

The complex exhibits the delocalized bond pattern of the s-nqdi ligand, which is similar to that of [Co(s-bqdi)₂] (Peng, Chen, Liaw, Chen & Wang, 1985) and of [Ni(s-bqdi)₂] (Hall & Soderberg, 1968) (Table 2). The average Co—N distance, 1.816 (3) Å, which is comparable to those in [Co(s-bqdi)₂] and [Ni(s-bqdi)₂], is short indicating a strong interaction between the Co atom and s-nqdi ligands. The average N—C(1) distance, 1.360 (5) Å, is very close to the aromatic C—N distance of pyridine. As for the C—C distances, the C(4)—C(5) distance, 1.355 (6) Å, is the shortest, but still comparable to those in corresponding naphthalene, 1.36 Å, and s-bqdi ligands (Table 2). The degree of delocalization is greater than that observed in [Fe(bqdi)₃]²⁺ (Peng, Chen, Liaw, Chen & Wang, 1985).

The authors would like to express their appreciation for the support of this work by the National Science Council. They also thank Professor Yu Wang for helpful discussions.

Acta Cryst. (1986). C42, 404–407

Structure of Sodium Iodide–Acetonitrile–Water (2/3/3)

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(Received 19 August 1985; accepted 18 November 1985)

Abstract. NaI.1½H₂O.1½C₂H₃N, *M_r* = 238.50, hexagonal, *P*62*m*, *a* = 8.707 (1), *c* = 6.424 (1) Å, *V* = 421.8 (1) Å³, *Z* = 2, *D_x* = 1.878 g cm⁻³, *Mo Kα*, λ = 0.71069 Å, μ = 38.21 cm⁻¹, *F*(000) = 224, *T* = 293 (1) K, final *R* = 0.032 for 288 non-zero reflections. Each sodium cation is octahedrally coordinated to three waters and three acetonitriles. Sodium-centred octahedra share opposite faces with two adjacent octahedra to form continuous chains. The shared faces consist of either three nitrogens or three oxygens, alternately along the chain, and in phase from one chain to another. Each iodide is at the centre of a trigonal prism on whose triangular-face edges are located acetonitrile molecules with the methyl groups nearest to the anions. In the equatorial plane of each prism lie the oxygens of three water molecules, which are bound to the iodides by I...H—O interactions, creating an effective coordination number of nine for iodide. Adjacent prisms, which share a common square face, are respectively left- and right-handed owing to the

different orientations of the acetonitriles. The sodium–iodide internuclear separations (5.270 Å) are even greater than the iodide–iodide contacts (5.027 Å) and are clearly nonbonding.

Introduction. In the course of Raman spectroscopic studies of alkali halides in aqueous and non-aqueous media (Irish, Hill, Archambault & Atkinson, 1985) we discovered, in the mixed-solvent system H₂O—CH₃CN and in the presence of sodium iodide, that crystals grew inside the sealed Raman capillary tubes. As sodium iodide is soluble in either water or acetonitrile alone we were intrigued by this result. With some difficulty, as the crystals are rapidly decomposed upon removal of their mother liquor, we have obtained the crystal and molecular structure of NaI.1½H₂O.1½CH₃CN. To our knowledge there are only three previous reports of X-ray-determined structures of compounds containing an alkali halide, water and an organic solvent [LiCl.1,4-dioxane.H₂O (Durant & Griffe, 1968); LiCl.2pyridine.H₂O (Durant, Piret & Van Meerssche, 1967); NaI.2glycine.H₂O (Verbist, Putzeys, Piret & Van

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Meerssche, 1971)], and none containing acetonitrile and a Group I halide. The title compound is thus an unusual species and its structure of considerable interest, especially as it appears to belong to the very rare space group $P\bar{6}2m$. To date we have not succeeded in obtaining similar mixed solvates of other Group I halides at room temperature. However, we have produced crystals of $\text{LiBr}\cdot x\text{CH}_3\text{CN}$, and of $\text{SrI}_2\cdot y\text{CH}_3\text{CN}$, and have embarked on structure determinations.

