

Neutron Diffraction Study of Sodium 1-Pyrrolidinecarbodithioate Dihydrate

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Abstract. $\text{Na}[\text{S}_2\text{CN}(\text{CH}_2)_4] \cdot 2\text{H}_2\text{O}$, $M_r = 205.3$, monoclinic, $P2_1/a$, $a = 12.121(4)$, $b = 5.789(1)$, $c = 14.008(2)$ Å, $\beta = 98.58(2)^\circ$, $V = 971.8(9)$ Å³, $Z = 4$, $D_x = 1.407$ g cm⁻³, $\lambda = 1.210$ Å, $R = 0.069$, $R_w = 0.082$ for 1132 observed reflexions. The 1-pyrrolidinecarbodithioate ion has two short intramolecular H...S contacts, 2.85(1) and 2.84(2) Å, somewhat shorter than the expected van der Waals distance. The S atoms and the water molecules form S...H—O hydrogen bonds. The S...H and S...O distances are in the range 2.22(1)–2.36(1) and 3.209(9)–3.308(9) Å, respectively. From a literature survey of O—H...S (O—D...S) bonds studied with neutron diffraction it is concluded that these hydrogen bonds have no detectable effects on the O—H distances.

Introduction. In a systematic study of the geometry of alkali dithiocarbamate compounds, the crystal structure of $\text{Na}[\text{S}_2\text{CN}(\text{CH}_2)_4] \cdot 2\text{H}_2\text{O}$ has been determined previously from X-ray intensities collected at 295, 150 and 27 K (Albertsson, Oskarsson, Ståhl, Svensson & Ymén, 1980). The structural models obtained imply short intramolecular H...S interactions and hydrogen bonding between the water molecules and the S atoms. In order to elucidate these matters a neutron diffraction study has been performed.

Large single crystals of the title compound were slowly grown from small crystals in a saturated aqueous solution placed in a desiccator. The thin, plate-like, colourless crystal used had a volume 23.7 mm³ and was bounded by {100}, {001} and {110}. The cell dimensions were taken from the previous study (Albertsson *et al.*, 1980).

The intensity data collection was made on a Hilger & Watts computer-controlled four-circle diffractometer, equipped with a double monochromator system (Cu₂₂₀), located at the Swedish Atomic Energy Reactor R2, Studsvik, Sweden. The radially output neutron beam has a wavelength of 1.210 Å. The neutron flux at the specimen is about 10⁶ cm⁻² s⁻¹. Table 1 gives information concerning the data collection, data reduction and the least-squares refinements.

About 10 min were spent measuring each reflexion with the ω -2 θ scan technique. Reflexions from slightly more than one quadrant (2147) were measured and reduced to 1967 independent reflexions. The agreement

between symmetry-dependent reflexions was usually better than 85%. Three standard reflexions were checked at regular intervals and no significant variations in their intensities were observed. Background corrections were made according to Lehmann & Larsen (1974). The values of I and $\sigma_c(I)$ were corrected for Lorentz and absorption effects, the latter by numerical integration [$\sigma_c(I)$ is based on counting statistics]. The linear absorption coefficient, μ , was determined from the mean value of absorption measurements on two different crystals, placed in the neutron beam. The value of the corresponding incoherent scattering cross-section for H, 3670 fm², is within the range 2640–5540 fm² given by Tellgren (1975).

The room-temperature parameters for the heavy atoms from the X-ray investigation (Albertsson *et al.*, 1980) were used as a starting point for the full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$ with weights $w = [\sigma_c^2/4|F_o|^2 + (C_1|F_o|)^2 + C_2]^{-1}$. The constants C_1 and C_2 were adjusted so that constant values of $\langle w(|F_o| - |F_c|)^2 \rangle$ were obtained in different $|F_o|$ and $\sin \theta$ intervals. A difference Fourier map revealed H atoms in the positions approximately given by the X-ray measurements. There were also some small minima which may be due to disordered H atoms. However, a refinement of the occupation factors including two positions for each of the H atoms on C(4) and C(5) was not successful. In the final calculations only the positions initially found were refined using anisotropic temperature factors, together

Table 1. *Data collection, data reduction and refinement parameters*

Crystal size (mm)	4.5 × 0.7 × 8.6
Total number of reflexions	2147
Number of independent reflexions	1967
Number of reflexions in final least-squares cycle ($I \geq 3\sigma$)	1132
Number of reflexions with $I < 3\sigma(I)$	799
θ -interval (°)	3–50
Wavelength (Å)	1.210
μ (mm ⁻¹)	0.263 (10)
Range of transmission factors	0.36–0.83
Number of parameters refined	210
$R = \sum AF / \sum F_o $	0.069
R (1931 reflexions)	0.129
$R_w = [\sum w(\Delta F)^2 / \sum w F_o ^2]^{1/2}$	0.082
$S = [\sum w(\Delta F)^2 / (m - n)]^{1/2}$	0.84
C_1 (weighting function)	0.05
C_2 (weighting function)	0.06
$g \times 10^{-4}$ (extinction)	0.36

with two scale factors and one isotropic extinction coefficient. A δR plot comparing observed and calculated structure amplitudes (Abrahams & Keve, 1971) resulted in $\delta R_{\text{observed}} = 0.763(2) \delta R_{\text{expected}} + 0.056(2)$ and a correlation coefficient 0.997.

