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The Structure of Sodium 1-Pyrrolidinecarbodithioate Dihydrate at 295, 150 and 27 K: A Study of Conformational Reorientation

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Abstract

The structure of $\text{Na}[\text{S}_2\text{CN}(\text{CH}_2)_4] \cdot 2\text{H}_2\text{O}$ has been determined at 295, 150 and 27 K. The crystals are monoclinic, space group $P2_1/a$, $Z = 4$ with: 295 K, $a = 12.121$ (4), $b = 5.789$ (1), $c = 14.008$ (2) Å, $\beta = 98.58$ (2)°; 150 K, $a = 12.050$ (4), $b = 5.767$ (2), $c = 13.937$ (5) Å, $\beta = 98.41$ (3)°; 27 K, $a = 11.938$ (22), $b = 5.716$ (6), $c = 13.893$ (48) Å, $\beta = 98.56$ (25)°. Final $R = 0.031$, 0.050 and 0.056 at 295, 150 and 27 K, respectively. Only minor changes in the crystal and molecular geometry are observed between the three temperatures. Conformational reorientation of the pyrrolidiny ring in the room-temperature solid persists down to 150 K, but at 27 K the molecules are ordered in only one of the orientations. As a result an apparent C–C distance of 1.39 Å at 295 K increases to 1.51 Å at 27 K. Each Na^+ ion is surrounded by four water O atoms and two S atoms forming a distorted octahedron. The coordination polyhedra share edges and corners in layers parallel to the ab plane. Along c the structure is held together by van der Waals forces between the pyrrolidiny rings. The carbodithioate ion acts as a unidentate ligand and each S atom is an acceptor of two hydrogen bonds.

Introduction

Substituted dithiocarbamate ligands, $-\text{S}_2\text{CN}(\text{RR}')$, form complexes with a variety of metals. The importance of this ligand in coordination chemistry stems partly from its ability to stabilize high formal oxidation states on

the metal. The dithiocarbamate ligand has a delocalized π -orbital system, in which electron density can be transferred from N to S. The net effect is a high electron density in the metal–sulphur bond, which is not reflected in the formal oxidation number.

It has been suggested that the anomalous magnetic behaviour of Fe^{III} dithiocarbamates is due to such an electronic rearrangement (Eley, Myers & Duffy, 1972; Gregson & Doddrell, 1975). One of our research projects aims to correlate magnetic behaviour with geometrical and bonding features for Fe^{III} dithiocarbamates (Albertsson, Elding & Oskarsson, 1979). Knowledge of the precise geometry of a dithiocarbamate ligand in a structure with small metal–ligand interaction would facilitate such a comparison. A sodium dithiocarbamate hydrate is suitable for the investigation since Na^+ does not interact with the delocalized π -orbital system of the ligand and forms weaker complexes with the S atoms than with water O atoms. Only one alkali-metal dithiocarbamate hydrate structure has so far been determined by X-ray crystallography (Colapietro, Domenicano & Vaciago, 1968).

Atomic parameters derived from room-temperature X-ray crystallographic experiments have systematic errors due to the thermal motion of the atoms. Bond distances and angles calculated from such parameters will thus also be in error. Corrections for libration and/or riding motion, when applicable, can improve the accuracy of bond distances and angles, but the problem is to find a good model for the correlation of atomic motion. Furthermore, these corrections are based on the usually inaccurate thermal parameters.

This paper reports the crystal structure of $\text{NaS}_2\text{CN}(\text{CH}_2)_4 \cdot 2\text{H}_2\text{O}$ at 295, 150 and 27 K and shows the advantage of low-temperature crystallography in that uncertain models of atomic motion can be avoided.

Experimental

Sodium 1-pyrrolidinecarbodithioate dihydrate, $\text{NaS}_2\text{CN}(\text{CH}_2)_4 \cdot 2\text{H}_2\text{O}$, was prepared by dissolving the ammonium salt in 1.0 M NaOH. Crystals were obtained on evaporation under reduced pressure at room temperature. Recrystallization from an aqueous solution gave colourless plates.

Weissenberg photographs taken at 295 and 100 K revealed the Laue class $2/m$ and the systematic extinctions $0k0$, $k \neq 2n$ and $h0l$, $h \neq 2n$, consistent with the space group $P2_1/a$. Cell dimensions (Table 1) were obtained by least squares from θ values determined as $\theta_{hkl} = (\omega_{hkl} - \omega_{\bar{h}\bar{k}\bar{l}})/2$, with a CAD-4 diffractometer in the bisecting mode and measuring $\omega_{\bar{h}\bar{k}\bar{l}}$ at negative θ angle.

