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Hydrogen Bonds in Sodium Dialkyldithiocarbamate Hydrates. X-ray Diffraction and Vibrational Spectroscopic Study

K. MEREITER, A. PREISINGER

Institut für Mineralogie, Kristallographie und Strukturchemie, Technische Universität Wien, A-1060 Vienna, Austria

W. MIKENDA and H. STEIDL

Institut für Organische Chemie der Universität Wien, A-1090 Vienna, Austria

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Abstract

Hydrogen bonds in the dithiocarbamates $Na[S_2CN(CH_2)_4]\cdot 2H_2O$, $Na[S_2CN(CH_3)_2]\cdot 2H_2O$ and $Na[S_2CN(C_2H_5)_2]\cdot 3H_2O$ have been studied. While the crystal structures of the first two compounds were known already in sufficient detail, the structure of the third compound has been redetermined by X-ray single crystal diffraction at 295 and 175 K. Crystal data: $Na[S_2CN(C_2H_5)_2]\cdot 3H_2O$, orthorhombic, space group *Pbca*, $Z = 8$; at 295 K $a = 7.612(1)$, $b = 28.583(4)$, $c = 10.457(2)$ Å, $R = 0.041$ for 1561 reflections; at 175 K $a = 7.577(2)$, $b = 28.356(5)$, $c = 10.365(2)$ Å, $R = 0.024$ for 2582 reflections. Besides one O–H···O bond the diethyldithiocarbamate contains five independent O–H···S bonds which with O···S distances of 3.257–3.343 Å (295 K) are similar in length to the O–H···S bonds of the first mentioned two compounds. The Raman spectra of H_2O and isotopically dilute HOD samples of the three given compounds were measured at 295 K and 75 K. The uncoupled O–D frequencies were found in the range $\nu = 2378–2496$ cm^{-1}. Reasonable assignments to the different O–H(D)···S groups are given.

Introduction

Within a systematic spectroscopic and structural study of O–H···S hydrogen bonds in solid hydrates, compounds with quite different kinds of sulfur as proton acceptors, like S^{2-}, PS_4^{3-}, AsS_4^{3-}, SbS_4^{3-} and $S_2O_3^{2-}$, have already been investigated [1–4]. In order to expand this series attention was paid to sodium dialkyldithiocarbamate hydrates. Three compounds were included in this study: (i) sodium tetramethylenedithiocarbamate dihydrate, $Na[S_2CN(CH_2)_4]\cdot 2H_2O$ (= sodium 1-pyrrolidinecarbodithioate dihydrate, denoted Na–1Py), the crystal structure of which is known from neutron and X-ray diffraction investigations [5, 6]; (ii) sodium dimethyldithiocarbamate dihydrate, $Na[S_2CN(CH_3)_2]\cdot 2H_2O$ (denoted Na–Dime), the structure of which was determined by X-ray diffraction [7]; (iii) sodium diethyldithiocarbamate trihydrate, $Na[S_2CN(C_2H_5)_2]\cdot 3H_2O$ (denoted Na–Diet), which also had been subjected to an X-ray diffraction study [8]; since only a preliminary report without atomic coordinates had been published, a redetermination of the crystal structure was, however, necessary. The three given compounds were investigated by Raman spectroscopy.

Experimental

Crystal Structure of $Na[S_2CN(C_2H_5)_2]\cdot 3H_2O$

Structure determination

Reagent grade Na–Diet was recrystallized and two crystals were ground to spheres for the measurements at room temperature (T = 295 K) and at T = 175 K. Cell dimensions and reflection data were measured on a PHILIPS PW1100 four-circle diffractometer with graphite monochromatized Mo-Kα radiation. For data collection at 175 K, which was performed in order to reduce thermal vibration effects and to look for structural changes, a Leybold–Heraeus gas-stream apparatus working with liquid N_2 was used. Salient experimental data are summarized in Table I.

The structure was solved by direct methods using the room temperature diffraction data, which were first available, and the program SHELX76 [9]. After anisotropic refinement of the heavy atoms the hydrogen atom could be located from a difference map. They were subsequently refined as parts of rigid H_2O molecules, CH_2 and CH_3 groups using O and C, respectively, as the reference points and O–H = 0.96 Å, H–O–H = 103.8–109° (calculated from H–O–H = 91.5 + 0.129 × A–O–A, where A–O–A is the angle subtended by the two hydrogen bond

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TABLE I. Crystal Data, Collection of Intensity Data and Least-Squares Refinements for $Na[S_2CN(C_2H_5)_2]\cdot 3H_2O$.