During the refinements it was observed that some of the weak reflexions had much larger $|F_{\text{obs}}|$ than $|F_{\text{calc}}|$. To see if this was due to the Renninger effect, the 36 most strongly affected reflexions were re-measured at four new ψ -angles. In none of the 4×36 cases could any significant intensity be found, and all 36 were deleted. Of the remaining 1931 reflexions, 16 had an isotropic extinction correction larger than 5% in $|F_{\text{obs}}|$, with the largest corrections for 003 (21%) and 202 (18%). These two reflexions were deleted. The coherent scattering lengths were taken from Bacon (1972).

Positional parameters are given in Table 2.* Half-normal probability plots comparing positional and thermal parameters for the non-H atoms obtained in the neutron and X-ray studies have been made (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972).

Both plots are linear with correlation coefficients 0.995 and 0.993 for the positional and thermal parameters, respectively. The intercepts 0.06(2) and 0.04(2) indicate very small systematic differences

* Lists of structure factors, anisotropic temperature factors and distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36906 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positional parameters and isotropic thermal parameters with e.s.d.'s in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Na	0.5780 (5)	0.7417 (11)	0.4809 (4)	2.7 (1)
S(1)	0.7403 (5)	0.4610 (13)	0.3864 (4)	2.3 (2)
S(2)	0.8435 (7)	0.2450 (16)	0.2241 (5)	3.3 (2)
O(1)	0.5952 (3)	0.4160 (8)	0.5912 (3)	2.9 (1)
O(2)	0.5394 (4)	1.0976 (7)	0.4025 (3)	2.8 (1)
N	0.6858 (2)	0.5628 (5)	0.2013 (1)	2.9 (1)
C(1)	0.7510 (2)	0.4341 (6)	0.2649 (2)	2.3 (1)
C(2)	0.6917 (4)	0.5602 (10)	0.0977 (3)	4.3 (1)
C(3)	0.6028 (4)	0.7266 (10)	0.2254 (3)	4.4 (1)
C(4)	0.6156 (7)	0.7593 (16)	0.0591 (3)	7.8 (2)
C(5)	0.5408 (9)	0.7958 (21)	0.1285 (4)	10.3 (3)
H(1C2)	0.6651 (13)	0.4029 (28)	0.0668 (7)	8.1 (4)
H(2C2)	0.7740 (10)	0.5932 (30)	0.0856 (8)	8.4 (4)
H(1C4)	0.5905 (11)	0.7580 (26)	-0.0164 (6)	8.1 (4)
H(2C4)	0.6718 (17)	0.9228 (38)	0.0759 (15)	11.8 (7)
H(1C5)	0.4759 (10)	0.6616 (37)	0.1079 (12)	9.3 (6)
H(2C5)	0.4933 (14)	0.9482 (29)	0.1279 (8)	9.7 (5)
H(1C3)	0.5487 (8)	0.6468 (24)	0.2690 (7)	6.8 (3)
H(2C3)	0.6438 (11)	0.8650 (23)	0.2681 (9)	7.2 (3)
H(1O1)	0.6187 (6)	0.5088 (14)	0.6502 (5)	4.1 (2)
H(2O1)	0.6488 (7)	0.2940 (15)	0.5944 (5)	4.2 (2)
H(1O2)	0.6008 (7)	1.1986 (14)	0.3950 (6)	4.3 (2)
H(2O2)	0.4857 (7)	1.1234 (15)	0.3454 (6)	4.4 (2)

between the two studies. The deviations from unity of the slopes, 1.46 (3) and 1.31 (2), are most probably caused by underestimated pooled standard deviations.