Intensities were collected with the diffractometer at 295, 150 and 27 K. All independent reflexions in the interval $4 < \theta < 70^\circ$ were measured with Ni-filtered Cu $K\alpha$ radiation at room temperature. The data set at 150 K was obtained with a gas-stream apparatus working with $\text{N}_2(I)$ (Danielsson, Grenthe & Oskarsson, 1976), and the data set at 27 K with a Be-walled conduction-cooling He(I) cryostat (Albertsson, Oskarsson & Ståhl, 1979). In the low-temperature experiments Zr-filtered Mo $K\alpha$ radiation was used, and all geometrically accessible independent reflexions in the interval $3 < \theta < 27^\circ$ were measured, while for $\theta > 27^\circ$ only reflexions with an intensity larger than a calculated minimum value (based on the room-temperature structure) were considered. Since the κ motion of the goniometer is restricted to $\pm 60^\circ$ by the He(I) transfer line and the goniometer head, the 27 K data set is not quite complete even though two crystals, mounted in different orientations, were used. Instrumental and crystal stabilities were checked by measuring three standard reflexions at regular intervals. Table 1 gives information concerning the collection and reduction of the data sets and the refinements of the crystal structures. The intensities (I) were calculated by the peak-location method (Lehmann & Larsen, 1974). The values of I and $\sigma_c(I)$ were corrected for Lorentz, polarization and absorption effects, the latter by numerical integration [$\sigma_c(I)$ is based on counting statistics]. The data set obtained with the Be-walled cryostat was corrected for absorption in the Be walls, and some weak reflexions close to strong Be powder lines were excluded (Albertsson, Oskarsson & Ståhl, 1979).

The positions of the non-hydrogen atoms were determined from the room-temperature data set with *MULTAN* (Germain, Main & Woolfson, 1971). The

Table 1. Crystal data, collection and reduction of intensity data and least-squares refinements at 295, 150 and 27 K

Temperature (K)	295	150	27
Crystal size (mm)	0.190 × 0.375 × 0.070	0.325 × 0.435 × 0.060	0.140 × 0.265 × 0.070 0.380 × 0.240 × 0.090
a (Å)	12.121 (4)	12.050 (4)	11.938 (22)
b (Å)	5.789 (1)	5.767 (2)	5.716 (6)
c (Å)	14.008 (2)	13.937 (5)	13.893 (48)
β (°)	98.58 (2)	98.41 (3)	98.56 (25)
V (Å ³)	971.8	958.0	937.5
D_x (Mg m ⁻³)	1.407	1.423	1.449
λ (Å)	1.5418	0.71069	0.71069
μ (mm ⁻¹)	4.9	0.54	0.55
Range of transmission factor	0.319–0.733	0.818–0.956	0.913–0.956
θ interval (°)	4–70	3–45	3–50
ω - 2θ scan width, $\Delta\omega$ (°)	0.85 + 0.4 tan θ	0.85 + 0.5 tan θ	1.0 + tan θ
$\sigma_c(I)/I$ requested in a scan	0.028	0.028	0.070
Maximum recording time (s)	180	180	120
Number of reflexions with zero weight	392	1700	1698
Number of reflexions in final LS cycle, m [$I > 2\sigma_c(I)$]	1522	2237	1461
Number of parameters refined, n	138	137	138
$R = \sum \Delta F / \sum F_o $ *	0.031	0.050	0.056
$R_w = [\sum w(\Delta F)^2 / \sum w F_o ^2]^{1/2}$	0.033	0.052	0.066
$S = [\sum w(\Delta F)^2 / (m - n)]^{1/2}$	0.72	0.89	0.99
Temperature (K)	295	150	27
C_1 (weighting function)	0.008	0.010	0.032
C_2 (weighting function)	0.800	1.200	2.000
$g \times 10^{-4}$ (extinction)	0.08 (2)	—	—

$$* \Delta F = |F_o| - |F_c|.$$

positions of the water H atoms were located in a difference synthesis and the positions of the methylene H atoms were calculated from geometrical considerations and included in the refinements. The refined room-temperature parameters were used as a starting point for the refinement of the 150 and 27 K data sets.

The structures were refined by full-matrix least squares, minimizing $\sum w(|F_o| - |F_c|)^2$ with weights $w = [\sigma_c^2/4|F_o|^2 + (C_1|F_o|^2 + C_2)]^{-1}$ and with C_1 and C_2 adjusted so that constant values of $\langle w(|F_o| - |F_c|)^2 \rangle$ were obtained in different $|F_o|$ and $\sin \theta$ intervals. Scattering factors, with corrections for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974). Only the room-temperature data were corrected for extinction, since no such effects were observed at the lower temperatures. The anisotropic temperature factors for O(1) and O(2) are not positive definite at 27 K. However, the eigenvalues are in both cases zero within 1σ . δR plots comparing observed and calculated structure amplitudes are given in Fig. 1 (Abrahams & Keve, 1971). The final positional and thermal parameters are given in Tables 2 and 3. Tables 4 and 5 give selected bond distances and angles.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35493 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final atomic coordinates at 295, 150 and 27 K*

The first line for each atom corresponds to 295 K, with following lines at decreasing temperatures. The B values for the non-hydrogen atoms were calculated from the anisotropic temperature factor coefficients.