$Na[S_2CN(C_2H_5)_2]\cdot 3H_2O$		
Orthorhombic, space group $Pbca - D_{2h}^{15}$, $Z = 8$		
Temperature	295 K	175 K
a (Å)	7.612(1)	7.577(2)
b (Å)	28.583(4)	28.356(5)
c (Å)	10.457(2)	10.365(2)
V (Å^3)	2275.2	2227.0
D_x (Mg m^{-3})	1.315	1.344
Crystal sphere diameter (mm)	0.33	0.42
λ (Å)	0.7107	0.7107
μ (mm^{-1})	0.46	0.47
θ intervall (°)	2–30	2–30
Absorption correction	small and therefore neglected	
ω scan width, $\Delta\omega$ (°)	1.2	1
Measuring time per reflection, (s)	72	25
Measured reflections	3382	4265
Independent non extinguished reflections	3345	3257
Reflections in final l.s. cycle ($F_o > 6\sigma F_o$)	1561	2582
Number of parameters	134	134
$R = \Sigma(F_o - F_c)/\Sigma F_o$	0.041	0.024
$Rw = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2}$	0.042	0.026
Weighting function		
$w = [\sigma^2(F_o) + C\cdot F_o^2]$, where C equals	0.0002	0.0001

acceptor atoms of each H_2O [10]), C–H = 1.08 Å and H–C–H = 109.5° for the nuclear H positions, while the centres of the usual spherical scattering function of H were placed at O–H = 0.8 Å and C–H = 1.0 Å in order to account for electron density deformation effects of bonded hydrogen [10]. The final refinement simultaneously adjusted 132 structural parameters, a scale factor and a correction for extinction. It converged to $R = 0.041$ for 1561 reflections with $F_o > 6\sigma(F_o)$.

The room temperature results were used as starting values for the l.s. refinement of the 175 K data. This refinement converged to $R = 0.024$ for the 2582 reflections with $F_o > 6\sigma(F_o)$. Neutral atom scattering functions with corrections for anomalous dispersion were used throughout [11].

Results and Discussion

Description of the Structure

Final positional and thermal parameters are given in Table II, selected distances and angles in Table III. The basic building principle of the structure is shown in Fig. 1.

Sodium is coordinated by one S(1) and five H_2O oxygen atoms which define a distorted octahedron. The $NaSO_5$ octahedra share edges and corners to build up the polyhedral layer shown in Fig. 2a. The dithiocarbamate groups are attached to both sides of the latter only via one of their S atoms thus forming puckered sandwich–like triple layers of the composition $Na[S_2CN(C_2H_5)_2]\cdot 3H_2O$. The triple layers extend parallel to (010) and are stacked one above the other in the direction of b via (100) b-glide planes; they are held together only by van der Waals interactions with interlayer H–H contacts $\geqslant 2.38$ Å. With respect to its architecture the structure closely resembles that of Na–1Py [5, 6] and of Na–Dime [7]. These structures are also built up from triple layers formed by the thiocarbamate groups and a network of NaS_2O_4 octahedra. The main differences from the structure of Na–Diet are: lower H_2O content causing different arrangement and connections of the Na coordination octahedra (Fig. 2b); the sulfur atoms equivalent to S(1) of Na–Diet are bonded to two rather than one Na in Na–1Py and Na–Dime; the stacking mode of the triple layers differs from that in Na–Diet, the triple layers in Na–1Py and Na–Dime repeat simply by translation (monoclinic space groups $P2_1/n$ and $P2_1/a$, four formula units per cell in each case).

The three independent water molecules of Na–Diet display approximately tetrahedral coordinations, each of them accepting two bonds and forming two essentially straight hydrogen bonds (Table IIIc).

