.2H ₂ O 295 K	NaCN.2H ₂ O 150 K	NaCl.2H ₂ O
Na-N'	x, y, z	2.472 (2) Å	2.448 (1) Å	2.7901 (3) Å
Na-N	$x - \frac{1}{2}, \frac{1}{2} - y, z$	2.761 (2)	2.730 (1)	2.7919 (3)
Na-C	$x - \frac{1}{2}, \frac{1}{2} - y, z$	2.923 (2)	2.899 (1)	
Na-O(1)	$x, y, z - 1$	2.449 (2)	2.436 (1)	2.3810 (4)
Na-O(1')	$x - \frac{1}{2}, \frac{1}{2} - y, z - 1$	2.477 (1)	2.451 (1)	2.4582 (4)
Na-O(2)	x, y, z	2.422 (2)	2.415 (1)	2.3789 (4)
Na-O(2')	$1 - x, 1 - y, -z$	2.405 (1)	2.392 (1)	2.3829 (5)

Table 3. Angles in the sodium coordination sphere

The atoms are labelled as in Table 2. The corresponding angles in NaCl.2H₂O are also given.

	NaCN.2H ₂ O	NaCl.2H ₂ O
N-Na-N'	95.34 (6)°	96.31°
C-Na-N'	100.31 (6)	
N-Na-O(1)	81.49 (5)	90.87
C-Na-O(1)	101.79 (5)	
N-Na-O(1')	171.29 (4)	172.18
C-Na-O(1')	165.21 (4)	
N-Na-O(2)	103.31 (5)	92.28
C-Na-O(2)	82.05 (4)	
N-Na-O(2')	88.88 (4)	90.83
C-Na-O(2')	81.24 (4)	
N'-Na-O(1)	96.84 (5)	90.88
N'-Na-O(1')	87.06 (5)	89.36
N'-Na-O(2)	91.65 (5)	93.27
N'-Na-O(2')	172.05 (5)	172.63
O(1)-Na-O(1')	89.91 (5)	94.39
O(1)-Na-O(2)	169.85 (4)	174.46
O(1)-Na-O(2')	90.43 (5)	90.87
O(1')-Na-O(2)	84.96 (4)	81.99
O(1')-Na-O(2')	89.76 (4)	83.36
O(2)-Na-O(2')	80.81 (5)	84.55

Results and discussion

The structure is shown in Fig. 1 where it is compared with that of NaCl.2H₂O (Klewe & Pedersen, 1974). In Table 2 the Na...X distances are compared with those found at 150 K and with those in NaCl.2H₂O. In Table 3 the angles in the Na coordination sphere are given. In Table 4 the distances and angles of the hydrogen-bonded intermolecular contacts are given and compared with the corresponding parameters at 150 K.

The structure of NaCN.2H₂O is closely similar to those of NaCl.2H₂O and NaBr.2H₂O (Culot, Piret & Van Meerssche, 1962; Haaf & Carpenter, 1964), which in turn are related to that of NaI.2H₂O (Verbist, Piret & Van Meerssche, 1970). Although the difference in cell dimensions, particularly in β , precludes calling the cyanide isomorphous with the chloride or bromide, an inspection of Fig. 1 shows that except for the difference in shape between cyanide and chloride the two structures are the same. In the chloride each Cl ion is in

Table 4. Distances and angles in hydrogen bonds

The first line in each case gives our results at 295 K; the second line gives the results of Bats (1977) at 150 K.

A	B	A-H (Å)	H-B (Å)	A-B (Å)	A-H-B (°)
O(1)	C	0.76 (2)	2.23 (2)	2.997 (2)	177 (2)
		0.85 (1)	2.14 (1)	2.989 (1)	173 (1)
O(1)	N	0.83 (3)	2.67 (3)	3.435 (2)	154 (3)
		0.85 (1)	2.51 (1)	3.347 (1)	168 (1)
O(2)	C	0.73 (3)	2.27 (3)	2.987 (2)	167 (2)
		0.79 (1)	2.21 (1)	2.969 (1)	160 (1)
O(2)	N	0.78 (3)	2.43 (2)	3.189 (2)	166 (2)
		0.76 (1)	2.39 (1)	3.120 (1)	165 (1)