Experimental. Well defined colourless crystals grown at room temperature (297 K) from CH_3CN solutions containing NaI (1 mol kg⁻¹) and H_2O (~0.1 mol kg⁻¹). Because the crystals desolvate immediately on exposure to air, the only practical way to obtain a crystal suitable for X-ray work was to transfer a crystal directly from the solution into rapidly-setting epoxy. Intensity data obtained using approximately spherical crystal 0.40 (3) mm diameter mounted on Syntex $P2_1$ diffractometer. Accurate cell constants obtained using 15 well distributed general reflections ($30 < 2\theta < 33^\circ$). Check of several sets of hkl indicated $hkl = khl = h\bar{k}l$ and fixed Laue symmetry as $6/mmm$. Data collected by θ - 2θ scan ($3.2 < 2\theta \leq 60.0^\circ$), variable scan rates 2.93–29.30° min⁻¹, scan width 0.95° below $K\alpha_1$ to 0.95° above $K\alpha_2$. During data collection, two standard reflections (600, 004), monitored every 100 measurements, exhibited only minor fluctuations. Data corrected for Lorentz and polarization effects and spherical absorption correction ($\mu R = 0.76$) applied to I . All $h\pm kl$ ($h = 0 \rightarrow 12$; $k = -12 \rightarrow 10$; $l = 0 \rightarrow 9$) collected for 1350 measured reflections. Resultant 290 unique data gave 288 non-zero reflections used in structure solution and refinement. No observed systematic absences, choice of five space groups ($P622$, $P6mm$, $P\bar{6}m2$, $P\bar{6}2m$ and $P6/mmm$). Wilson plot strongly suggested non-centrosymmetric distribution of E values. Patterson function indicated the I–I vector at $\frac{1}{3}, \frac{2}{3}, 0$, I–Na at $\frac{1}{3}, \frac{2}{3}, 0.24$ and Na–Na at $0, 0, 0.5$. Although all these space groups could accommodate solution of vectors with $Z = 2$, $P622$, $P6mm$ and $P6/mmm$ eliminated on basis of unlikelihood that sodium could possess 6 or $6mm$ symmetry. In spite of space-group rarity, successful solution obtained using $P\bar{6}2m$ (No. 189– D_{3h}^3) with iodine and sodium atoms on $\bar{6}$ and $3m$ sites, respectively. From Fourier synthesis phased with these atoms, water and acetonitrile molecules located on mm sites $x00$ and $x0\frac{1}{2}$, respectively. Choice of $P\bar{6}2m$ rather than $P\bar{6}m2$ consistent with the more desirable $\bar{6}$ packing of acetonitrile molecules about iodine rather than $\bar{6}m2$ packing required in latter space group, supported by least-squares refinement based on F of atomic positions and anisotropic thermal parameters, which converged at R and wR values of 0.032 and 0.041 respectively. Empirical weighting scheme $w^{-1} = 3.06 - 0.1|F_o| + 0.004|F_o|^2$ employed in final cycles of refinement. Max.

Table 1. Atomic coordinates (fractional, $\times 10^4$) and U_{eq} (\AA^2)

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	U_{eq}
I	3333	6667	0	53.7
Na	0	0	2460 (6)	41
O	-2099 (10)	0	0	47
N	2211 (15)	0	5000	56
C(1)	3522 (14)	0	5000	41
C(2)	5094 (32)	0	5000	61

Table 2. Bond lengths (\AA), non-bonding contacts (\AA) and bond angles ($^\circ$)

Na–O	2.416 (7)	Na–N	2.523 (10)
N–C(1)	1.142 (18)	C(1)–C(2)	1.368 (30)
I...I	5.027	I...Na	5.270 (3)
I...O	3.564 (6)	I...C(2)	4.079 (15)
Na...Na ^I	3.161 (6)	Na...Na ^{II}	3.263 (6)
O–Na–O ^{III}	81.9 (2) ($\times 3$)*	O–Na–N	179.4 (2) ($\times 3$)
O–Na–N ^{III}	97.7 (2) ($\times 6$)	N–Na–N ^{III}	82.7 (2) ($\times 3$)
Na–O–Na ^I	81.7 (1)	Na–N–Na ^{II}	80.6 (1)
Na–N–C(1)	139.7 (2)		

Symmetry code: (i) 0, 0, $-z$; (ii) 0, 0, $1-z$; (iii) y, x, z .

* The number of times an angle occurs about sodium is given by ($\times 3$) or ($\times 6$).

parameter shifts in final cycle 0.09σ . Final difference Fourier map indicated max. residuals of 0.6 e \AA^{-3} in vicinity of iodine atom and unique water proton at $-0.305, -0.095, 0$. Scattering factors from *International Tables for X-ray Crystallography* (1974) including anomalous-dispersion corrections for iodine. Programs used are described elsewhere (Taylor, Jacobson & Carty, 1975).*

Discussion. Final positional parameters are listed in Table 1. U_{33} values for oxygen and nitrogen are somewhat larger than for C(1) or sodium. Although this may be just a consequence of data limitations the possibility exists that these bridging atoms are in fact closer to one sodium than the other at any particular time, and that this thermal parameter elongation is due to an unresolvable disorder over two sites. Bond lengths and angles are shown in Table 2.