TABLE II. Atomic Coordinates ($\times 10^5$) and Thermal Parameters U_{ij} ($\times 10^4$) for $Na[S_2CN(C_2H_5)_2]\cdot 3H_2O$.[a]

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na	13095(15)	49335(4)	13855(11)	398(7)	459(7)	360(7)	−20(6)	−30(6)	49(6)
	13048(5)	49345(2)	13816(4)	217(2)	233(2)	199(2)	−11(2)	−17(2)	23(2)
S(1)	35121(10)	42654(3)	−2285(8)	359(4)	366(4)	383(4)	0(4)	21(4)	19(4)
	35170(4)	42646(1)	−2271(3)	195(1)	186(1)	207(1)	−3(1)	11(1)	13(1)
S(2)	9754(11)	35191(3)	5275(9)	346(5)	441(5)	664(6)	−44(4)	116(4)	−11(4)
	9750(4)	35049(1)	5299(3)	181(1)	221(1)	342(2)	−22(1)	52(1)	−7(1)
C(1)	30378(37)	36825(10)	482(25)	319(16)	397(17)	284(17)	−5(13)	−9(12)	−10(14)
	30455(14)	36712(4)	438(9)	178(5)	219(5)	145(5)	−7(4)	−9(4)	−11(4)
N	42843(32)	33567(8)	−1037(24)	352(14)	346(14)	393(15)	7(11)	−3(12)	−22(12)
	43141(12)	33483(3)	−1238(9)	180(5)	179(4)	227(5)	−4(3)	3(4)	−14(4)
C(2)	39578(44)	28576(11)	1026(36)	462(20)	359(17)	691(25)	26(16)	−21(20)	−29(17)
	39821(16)	28413(4)	638(12)	245(6)	181(5)	369(7)	10(5)	−3(5)	−13(5)
C(3)	61176(39)	34692(12)	−4435(33)	280(17)	500(20)	543(22)	15(16)	−25(16)	−44(17)
	61564(14)	34659(4)	−4427(11)	153(5)	253(6)	278(6)	10(4)	1(4)	−38(4)
C(4)	42864(57)	27151(14)	14606(41)	827(30)	577(26)	869(33)	24(22)	−23(26)	264(25)
	42898(19)	26923(5)	14488(14)	420(8)	305(7)	450(6)	12(6)	−16(7)	131(6)
C(5)	64743(44)	34252(14)	−18563(35)	468(21)	723(26)	612(24)	−19(20)	145(20)	−110(21)
	65332(16)	34313(5)	−18770(12)	253(6)	354(7)	308(6)	−6(5)	63(5)	−54(5)
O(1)	13109(29)	43117(8)	28652(19)	465(14)	561(15)	344(13)	−20(13)	29(11)	32(10)
	13219(10)	43063(3)	28648(7)	255(4)	288(4)	193(4)	−11(3)	20(3)	9(3)
O(2)	38539(31)	53071(7)	24141(22)	441(14)	469(12)	390(13)	−24(12)	58(11)	14(11)
	38543(11)	53035(3)	24156(8)	240(4)	248(4)	217(4)	−12(4)	29(3)	4(3)
O(3)	10665(27)	54841(7)	−2628(21)	367(13)	457(13)	425(13)	33(10)	38(11)	65(11)
	10606(11)	54902(3)	−2691(8)	212(4)	232(4)	230(4)	29(3)	25(3)	9(3)

Atom	x/a	y/b	z/c	U_{iso}	Atom	x/a	y/b	z/c	U_{iso}
H(1)	26324	27731	−1845	551(50)	H(9)	56263	36625	−23709	
	26440	27681	−2341	251(16)		57017	36758	−23956	
H(2)	48773	26841	−5249		H(10)	62039	30704	−21519	
	48911	26632	−5739			62774	30769	−22098	
H(3)	63205	38254	−1318		H(11)	3877	42722	34812	660(53)
	64069	38192	−995			3183	42907	34285	456(19)
H(4)	68532	32346	1636		H(12)	12729	40435	23133	
	69212	32177	1158			12435	40395	22976	
H(5)	41175	23400	14816		H(13)	44361	55075	18116	
	41462	23137	14939			44075	54966	17712	
H(6)	33595	28766	21060		H(14)	33363	54958	30735	
	33344	28561	20789			33279	55036	30561	
H(7)	56075	28020	17529		H(15)	4014	57693	−2367	
	56045	27894	17512			4014	57821	−2067	
H(8)	78294	35088	−20597		H(16)	19552	55445	−8929	
	79019	35182	−20446			19228	55495	−9281	

[a] The first line for each atom corresponds to 295 K, the second to 175 K. The temperature factor is of the form $\exp[-2\pi^2(U_{11}h^2 a^{*2} + \ldots + 2U_{23}klb^*c^*)]$. The coordinates of the H atoms were obtained by refining rigid H_2O molecules, CH_2 and CH_3 groups (see text). The e.s.d.s of the rotation angles average for H_2O 2.5° (295 K) and 1.0° (175 K), for CH_2 and CH_3 1.7° (295 K) and 0.6° (175 K).