contact with two Na ions, both at a distance of 2.79 Å, which is just slightly shorter than the distance in anhydrous sodium chloride, 2.82 Å. For the bromides the distances are 2.96 and 2.98 Å in the dihydrate versus 2.99 Å in the anhydrous salt. In the cyanide the distances are quite different. One is an end-on Na-NC contact (Na-N-C angle, 172°) with a distance of 2.47 Å. There is no corresponding distance in the orthorhombic anhydrous NaCN structure (see Britton, 1967, and references therein, for a discussion of the ionic cyanide structures), but a comparison with the ionic radius for the Na ion, the axial ionic radius for the CN ion, and the C-N distance gives reasonable agreement ($0.95 + 2.15 - 1.16/2 = 2.52$ Å). The second contact is a sideways one (Na-C-N angle, 88°; Na-N-C angle, 71°) with distances of 2.76 (Na-N) and 2.92 (Na-C) Å. The average of these two distances, 2.84 Å, can be compared with the corresponding distance in orthorhombic anhydrous NaCN, 2.82 Å.

Our original intention was to look for the effects of bonding electrons in the CN group on a difference electron density map. The disorder of the CN groups makes this pointless for our room-temperature results. These effects have been found in the low-temperature work and are discussed at length there (Bats, 1977). If we take the extent of the disorder as between 12.5% and 25%, assume equilibrium in the disorder, and

further assume that there is no entropy difference between the two orientations, then $-\Delta H = RT \ln K$, and the energy difference between the two orientations is between 0.6 and 1.2 kcal mol⁻¹.

If we use our estimate of the energy to calculate the disorder we would expect to find at 150 K, the results are 2% disorder (for 1.2 kcal mol⁻¹) to 12% disorder (for 0.6 kcal mol⁻¹). Bats (private communication) has refined his data further allowing for the possibility of disorder and finds $0.8 \pm 0.6\%$ disorder using all the data and $27 \pm 24\%$ disorder using only the high-angle data. (The ambiguity from the high-angle data is discussed below.) The 0.8% disorder corresponds to an energy difference between the orientations of 1.4 kcal mol⁻¹. Thus, while there is no significant disorder at 150 K, the results at the two temperatures are not inconsistent.

The apparent disorder bears further discussion. Under *Solution and refinement* we described the refinement assuming that the atoms referred to as N and C in Table 1 and Fig. 1 were in fact each mixtures of N and C (or C and N) in the proportions 1/0, 0.875/0.125, 0.75/0.25, and 0/1. Henceforth, we shall use a parameter, X , corresponding to the fraction of N atom assumed at the N position to describe the mixtures; e.g. $X = 1, 0.875, 0.75$, and 0, respectively, in the mixtures just mentioned. We also repeated the refinement using 794 high-angle data ($\sin \theta/\lambda \geq 0.55$) with the H atom parameters fixed at the values found using all the data. As it happened these high-angle data do not include reflections for which $I < 2\sigma(I)$ so that the r values are all lower than for the more complete data set. This was done for mixtures with $X = 1, 0.875, 0.75, 0.5, 0.25$, and 0 with r values after refinement of 0.0082, 0.0081, 0.0081, 0.0080, 0.0081, and 0.0081, respectively. Using Hamilton's \mathcal{R} factor test, $\mathcal{R} = (0.0082/0.0080)^{1/2} = 1.012$, which should be compared with $\mathcal{R}_{1,744,0.005} = 1.006$. Again the test says that the improvement is unlikely to be due to chance. These results are shown graphically in Fig. 2 where it can be seen that the minimum in the curve for all the data is much more convincing than that for the high-angle data only even though the \mathcal{R} factor test says that both are significant.

Also shown in Fig. 2 are the equivalent isotropic B values (calculated from the anisotropic B_{ij} values found in the refinement) for the atoms at the N and C positions as a function of X . It can be seen that the approximate constancy of r for the high-angle data arises because the decrease in $B(N)$ and the increase in $B(C)$ compensate almost completely for the change in the scattering factors used for the atoms at the N and C positions. In spite of the result of the \mathcal{R} factor test our opinion is that the high-angle data do not convincingly distinguish between order and disorder or even between whether CN or NC is the better description if order is assumed.