	x	y	z	B (Å ²)
Na	0.5778 (1)	0.7407 (2)	0.4809 (1)	2.73 (3)
	0.5775 (1)	0.7410 (2)	0.4808 (1)	1.73 (2)
	0.5773 (2)	0.7417 (4)	0.4809 (1)	0.49 (6)
O(1)	0.5948 (2)	0.4165 (3)	0.5911 (1)	3.02 (5)
	0.5955 (2)	0.4168 (4)	0.5906 (2)	1.98 (5)
	0.5974 (4)	0.4161 (8)	0.5903 (3)	0.75 (12)
O(2)	0.5400 (2)	1.0968 (3)	0.4030 (1)	3.08 (5)
	0.5388 (2)	1.0974 (4)	0.4024 (2)	1.92 (5)
	0.5365 (4)	1.0983 (7)	0.4012 (3)	0.58 (11)
S(1)	0.7402 (1)	0.4625 (1)	0.3868 (1)	2.45 (2)
	0.7401 (1)	0.4616 (1)	0.3871 (1)	1.63 (1)
	0.7386 (1)	0.4596 (3)	0.3872 (1)	0.42 (3)
S(2)	0.8437 (1)	0.2475 (1)	0.2250 (1)	3.66 (2)
	0.8437 (1)	0.2433 (2)	0.2240 (1)	2.37 (2)
	0.8391 (1)	0.2355 (3)	0.2221 (1)	0.55 (4)
C(1)	0.7513 (2)	0.4339 (4)	0.2653 (2)	2.39 (6)
	0.7506 (2)	0.4332 (5)	0.2646 (2)	1.55 (6)
	0.7467 (5)	0.4270 (11)	0.2636 (4)	0.83 (15)
N	0.6863 (2)	0.5625 (4)	0.2018 (1)	3.02 (6)
	0.6856 (2)	0.5607 (5)	0.2010 (2)	1.99 (6)
	0.6795 (4)	0.5561 (9)	0.2002 (3)	0.56 (12)
C(2)	0.6907 (3)	0.5622 (7)	0.0969 (2)	4.39 (9)
	0.6897 (3)	0.5598 (8)	0.0958 (2)	2.77 (8)
	0.6829 (5)	0.5543 (11)	0.0934 (4)	0.71 (15)
C(3)	0.6025 (3)	0.7279 (7)	0.2256 (2)	4.53 (9)
	0.6008 (3)	0.7289 (8)	0.2253 (3)	3.00 (9)
	0.5913 (6)	0.7207 (13)	0.2254 (5)	1.04 (17)
C(4)	0.6152 (5)	0.7572 (9)	0.0604 (2)	7.72 (16)
	0.6147 (5)	0.7604 (11)	0.0595 (3)	5.28 (15)
	0.6089 (6)	0.7610 (13)	0.0578 (4)	1.22 (17)
C(5)	0.5451 (6)	0.8056 (13)	0.1281 (3)	11.02 (30)
	0.5390 (5)	0.7893 (13)	0.1275 (3)	6.55 (19)
	0.5215 (6)	0.7755 (13)	0.1259 (4)	1.18 (17)
H(1O1)	0.612 (5)	0.501 (10)	0.637 (4)	5.0
	0.613 (4)	0.475 (10)	0.640 (4)	3.0
	0.626 (8)	0.486 (16)	0.624 (6)	1.0
H(2O1)	0.640 (3)	0.316 (7)	0.591 (3)	5.0
	0.642 (4)	0.332 (10)	0.592 (4)	3.0
	0.643 (8)	0.319 (16)	0.586 (6)	1.0
H(1O2)	0.602 (3)	1.197 (7)	0.397 (3)	5.0
	0.590 (4)	1.171 (10)	0.396 (4)	3.0
	0.589 (8)	1.193 (15)	0.391 (6)	1.0
H(2O2)	0.509 (3)	1.111 (7)	0.364 (3)	5.0
	0.500 (4)	1.119 (9)	0.348 (4)	3.0
	0.503 (8)	1.091 (15)	0.346 (6)	1.0
H(1C2)	0.663 (3)	0.405 (7)	0.073 (3)	5.0
	0.657 (4)	0.435 (9)	0.065 (4)	3.0
	0.652 (7)	0.397 (15)	0.063 (6)	1.0
H(2C2)	0.762 (3)	0.569 (7)	0.085 (3)	5.0
	0.762 (4)	0.569 (9)	0.088 (4)	3.0
	0.754 (8)	0.568 (15)	0.080 (6)	1.0
H(1C3)	0.558 (3)	0.648 (7)	0.270 (3)	5.0
	0.556 (4)	0.654 (9)	0.271 (4)	3.0
	0.555 (8)	0.650 (15)	0.270 (6)	1.0
H(2C3)	0.642 (3)	0.864 (7)	0.254 (3)	5.0
	0.634 (4)	0.857 (10)	0.258 (4)	3.0
	0.614 (8)	0.861 (15)	0.243 (6)	1.0
H(1C4)	0.589 (4)	0.751 (3)	-0.007 (3)	5.0
	0.593 (4)	0.745 (9)	-0.008 (4)	3.0
	0.589 (7)	0.753 (15)	-0.002 (6)	1.0

Table 2 (cont.)

	x	y	z	B (Å ²)
H(2C4)	0.659 (3)	0.933 (7)	0.078 (3)	5.0
	0.674 (4)	0.948 (9)	0.080 (4)	3.0
	0.651 (7)	0.923 (15)	0.078 (6)	1.0
H(1C5)	0.520 (3)	0.725 (7)	0.104 (3)	5.0
	0.468 (4)	0.656 (9)	0.096 (4)	3.0
	0.486 (8)	0.655 (15)	0.110 (6)	1.0
H(2C5)	0.506 (4)	0.955 (8)	0.134 (3)	5.0
	0.507 (4)	0.922 (10)	0.127 (4)	3.0
	0.483 (7)	0.956 (15)	0.135 (5)	1.0