There are five O–H···S bonds and one O–H···O bond. Function, coordination and bond distances of the water molecules in Na–Diet are similar to the molecules in Na–1Py and Na–Dime, except that these salts exhibit exclusively O–H···S bonds.

The diethyldithiocarbamate anion is shown in Fig. 3. The numbering of the atoms in the S_2CNC_2 moiety follows [8] and the usage of Ymén [5–7, 12]. Bond lengths and angles within the moiety at 295 K agree well with the previously reported values [8]. They also compare well with the figures found for Na–Dime, Na–1Py [5–7] and several other alkali dialkyldithiocarbamate hydrates [12]. The S_2CN moiety is almost exactly planar while moderate deviations from this plane are observed for C(2) and C(3) indicating a small torsion about

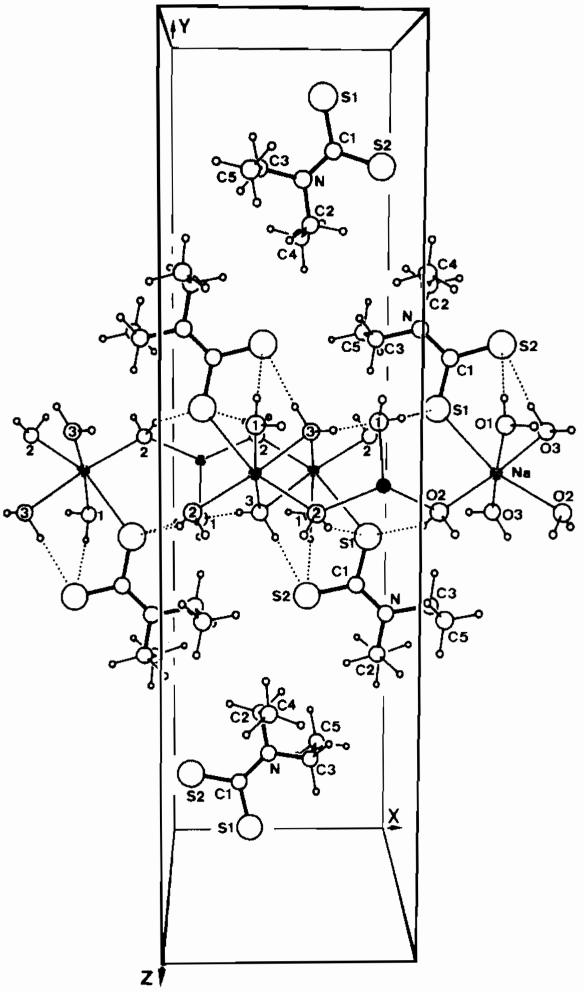

Fig. 1. $Na[S_2CN(C_2H_5)_2]\cdot 3H_2O$. A partial view of the structure.

the C(1)–N bond of ~2° at 295 K and ~3° at 175 K. The difference in length between S(1)–C(1) and S(2)–C(1), considered already by [8], is significant, especially at 175 K, and can be explained by the fact that S(1) is involved in one Na–S and three O–H···S bonds, while S(2) protrudes in the non-polar part of the structure and has only two O–H···S interactions. A very similar situation is met in Na–Dime and Na–1Py where the S(1) atoms with two Na–S and two O–H···S bonds also exhibit significantly larger C–S bond distances than the S(2) atoms which receive two O–H···S bonds.

At room temperature the structure of Na–Diet displays appreciable thermal motion effects which are considerably lowered at 175 K, the U_{ij} values becoming approximately one half of the room temperature values. These changes are accompanied by a decrease of the unit cell dimensions (Table I), increasing bond lengths uncorrected for thermal motion within the $S_2CN(C_2H_5)_2$ group (by 0.007 Å on the average, excluding C–H bonds) and decreasing lengths of the Na–S, O bonds (0.014 Å on the average), hydrogen bonds (0.017 Å on the average) and the van der Waals contacts. Due to lower thermal vibration effects and higher precision of the diffraction data, bond lengths at 175 K are more significant than the room temperature values.