As shown in Fig. 1 each sodium is octahedrally coordinated to three waters and three acetonitriles. Sodium-centred octahedra share opposite faces with two adjacent octahedra so as to form continuous chains along the z axis. These shared faces consist of either three nitrogens or three oxygens, alternately along the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42649 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

chain, and in phase from one chain to the next as seen in Fig. 2, which also shows the packing about a central $(\text{CH}_3\text{CN})_3\text{Na}(\text{H}_2\text{O})_3\text{Na}(\text{CH}_3\text{CN})_3$ portion of a chain and clearly reveals the hexagonal symmetry, even though the view is from slightly off the z axis to enable recognition of other features. Fig. 3 shows the coordination about iodide to emphasize the trigonal prismatic geometry and to illustrate the apparent left- and right-handedness of the two iodide coordination polyhedra in the unit cell, which are related by the (110) mirror plane. The ninefold coordination of each iodide (six methyls and three H-bonded waters) can be described as distorted tricapped trigonal prismatic with the water molecules located off-centre in each square face of the prism. The iodides and oxygens are coplanar, forming sheets in the xy plane, with each iodide forming $\text{I}\cdots\text{H}-\text{O}$ bonds to three waters, one in each of three neighbouring chains. The structure is basically similar to that of $\text{NaI}\cdot 3\text{CH}_3\text{OH}$ (Piret & Mesureur, 1965) in which the sodiums are octahedrally surrounded by six oxygens at 2.47 Å (compared to 2.416 Å in this work), and the iodides by six methyl and three hydroxy groups. In each case there is clearly no sodium-to-iodide interaction, the Na-I distance being 5.27 Å in both structures; in fact the I-I distances (5.027 Å) are smaller than the Na-I separations (5.270 Å). This may be contrasted with the situation in $\text{NaI}\cdot 2\text{H}_2\text{O}$ (Verbist, Piret & Van Meerssche, 1970), where the Na-I distances are in the range 3.209–3.259 Å. Other related structures are $\text{NaI}\cdot 3(\text{CH}_3)_2\text{CO}$ and $\text{NaI}\cdot 3(\text{CH}_3)_2\text{NCHO}$ (Gobillon & Piret, 1962), $\text{NaI}\cdot 3$ dioxane (Barnes & Duncan, 1972) and $\text{LiI}\cdot 3\text{H}_2\text{O}$ and $\text{LiClO}_4\cdot 3\text{H}_2\text{O}$ (West, 1934; Wells, 1975). $\text{NaI}\cdot 2$ glycine $\cdot\text{H}_2\text{O}$ (Verbist *et al.*, 1971), and $\text{LiCl}\cdot 1,4$ -dioxane $\cdot\text{H}_2\text{O}$ (Durant & Griffé, 1968) contain similar infinite chains of oxygen-linked cation-centred octahedra but the structures are otherwise not closely related to $\text{NaI}\cdot 1\frac{1}{2}\text{H}_2\text{O}\cdot 1\frac{1}{2}\text{CH}_3\text{CN}$. The existence of $\text{O}-\text{H}\cdots\text{I}^-$ hydrogen bonds in $\text{NaI}\cdot 3\text{CH}_3\text{OH}$ has been discussed (Piret, 1965; Piret & Mesureur, 1965) and clearly the situation is comparable in our material whose OH stretching mode region has a single Raman band at 3387 cm^{-1} at room temperature which is relatively sharp (FWHM = 57 cm^{-1}) reflecting hydrogen bonding of water in a highly ordered structure. The $\text{I}\cdots\text{O}$ separations (3.564 and 3.60 Å, respectively) are essentially identical in the two compounds. Distances within the acetonitriles reveal apparent shortenings of the C-N and C-C bonds compared to the free ligand [C-N: 1.142 (18) compared to 1.155 (30) and C-C 1.368 (30) compared to 1.465 (20) Å; Danford & Livingston, 1955]. The upward shift in the C-N stretch ($2252\rightarrow 2260\text{ cm}^{-1}$, Raman) is consistent with this shortening, though the bridging character of the attachment complicates the issue. Currently we are engaged in a detailed Raman and IR study of $\text{NaI}\cdot 1\frac{1}{2}\text{H}_2\text{O}\cdot 1\frac{1}{2}\text{CH}_3\text{CN}$.