Table 3. *Thermal parameters ($\times 10^4$) with e.s.d.'s*

The form of the temperature factor is $\exp(-\beta_{11}h^2 - 2\beta_{12}hk - \dots)$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
(a) 295 K						
Na	45 (1)	186 (3)	40 (1)	0 (1)	5 (0)	2 (1)
S(1)	39 (1)	233 (3)	26 (0)	3 (1)	5 (0)	7 (1)
S(2)	73 (1)	325 (3)	32 (0)	61 (1)	9 (0)	2 (1)
O(1)	54 (2)	198 (6)	41 (1)	10 (2)	-1 (1)	-11 (2)
O(2)	53 (2)	220 (6)	42 (1)	11 (2)	5 (1)	-6 (2)
N	51 (2)	296 (8)	28 (1)	31 (3)	7 (1)	12 (2)
C(1)	37 (2)	201 (7)	30 (1)	-7 (3)	3 (1)	6 (2)
C(2)	89 (3)	450 (13)	26 (1)	65 (5)	7 (2)	23 (3)
C(3)	80 (3)	436 (13)	40 (1)	98 (5)	6 (2)	22 (4)
C(4)	183 (6)	719 (21)	40 (2)	211 (10)	17 (3)	62 (6)
C(5)	233 (10)	1188 (48)	47 (2)	413 (19)	10 (3)	62 (8)
(b) 150 K						
Na	29 (1)	107 (3)	28 (1)	-1 (1)	4 (0)	0 (1)
S(1)	27 (0)	141 (2)	20 (0)	2 (1)	4 (0)	3 (1)
S(2)	48 (1)	202 (3)	23 (0)	38 (1)	7 (0)	1 (1)
O(1)	37 (1)	113 (7)	29 (1)	4 (3)	-1 (1)	-5 (2)
O(2)	35 (1)	125 (6)	28 (1)	8 (3)	6 (1)	-3 (2)
N	36 (2)	182 (9)	21 (1)	20 (3)	5 (1)	3 (3)
C(1)	26 (1)	121 (8)	20 (1)	-7 (3)	2 (1)	2 (3)
C(2)	56 (2)	262 (13)	21 (1)	42 (5)	5 (1)	11 (4)
C(3)	55 (2)	290 (14)	26 (1)	79 (5)	5 (1)	13 (4)
C(4)	129 (5)	477 (22)	30 (2)	141 (10)	16 (3)	44 (6)
C(5)	134 (6)	701 (32)	33 (2)	241 (12)	3 (3)	25 (7)
(c) 27 K						
Na	6 (2)	19 (8)	11 (1)	-6 (3)	-1 (1)	3 (2)
S(1)	7 (1)	37 (5)	5 (1)	1 (2)	0 (1)	2 (1)
S(2)	13 (1)	33 (5)	7 (1)	11 (2)	2 (1)	4 (1)
O(1)	16 (3)	6 (17)	15 (2)	1 (5)	-5 (2)	-10 (4)
O(2)	10 (3)	1 (16)	14 (2)	2 (5)	-3 (2)	6 (4)
N	11 (4)	28 (17)	10 (3)	2 (6)	1 (2)	-8 (5)
C(1)	14 (5)	30 (21)	16 (3)	-11 (7)	-3 (3)	1 (6)
C(2)	17 (5)	41 (21)	9 (3)	16 (8)	2 (3)	12 (6)
C(3)	16 (5)	87 (26)	14 (3)	23 (8)	1 (3)	2 (7)
C(4)	34 (6)	87 (24)	7 (3)	25 (9)	-1 (3)	-3 (7)
C(5)	30 (5)	68 (26)	11 (3)	29 (8)	-3 (3)	-3 (6)

Results

Crystal packing and Na coordination

The main features of the structure are very similar at the three temperatures. The structure is shown in

Fig. 2 and the atoms within the organic ligand are designated in Fig. 3. Each Na⁺ ion is coordinated by four water O and two S atoms forming a distorted octahedron. Fig. 4 shows a projection of the coordination polyhedron along a pseudo threefold axis. The polyhedra share the edges O(1)—O(1ⁱ) and O(2)—O(2ⁱⁱⁱ) and form zig-zag chains running along *b*.

These chains of octahedra are linked through corner sharing of S(1) to a layer parallel to the *ab* plane (Fig. 5). Along *c* the structure is kept together by van der Waals forces between the pyrrolidinyl rings, the closest contact between methylene H atoms being 2.45 Å; distances given in the text refer to 27 K unless otherwise stated.

One of the triangular faces normal to the projection of Fig. 4 is capped by the non-coordinated S(2ⁱⁱ), which accepts one hydrogen bond (Table 4) from each of the two water molecules O(1) and O(2ⁱⁱⁱ) (Pimentel & McClellan, 1971). On its other side S(2) has no strong interactions but protrudes into a region delimited by pyrrolidinyl rings. The shortest intermolecular S(2)—C distance, to C(5), is 3.900 (9) Å with S(2)—H(2C5) just about equal to the sum of the van der Waals radii.