Raman Spectra

Na–1Py was prepared by a literature method [13]; crystals of Na–Dime were kindly provided by I. Ymén, University of Lund; for Na–Diet commercially available material was used. These substances were recrystallized from H_2O and from 95% H_2O + 5% D_2O, respectively. Raman spectra

TABLE III. Selected Distances (Å) and Angles (°) for $Na[S_2CN(C_2H_5)_2]\cdot 3H_2O$.[a]

(a) The $NaS(H_2O)_5$ coordination octahedron

	295 K	175 K
Na–S(1)	3.051(2)	3.033(1)
Na–O(1)	2.356(3)	2.353(1)
Na–O(2)	2.459(3)	2.444(1)
Na–O(2^{i})	2.492(3)	2.469(1)
Na–O(3)	2.341(3)	2.333(1)
Na–O(3^{ii})	2.465(3)	2.448(1)
mean value Na–O	2.423	2.409

(b) The $S_2CN(C_2H_5)_2$ group[b]

	295 K	175 K		295 K	175 K
S(1)–C(1)	1.729(3)	1.743(1)	S(1)–C(1)–S(2)	120.2(2)	120.0(1)
S(2)–C(1)	1.713(3)	1.714(1)	S(1)–C(1)–N	120.2(2)	119.5(1)

(continued on facing page)

TABLE III. *(continued)*

	295 K	175 K		295 K	175 K
C(1)–N	1.339(4)	1.339(2)	S(2)–C(1)–N	119.6(2)	120.5(1)
N–C(2)	1.464(4)	1.472(2)	C(1)–N–C(2)	122.7(3)	121.9(1)
N–C(3)	1.476(4)	1.473(2)	C(1)–N–C(3)	123.2(3)	123.7(1)
C(2)–C(4)	1.498(6)	1.514(2)	C(2)–N–C(3)	114.1(3)	114.4(1)
C(3)–C(5)	1.507(5)	1.517(2)	N–C(2)–C(4)	112.1(3)	111.8(1)
S(1)–S(2)	2.984(1)	2.994(1)	N–C(3)–C(5)	112.8(3)	112.6(1)
S(1)–C(3)	3.027(4)	3.030(1)	S(1)–C(1)–N–C(2)	–179.3(3)	–178.7(1)
S(2)–C(2)	2.988(4)	2.994(1)	S(1)–C(1)–N–C(3)	3.1(3)	4.5(1)
S(1)–H(3)	2.482(31)	2.531(11)	S(2)–C(1)–N–C(2)	1.1(3)	1.7(1)
S(2)–H(1)	2.587(30)	2.567(11)	S(2)–C(1)–N–C(2)	–176.5(3)	–175.2(1)
			C(1)–N–C(2)–C(4)	–89.4(4)	–88.7(2)
			C(1)–N–C(3)–C(5)	–96.7(4)	–97.0(2)

(c) Water molecules and hydrogen bonds[c]
Each first line for 295 K, each second line for 175 K

O H A	H–A	O–A	O–H–A	H–O–H	A–O–A	L	L–O	L–O–L
O(1)–H(11)···$S(1^{i})$	2.319(9)	3.266(2)	169(4)	106.7	118.4(1)	Na	2.356(3)	107.2(1)
	2.312(5)	3.244(1)	164(2)	106.7	118.2(1)		2.353(1)	107.2(1)
O(1)–H(12)···S(2)	2.405(11)	3.343(2)	165(4)			$O(3^{iii})$	2.856(3)	
	2.387(4)	3.330(1)	167(2)				2.830(1)	
O(2)–H(13)···$S(1^{iv})$	2.367(16)	3.277(2)	158(4)	109.0	136.0(1)	Na	2.459(3)	128.7(1)
	2.344(6)	3.258(1)	159(2)	109.0	135.7(1)		2.444(1)	129.4(1)
O(2)–H(14)···$S(1^{iii})$	2.366(14)	3.288(2)	161(4)			Na^{v}	2.492(3)	
	2.356(6)	3.271(1)	159(2)				2.469(1)	
O(3)–H(15)···$S(2^{ii})$	2.308(8)	3.257(2)	170(4)	103.8	95.5(1)	Na	2.341(3)	94.8(1)
	2.307(4)	3.251(1)	168(2)	103.8	95.6(1)		2.333(1)	94.1(1)
O(3)–H(16)···$O(1^{ii})$	1.897(2)	2.856(3)	178(4)			Na^{ii}	2.465(3)	
	1.871(2)	2.830(1)	176(2)				2.448(1)	