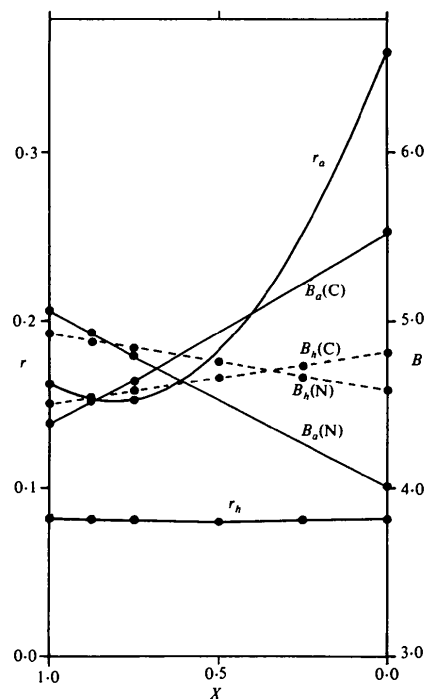


Fig. 2. Effect of apparent disorder on r and B . The abscissa is X , an orientation parameter ($X = 1$ corresponds to CN as shown in Table 1 and Fig. 1, $X = 0$ corresponds to the opposite arrangement, $X = 0.5$ corresponds to a 50/50 mixture of the two extremes, etc.). The ordinate is r (left) or B (right). The curves are labelled. The subscripts a and h refer to all-angle data and high-angle data, respectively. See text for discussion.

On the other hand, the minimum in r based on all the data is convincing and might be expected since the values of the scattering factors for C and N are fixed at $\sin \theta/\lambda = 0$, and at low angles cannot be compensated for by adjustments in the B 's. It should be noted, however, that this minimum in r occurs at that value of X where the B values determined from the high-angle data alone agree with the B values determined from all the data. It seems quite possible that this agreement causes the minimum in r , which does not then necessarily reflect the actual amount of disorder. If the minimum in r_a and r_h (see Fig. 2) occurred at the same value of X , we would not have this reservation.

If we examine the individual B_{ii} values as a function of X , these add to the uncertainty. B_{11} , B_{22} , and B_{33} are affected quite differently by the change in X , which suggests that the anisotropy in the valence electron arrangement is mixed up with the anisotropy in the thermal motion to an undetermined extent.

In summary, the data are better fitted by using average scattering factors corresponding to X equal to approximately 0.8. The simplest interpretation of this is that 20% of the CN have the opposite orientation. It might, however, be an artificial effect arising because

the average scattering factors plus the apparent anisotropic thermal motion better approximate the anisotropic valence electron distribution plus the actual thermal motion of CN groups that are completely ordered or have some other degree of disorder. It does not appear to us that this question can be resolved readily by X-ray diffraction techniques. Since the high-angle data have little bearing on the question of disorder, as discussed above, it would require considerably better low-angle data to decide the question. A neutron diffraction study of this compound would appear to be more useful than further X-ray work.

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Die Kristallstruktur von Trisamariumtetrasulfid, eine allgemeine kristallchemische Betrachtung über den Th₃P₄-Typ und eine Diskussion über den ungewöhnlichen Valenzzustand des Samariums in Sm₃S₄

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Confirming earlier results from powder diffraction studies the present single-crystal X-ray structure determination (Mo K α radiation, 866 reflexions, $R = 4.9\%$) has shown that Sm₃S₄ crystallizes with the Th₃P₄-type structure: space group *I43d*, $a = 8.523$ (1) Å. The only free positional parameter of this structure, $x(S) = 0.0722$ (2), is considerably smaller than the originally assumed ideal value of $x = \frac{1}{2}$. The stoichiometric composition of Sm₃S₄ has been corroborated by refinement of the atomic occupation factors, *i.e.* Sm₃S₄ does not belong to the relatively large group of defect structures known for many Th₃P₄-type compounds. Some physical properties of Sm₃S₄ are unique; they suggest an unusual valence state of the Sm ions. Within the context of theoretical concepts presently under discussion, Sm₃S₄ may be called a homogeneously mixed-valent compound. An intermediate valence of +2.78 per cation has been derived from a detailed comparison of lattice dimensions of Sm₃S₄ and some similar rare-earth sulphides. Although the Th₃P₄ structure has been known since 1939 a thorough understanding based on simple ideas of crystal chemistry is as yet to be gained. In order to overcome this situation another interpretation of this structure is presented along with a demonstration of topological relations with well-known structures.

Einleitung

In einer grundlegenden Arbeit über das System Ce/S konnte Zachariasen (1949) zeigen, dass Ce₃S₄ im Th₃P₄-Typ (Meisel, 1939) kristallisiert und dass diese

Phase ein breites Homogenitätsgebiet bis zur Zusammensetzung Ce_{2,67}S₄, also bis hin zum Sesquisulfid Ce₂S₃ aufweist. Völlig analoge Verhältnisse wurden später bei einer Vielzahl von anderen Seltenerdmetall-Chalkogen-Systemen gefunden (vgl.