The two-dimensional net of Na coordination polyhedra is stabilized by OH...S(1) hydrogen bonds, Fig. 2. The surrounding of S(1) is trigonal bipyramidal with C(1) and two Na⁺ ions in the equatorial plane (Fig. 3) and with the water molecules apical. Thus the system OH...S...HO is approximately linear with O—S distances of 3.204 (6) and 3.249 (6) Å.

Table 4. Selected bond distances (Å) with e.s.d.'s at 295, 150 and 27 K

The superscripts (i)–(vi) denote the following transformations applied to the *x, y, z* values given in Table 2:

- (i) $1-x, 1-y, 1-z$
- (ii) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$
- (iii) $1-x, 2-y, 1-z$
- (iv) $\frac{1}{2}-x, y-\frac{1}{2}, 1-z$
- (v) $x+\frac{1}{2}, \frac{1}{2}-y, z$
- (vi) $x, y-1, z$

	295 K	150 K	27 K
S(1)—S(2)	3.018 (1)	3.022 (1)	3.027 (8)
Na—O(1)	2.419 (2)	2.406 (3)	2.392 (6)
Na—O(1 ⁱ)	2.365 (2)	2.357 (3)	2.351 (7)
Na—O(2)	2.345 (2)	2.342 (3)	2.336 (5)
Na—O(2 ⁱⁱⁱ)	2.502 (2)	2.480 (3)	2.455 (8)
Na—S(1)	2.997 (1)	2.982 (2)	2.958 (6)
Na—S(1 ⁱⁱ)	2.954 (1)	2.942 (2)	2.922 (8)
S(1)—C(1)	1.734 (2)	1.737 (3)	1.745 (8)
S(2)—C(1)	1.711 (2)	1.721 (3)	1.713 (7)
C(1)—N	1.326 (3)	1.318 (4)	1.324 (8)
C(2)—N	1.478 (3)	1.473 (4)	1.490 (9)
C(3)—N	1.471 (4)	1.484 (5)	1.492 (9)
C(2)—C(4)	1.495 (6)	1.509 (7)	1.513 (10)
C(3)—C(5)	1.506 (6)	1.496 (6)	1.537 (10)
C(4)—C(5)	1.394 (8)	1.419 (8)	1.511 (10)
S(1)—O(1 ⁱⁱ)	3.290 (2)	3.276 (2)	3.249 (6)
S(1)—O(2 ^{iv})	3.254 (2)	3.239 (2)	3.204 (6)
S(2)—O(1 ⁱⁱⁱ)	3.208 (2)	3.195 (3)	3.180 (9)
S(2)—O(2 ^v)	3.304 (2)	3.293 (3)	3.302 (11)
O(1)—H(1O1)	0.82 (4)	0.77 (5)	0.67 (9)
O(1)—H(2O1)	0.80 (4)	0.74 (5)	0.79 (9)
O(2)—H(1O2)	0.97 (4)	0.76 (5)	0.86 (9)
O(2)—H(2O2)	0.62 (4)	0.83 (5)	0.81 (9)

Table 5. Selected bond angles (°) with e.s.d.'s at 295, 150 and 27 K

	295 K	150 K	27 K
S(1)—C(1)—S(2)	122.30 (14)	121.81 (16)	122.13 (38)
S(1)—C(1)—N	118.69 (18)	119.19 (21)	118.59 (47)
S(2)—C(1)—N	119.01 (17)	119.01 (21)	119.28 (46)
C(1)—N—C(2)	124.12 (23)	124.39 (27)	123.67 (52)
C(1)—N—C(3)	125.06 (20)	124.87 (25)	125.04 (50)
N—C(2)—C(4)	103.16 (26)	103.07 (31)	102.65 (49)
N—C(3)—C(5)	103.30 (33)	102.21 (34)	102.94 (52)
C(3)—C(5)—C(4)	108.13 (54)	107.37 (48)	102.70 (58)
C(2)—C(4)—C(5)	108.90 (39)	106.11 (44)	105.18 (53)
C(2)—N—C(3)	110.81 (22)	110.72 (27)	111.29 (49)
H(1O1)—O(1)—H(2O1)	110 (4)	99 (6)	101 (10)
H(1O2)—O(2)—H(2O2)	103 (5)	100 (6)	98 (8)