[a] Symmetry code: (i) x – ½, y, ½ – z; (ii) –x, 1 – y, –z; (iii) ½ – x, 1 – y, ½ + z; (iv) 1 – x, 1 – y, –z; (v) ½ + x, y, ½ – z. [b] C–H = 1.08 Å and H–C–H = 109.4° were fixed in the refinement of rigid CH_2 and CH_3 groups. [c] O–H = 0.96 Å and H–O–H (°) = 91.5 + 0.129 × A–O–A, where A–O–A is the acceptor–oxygen–acceptor angle, were fixed during the rigid-body refinement of the H_2O molecules.

TABLE IV. Hydrogen Bond Geometry (Room Temperature) and Assignments of Uncoupled O–D Stretching Frequencies (75 K) in Sodium Dialkyldithiocarbamate Hydrates

	H···S	O···S	$\sphericalangle$O–H···S	$\tilde{\nu}_{OD}$
Na[$S_2CN(CH_2)_4$]·$2H_2O$	2.222 Å	3.209 Å	173°	2378 cm^{-1}
(neutron diffraction, [5])	2.290	3.251	175	2467
	2.343	3.291	171	2496
	2.359	3.308	168	2496
Na[$S_2CN(CH_3)_2$]·$2H_2O$		3.210		2418
(X-ray diffraction, [7])		3.261		2422
		3.282		2494
		3.312		2494
Na[$S_2CN(C_2H_5)_2$]·$3H_2O$	2.308	3.257	170	2428
(X-ray diffraction, this work)	2.319	3.266	169	2428
	2.366	3.288	161	2474
	2.367	3.277	158	2474
	2.405	3.343	165	2484
O–H···O bond	1.897	2.856	178	2493