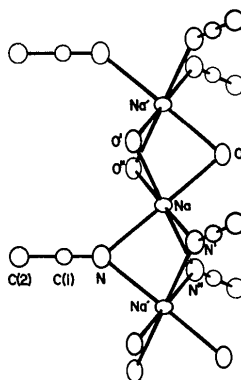


Fig. 1. Arrangement around each Na^+ and the sharing of alternate $(\text{O})_3$ and $(\text{N})_3$ faces of the octahedra that make up the infinite chains of cations.

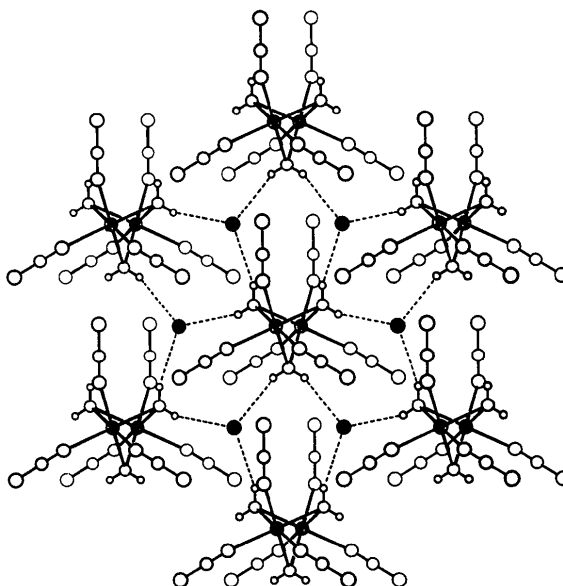


Fig. 2. The packing of the chains of Fig. 1 around the I^- ions (solid circles). The dashed lines indicate the $\text{O}-\text{H}\cdots\text{I}^-$ interactions.

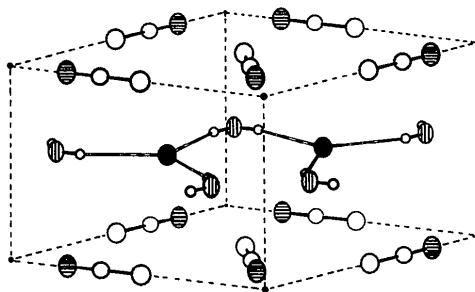


Fig. 3. Details of the coordination about iodine (solid circles).

We thank the Natural Sciences and Engineering Research Council of Canada and the Defence Research Establishment, Ottawa, for financial support.

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Acta Cryst. (1986). **C42**, 407–410

Structure of Bis(4-amino-1,2-dihydro-1-methyl-5-nitroso-2-oxo-6-pyrimidinolato-*O,N*)-diaquazinc(II) Dihydrate

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(Received 20 June 1985; accepted 12 November 1985)

Abstract. $[\text{Zn}(\text{C}_5\text{H}_5\text{N}_4\text{O}_3)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, $M_r = 475.68$, triclinic, $P1$, $a = 11.4430$ (6), $b = 9.5610$ (4), $c = 8.1430$ (2) Å, $\alpha = 102.1$ (1), $\beta = 94.1$ (1), $\gamma = 97.6$ (1)°, $V = 858.7$ (4) Å³, $Z = 2$, $D_m = 1.79$ (6), $D_x = 1.840$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu = 15.35$ cm⁻¹, $F(000) = 488$, room temperature, final $R = 0.042$ for 4280 observed reflections. The Zn^{II} ion is involved in a distorted octahedral coordination, in which the equatorial positions are occupied by two bidentate ligands through the nitrogen and oxygen atoms of the substituents in 5 and 6 positions, respectively. Two molecules of water are in the axial positions of the octahedron, whereas the other two are involved in the formation of hydrogen bonds.

Introduction. The study of transition-metal complexes with pyrimidine derivatives has received increasing

attention in the last few years from both inorganic and biological points of view (Hodgson, 1977; Martin & Mariam, 1973), since it has been found that the metal ions play a vital role in the biochemistry of living systems and some of these complexes have shown chemotherapeutic effects (Rosenberg, 1971, 1973).

There are only a few crystallographic reports on 5-nitrosopyrimidine complexes (Romero-Molina, Martin-Ramos, López-González & Valenzuela-Calahorra, 1983; Ruiz-Valero, Monge, Gutiérrez-Puebla & Gutiérrez-Rios, 1983, 1984) and all of them are referred to metal complexes with 1,3-dimethyl-violuric acid. They show that this pyrimidine derivative is bound to metal ions, in bidentate form, through the oxygen and nitrogen atoms of the 6-oxide and 5-nitroso groups, respectively.

As a new example of this type of compound, we report in this paper the crystal structure of bis(4-amino-1,2-dihydro-1-methyl-5-nitroso-2-oxo-6-pyrimidinolato)diaquazinc(II) dihydrate.

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