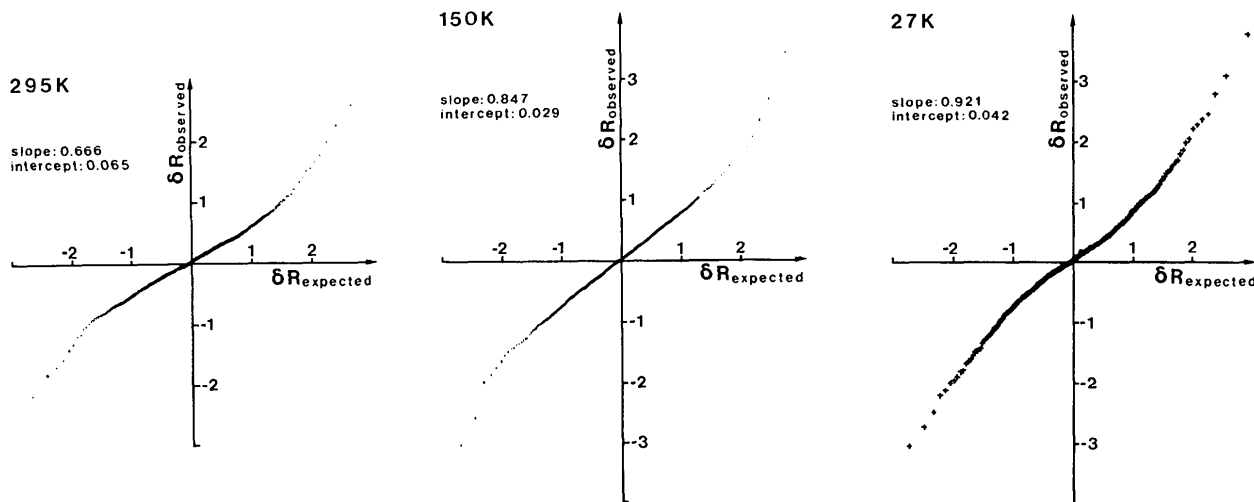


Fig. 1. δR plots comparing model and data after the last cycles of refinement.

Bond distances

The difference in the two C—S distances is consistent with a greater double-bond character of C(1)—S(2), though the latter bond appears shortened due to the libration of S(2). All Na to ligand distances decrease with temperature. The average decreases in the interval 295–27 K are 0.024 (7) for the Na—O and 0.037 (7) Å for the Na—S distances. Within the organic ligand the increases in bond lengths in the interval 295–27 K are <0.03 Å except for C(4)—C(5) which shows a remarkable and highly significant increase of 0.12 Å. The donor–acceptor distances for the hydrogen bonds show the same trend as observed within the coordination polyhedron.

Conformation of the organic ligand

The delocalized π -orbital system should force S(1), S(2), C(1) and N to be coplanar. Deviations from the least-squares plane defined by these atoms are given in Table 6 and it is concluded that this group is equally planar at the three temperatures. C(2), C(3) and C(4), C(5) deviate significantly from this plane (Table 6, Fig. 6) and the deviations increase with decreasing temperature. The interaction between non-bonded methylene H

Table 6. Deviations ($\text{Å} \times 10^4$) with *e.s.d.*'s from the least-squares plane through S(1), S(2), C(1) and N at 295, 150 and 27 K

	295 K	150 K	27 K
S(1)	0 (6)	0 (7)	1 (14)
S(2)	1 (7)	0 (8)	1 (15)
C(1)	-36 (23)	-5 (28)	-32 (59)
N	14 (21)	2 (26)	9 (48)
C(2)*	571 (34)	559 (39)	-763 (62)
C(3)*	-141 (34)	-173 (40)	-696 (70)
C(4)*	2454 (48)	2695 (55)	3277 (66)
C(5)*	-1513 (68)	-2589 (64)	-3726 (68)

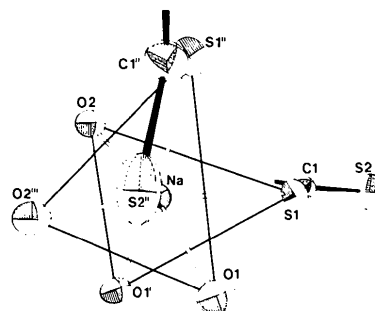


Fig. 4. The coordination polyhedron about Na.

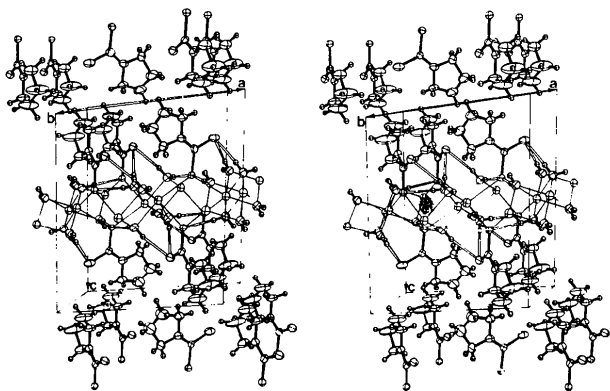


Fig. 2. Stereoscopic view of the unit-cell contents of $\text{NaS}_2\text{CN}(\text{CH}_2)_4 \cdot 2\text{H}_2\text{O}$ at 295 K.

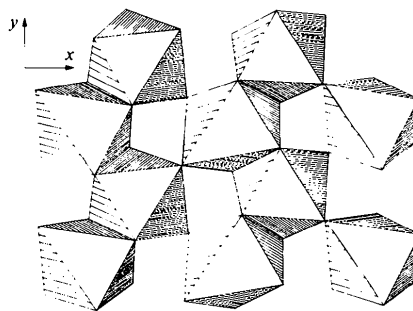


Fig. 5. Packing of the distorted octahedral in the *ab* plane.