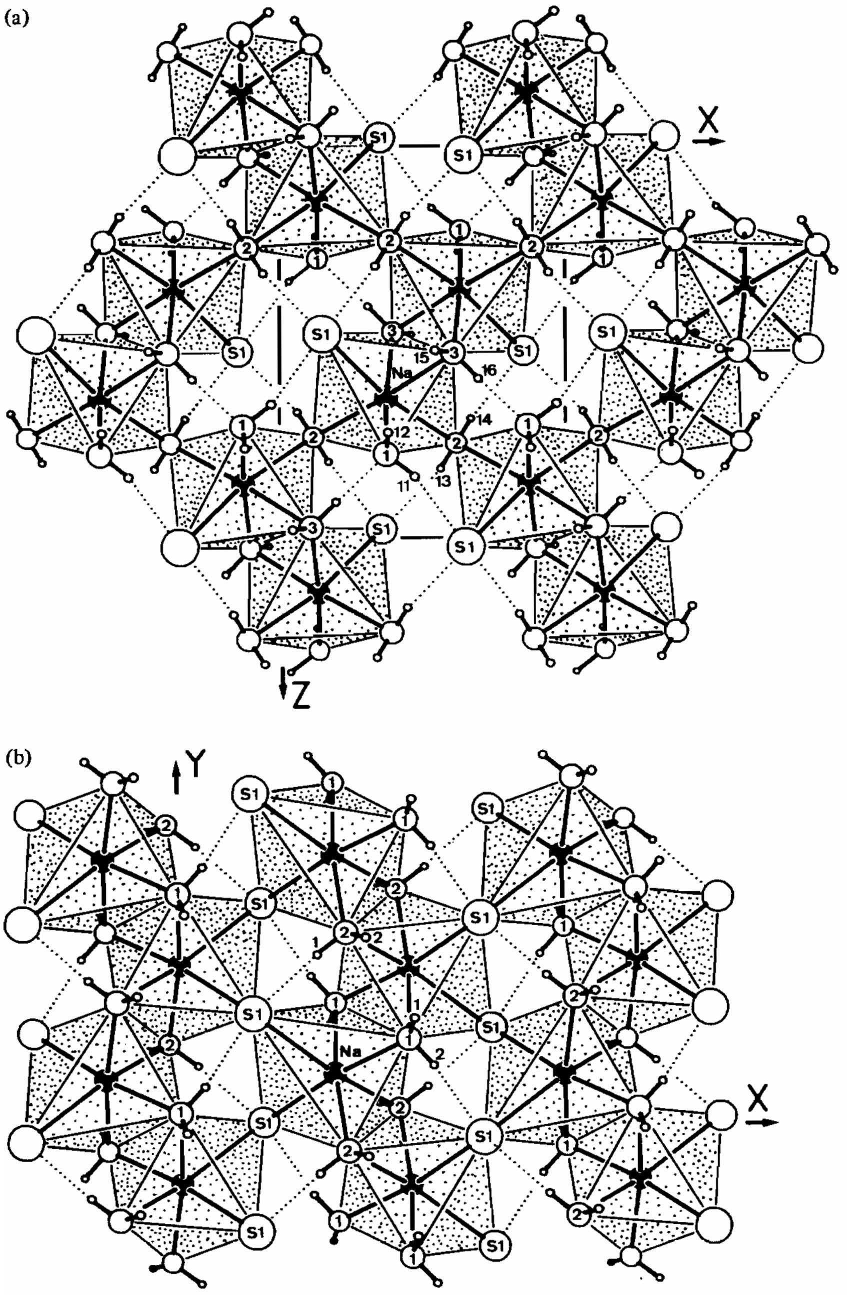

Fig. 2. Arrangement and connection of the Na coordination octahedra in (a) $Na[S_2CN(C_2H_5)_2]\cdot 3H_2O$ and in (b) $Na[S_2CN(CH_2)_4]\cdot 2H_2O$ [ref. 7].

of the H_2O and of the isotopically dilute HOD containing crystals were measured at 295 K and 75 K with standard Raman spectroscopic and low temperature equipment [3]. For the advantages of the isotopic dilution technique the reader is referred to [14].

Since a detailed consideration of the total spectra is outside the scope of this paper, only the O–D(H) stretching frequencies will be discussed here. It should be noted, however, that no unusual differences were observed between the room temperature and the low temperature spectra of either of the three compounds within the entire frequency range. Phase transitions can, therefore, be excluded as shown already for Na–1Py by the X-ray diffraction work at 295, 150 and 27 K [6]. The ranges of O–D(H) stretching frequencies of isotopically dilute HOD molecules ('uncoupled frequencies') and of the H_2O molecules, respectively, in all three compounds are depicted in Fig. 4.

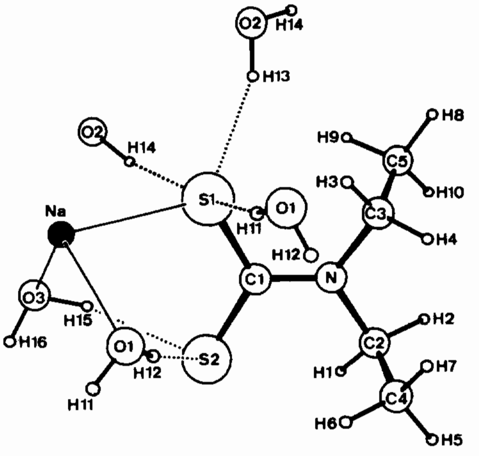

Fig. 3. Na[$S_2CN(C_2H_5)_2$]·$3H_2O$. View of the diethyldithiocarbamate group with the Na and H_2O bonded to its S atoms.

The structures of Na–1Py and Na–Dime each contain two independent water molecules which form pairs of O–H···S bonds [5–7]. Na–Diet contains three independent water molecules with five O–H···S and one O–H···O bonds. Hydrogen bond lengths are given in Table IV together with the assignments of the uncoupled O–D frequencies to the different O–D···S,O groups. These assignments were obtained as in previous works [3] by assuming a fairly monotonic relationship between bond distances and O–D frequencies for a given kind of proton acceptor. In either of the three compounds studied here, the number of O–D frequencies observed in the spectra was less than the number of crystallographically independent O–H(D) groups, which is obviously due to overlap of closely adjacent lines. Comparing the geometric and spectroscopic data of Table IV with corresponding data on O–H(D)···S bonds previously obtained [1–4, 10, and references cited therein], one may note two facts. (i) In previously investigated compounds O···S bond distances of 3.19–3.54 Å (mean value 3.34 Å; these figures are from 47 O–H(D)···S bonds excluding bifurcated ones) were found, while O···S values in the dithiocarbamates cover only the lower range of 3.21–3.34 Å (mean value 3.27 Å). (ii) At comparable bond distances the uncoupled O–D frequencies of the sodium dithiocarbamate hydrates are very similar to those of the XS_4^{3-} (X = P, As, Sb) compounds [2, 3].

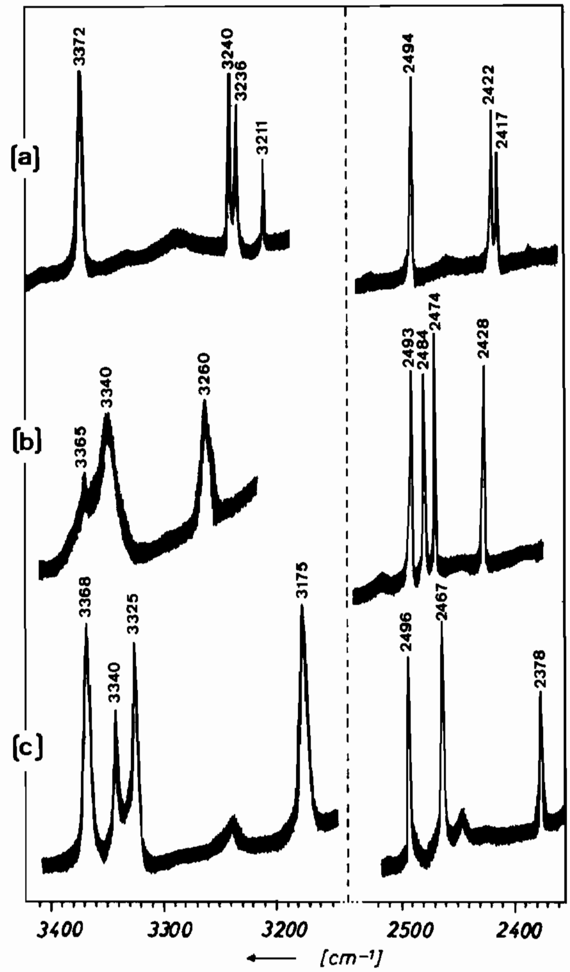

Fig. 4. Raman spectra (T = 75 K; λ_{exc} = 647.1 nm; slit width < 3 cm^{-1}). Range of O–H and O–D stretching frequencies of isotopically diluted samples (95% H_2O + 5% D_2O) of: (a) Na[$S_2CN(CH_2)_4$]·$2H_2O$, (b) Na[$S_2CN(C_2H_5)_2$]·$3H_2O$ and (c) Na[$S_2CN(CH_3)_2$]·$2H_2O$.

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References

1 K. Mereiter, A. Preisinger, A. Zellner, W. Mikenda and H. Steidl, *J. Chem. Soc., Dalton Trans.*, 1275 (1984).
2 K. Mereiter, A. Preisinger, A. Zellner, W. Mikenda and H. Steidl, *Inorg. Chim. Acta, 72,* 67 (1983).
3 W. Mikenda, H. Steidl and A. Preisinger, *J. Raman Spectrosc., 12,* 217 (1982).
4 W. Mikenda and H. Steidl, *Spectrochim. Acta, Part A:, 38,* 1059 (1982).
5 I. Ymén, *Acta Crystallogr., Sect. B:, 38,* 2671 (1982).
6 J. Albertsson, N. Oskarsson, K. Ståhl, C. Svensson and I. Ymén, *Acta Crystallogr., Sect. B:, 36,* 3072 (1980).
7 A. Oskarsson and I. Ymén, *Acta Crystallogr., Sect. C:, 39,* 66 (1983).

8 M. Colapietro, A. Domenicano and A. Vaciago, *Chem. Commun.*, 572 (1968).

9 G. M. Sheldrick, 'SHELX76', University of Cambridge, 1976.

10 K. Mereiter, A. Preisinger, O. Baumgartner, G. Heger, W. Mikenda and H. Steidl, *Acta Crystallogr., Sect. B:, 38,* 401 (1982).

11 'International Tables for X-ray Crystallography, Vol. IV', Kynoch Press, Birmingham, 1974.

12 I. Ymén, *Ph.D. Thesis,* University of Lund, 1983.

13 K. Glen and R. Schwab, *Angew. Chem., 62,* 320 (1950).

14 H. Falk and O. Knop, in F. Franks (ed.), 'Water, a Comprehensive Treatise, Vol. 2', Plenum, New York, 1973, p. 55.