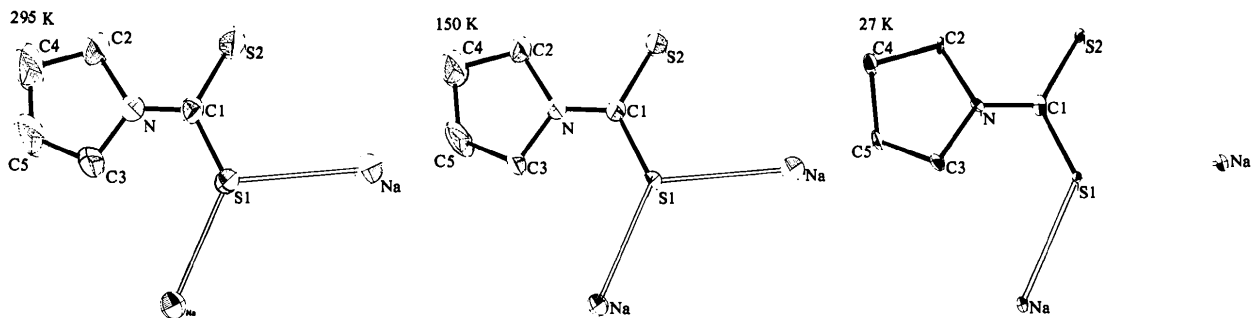


Fig. 3. The ligand viewed along the normal to the least-squares plane at the three different temperatures.

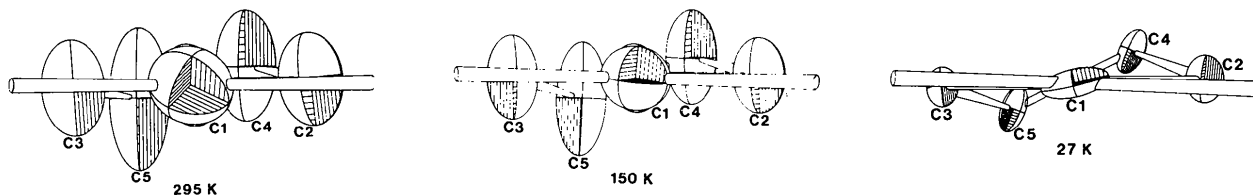


Fig. 6. The ligand viewed along the C(1)–N bond at the three different temperatures. The N atom is hidden by C(1).

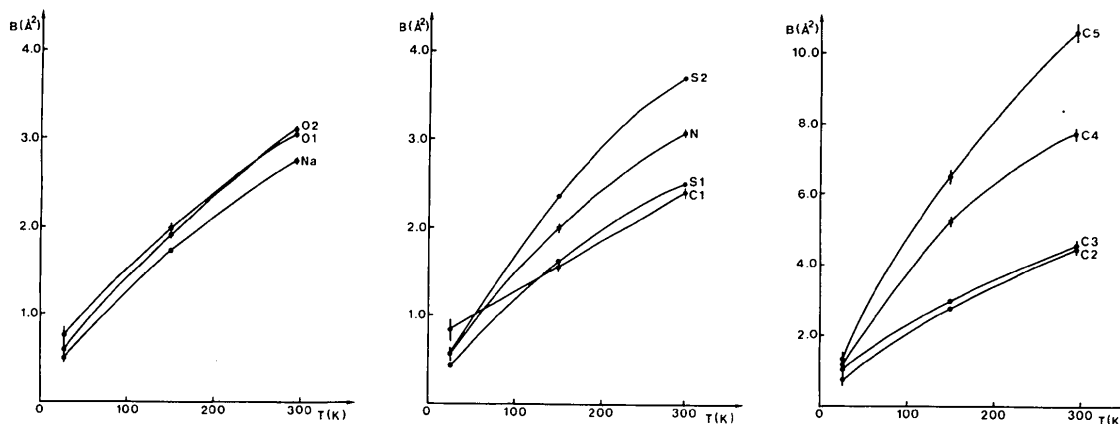


Fig. 7. The isotropic temperature factor coefficients B (Å^2) for the non-H atoms plotted against temperature.

Table 7. Torsion angles ($^\circ$) in the ligand with *e.s.d.*'s at 295, 150 and 27 K

	295 K	150 K	27 K
S(1)–C(1)–N–C(2)	177.3 (2)	177.4 (3)	176.4 (4)
S(2)–C(1)–N–C(3)	179.4 (2)	179.2 (3)	176.8 (5)
S(2)–C(1)–N–C(2)	–2.2 (3)	–2.6 (4)	–3.2 (8)
S(1)–C(1)–N–C(3)	–1.2 (3)	–0.9 (4)	–3.7 (8)
C(1)–N–C(2)–C(4)	–171.9 (3)	–170.7 (3)	–169.1 (5)
C(1)–N–C(3)–C(5)	–174.1 (3)	–170.1 (4)	–166.8 (6)
N–C(2)–C(4)–C(5)	–19.8 (5)	–25.3 (5)	–31.3 (6)
N–C(3)–C(5)–C(4)	–19.9 (5)	–27.9 (5)	–31.8 (6)
C(2)–C(4)–C(5)–C(3)	25.3 (6)	33.9 (6)	39.9 (6)
C(3)–N–C(2)–C(4)	6.8 (4)	7.8 (4)	10.9 (6)
C(2)–N–C(3)–C(5)	7.3 (4)	11.4 (4)	13.1 (7)

atoms may cause the relatively small deviations of C(2) and C(3). Table 7 gives the conformation in terms of torsion angles and, with both the asymmetry parameters of Duax & Norton (1975) and the pseudorotation parameters of Altona, Geise & Romers (1968), it can be seen that the pyrrolidiny ring conformation is best described as a C(4), C(5) half-chair at 27 K. The pseudorotation parameters are $\Delta = -2.5^\circ$ and $\varphi_{\max} = 39.9^\circ$.

Thermal parameters

The influence of temperature on the thermal vibration parameters of the organic ligand is unusually strong and is illustrated in Figs. 3 and 6. The

implication of the C(4) and C(5) parameters on the structural model is discussed below. Thermal parameters are very sensitive to changes in temperature as long as intermolecular, or intramolecular torsional, vibrations are of importance. Isotropic B values, calculated from the anisotropic β_{ij} 's, are plotted as a function of the temperature in Fig. 7. The unexpected curvature may be caused by the larger $\sin \theta/\lambda$ intervals used at lower temperatures and other systematic errors (Albertsson, Oskarsson & Ståhl, 1979).

Discussion

Two models are widely used for making corrections to bond lengths for thermal motion. In the rigid-body model the atoms are tightly bound so that the molecule, or part thereof, vibrates as a rigid body. Bond distances at 295 K corrected for librational motion are compared in Table 8 with both the uncorrected distances and the distances obtained at 27 K. The corrections are based on a TLS analysis of the non-H atoms of the ligand (Schomaker & Trueblood, 1968). Distances are both over- and undercorrected so, on the whole, the uncorrected distances are as good as the corrected ones. This failure of the rigid-body analysis may be caused by the behaviour of C(4) and C(5), which both move individually. The riding-motion model for corrections of bond lengths can be applied on terminating bonds in a molecule. For the present molecule such a

Table 8. Distances (Å) at 295 K, d_o , compared to distances corrected for libration of the molecule, d_r , and to distances at 27 K

$d_r = (r^t M^2 r)^{1/2}$ where $r = (\Delta x', \Delta y', \Delta z')$ in an orthonormalized coordinates system, $M = |1 + \frac{1}{2} \text{Tr}(\mathbf{L})\mathbf{I} - \frac{1}{2}\mathbf{L}|$, and \mathbf{L} is the libration matrix in the same coordinate system (Johnson, 1970).

	d_o (295 K)	d_r	d_o (27 K)
S(1)—C(1)	1.734 (2)	1.734	1.745 (8)
S(2)—C(1)	1.711 (2)	1.722	1.713 (7)
C(1)—N	1.326 (3)	1.344	1.324 (8)
N—C(2)	1.478 (3)	1.478	1.490 (9)
N—C(3)	1.471 (4)	1.483	1.492 (9)
C(2)—C(4)	1.495 (6)	1.520	1.513 (10)
C(3)—C(5)	1.506 (6)	1.516	1.537 (10)
C(4)—C(5)	1.394 (6)	1.394	1.511 (10)

correction results in C(1)—S(1) = 1.737 (2) and C(1)—S(2) = 1.726 (3) Å at 295 K.

Both the hydrogen-bond distances and the metal-donor distances within the coordination polyhedra decrease with decreasing temperature. The S atoms, which accept the hydrogen bonds, are strongly covalently bonded in the organic ligand. Compared to the covalent C—S bond, the hydrogen bond O—H...S must be considered as very weak, and the thermal effect on the O...S distance will be the same as for an intermolecular interaction. The Na—O and Na—S bonds, which are of electrostatic character, may be as strong as the covalent bonds within the organic ligand from the point of view of binding energy, but they do not cause the high correlation between atomic motion as found in the covalent case. Consequently, there should be no observable increase in these bond lengths with decreasing temperature.

Neither the rigid-body nor the riding-motion model can adequately be used for correcting the C(4)—C(5) distance. However, the answer to the problem is obtained from the 27 K experiment. Obviously, the pyrrolidiny ring undergoes conformational re-orientation in the room-temperature solid and down to at least 150 K (Fig. 6). The five-membered ring flips between the two possible C(4),C(5) half-chair conformations. In spite of the anisotropic surrounding of the molecule there is only a small energy difference between the two conformers. At 27 K the conformer with the lowest energy dominates in the structure. The van der Waals contact H(2C5)—S(2) mentioned earlier may have an important role in favouring an ordered arrangement of the rings. The barrier to pseudo-rotation in the pyrrolidine molecule has been estimated to be 2.1×10^{-21} J (McCullough *et al.*, 1959), which is of the same magnitude as kT at 150 K. As the temperature increases from 27 K both conformers will be present in the structure. The transition frequency must be low compared to the X-ray frequency so the

X-ray data at the higher temperatures show for each atom of the ring the convolution of two distinct electron distributions and the thermal vibrations at each site. The resolution of the data, about 0.5 Å at 150 K and 0.8 Å at 295 K, is too low for resolving the two conformers clearly.

It is doubtful if comparison of the geometry of the 1-pyrrolidinecarbodithioate ligand in different crystal structures is meaningful. The C(4)—C(5) distance observed in different structures at room temperature varies from 1.39 to 1.53 Å. The longest distance is found in Ni[S₂CN(CH₂)₄]₂ (Newman, Raston & White, 1973) where an efficient packing restricts the pyrrolidiny ring to one conformation.

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