Discussion. Selected bond distances and bond angles are given in Table 3. In Fig. 1 the atoms in the asymmetric unit are depicted. The dithiocarbamate ion acts as a monodentate ligand. Na⁺ is surrounded by four water O atoms and two S atoms forming a distorted octahedron. These polyhedra share edges and corners to form layers parallel to the *ab* plane. Along *c* the structure is kept together by van der Waals bonds between the pyrrolidiny rings (Albertsson *et al.*, 1980). Both S atoms are involved in the S...H—O hydrogen-bond system, where they each accept two hydrogen bonds. The O...S distances vary from 3.21 (1) to 3.30 (1) Å and the H...S distances from 2.22 (1) to 2.36 (1) Å (Table 4). Expected van der Waals distances are 3.3 and 3.0 Å, respectively (Bondi, 1964). Thus, the operational criterion for hydrogen bonds given by Hamilton & Ibers (1968) is fulfilled. Both water O atoms are approximately tetrahedrally surrounded by their two H atoms and two Na atoms (class 2A water molecules according to Ferraris & Franchini-Angela, 1972). The O—H distances range from 0.96 (1) to 0.99 (1) Å with a mean value of 0.97 (1) Å. The H—O—H angles are the same within experimental errors, with an average of 104.6 (1)°. At room temperature the dimensions of an isolated water molecule are O—H = 0.9724 Å and H—O—H = 104.52° (Kuchitsu, 1966, 1971). It is concluded that the coordination to Na⁺ and the hydrogen bonding to S have no detectable effects on the geometry of the water molecules.

The hydrogen-bond parameters from this study, together with those obtained from six other crystal structures examined by neutron diffraction, are compiled in Table 4. From this table the O...S distances have been plotted against the H...S distances in Fig. 2. The equation for the straight line is $y = 1.16(11)x +$

Table 3. *Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses*

Symmetry code: (i) $1 - x, 1 - y, 1 - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (iii) $1 - x, 2 - y, 1 - z$.

S(1)—S(2)	3.024 (10)	S(1)—C(1)	1.732 (7)
Na—O(1)	2.426 (8)	S(2)—C(1)	1.724 (9)
Na—O(1 ⁱ)	2.372 (7)	C(1)—N	1.328 (4)
Na—O(2)	2.349 (8)	C(2)—N	1.464 (4)
Na—O(2 ⁱⁱⁱ)	2.500 (7)	C(3)—N	1.459 (6)
Na—S(1)	3.007 (9)	C(2)—C(4)	1.523 (10)
Na—S(1 ⁱⁱ)	2.949 (9)	C(4)—C(5)	1.440 (11)
		C(3)—C(5)	1.505 (8)
S(1)—C(1)—S(2)	122.1 (4)	N—C(2)—C(4)	103.1 (4)
S(1)—C(1)—N	119.0 (3)	N—C(3)—C(5)	103.4 (5)
S(2)—C(1)—N	119.0 (3)	C(3)—C(5)—C(4)	106.8 (7)
C(1)—N—C(2)	123.2 (3)	C(2)—C(4)—C(5)	106.3 (6)
C(1)—N—C(3)	124.8 (2)	C(2)—N—C(3)	111.9 (3)

Table 4. A survey of some O—H...S hydrogen bonds measured by neutron diffraction

Bonds marked with no or one x were used in the calculation of the mean value. The mean value 0.963 (2) Å is calculated as

$$\bar{x} = \frac{\sum (w_i \cdot x_i)}{\sum (w_i)} \text{ and } \sigma = \left\{ \frac{1}{(n-1)} \left[\frac{\sum (w_i \cdot x_i^2)}{\sum w_i} - \bar{x}^2 \right] \right\}^{1/2} \text{ where } w_i = 1/\sigma_{\text{obs}}^2 \text{ and } x_i = d_{\text{O-H}}$$

x: Deuterium instead of hydrogen, no isotope effects observed.
 xx: Very weak, bifurcated bond.
 xxx: Strong intramolecular bond, $T = 20$ K.

	O—H	H...S	O...S	O—H...S	Reference
	0.991 (9) Å	2.222 (11) Å	3.209 (9) Å	173.5 (7)°	(a)
	0.957 (9)	2.343 (11)	3.291 (8)	170.9 (7)	(a)
	0.964 (9)	2.290 (11)	3.251 (8)	174.9 (7)	(a)
	0.965 (9)	2.359 (12)	3.308 (9)	167.9 (8)	(a)
	0.958 (4)	2.399 (4)	3.351 (3)	172.1 (3)	(b)
	0.960 (4)	2.390 (4)	3.337 (3)	168.4 (3)	(b)
	0.956 (4)	2.418 (5)	3.336 (3)	160.8 (3)	(b)
	0.956 (4)	2.408 (4)	3.359 (3)	172.8 (3)	(b)
	0.960 (5)	2.367 (4)	3.298 (4)	163.0 (3)	(c)
x	0.967 (4)	2.379 (6)	3.343 (6)	175.4 (4)	(d)
x	0.959 (5)	2.403 (7)	3.358 (6)	173.9 (4)	(d)
x	0.961 (5)	2.362 (6)	3.319 (6)	173.2 (4)	(d)
x	0.957 (5)	2.338 (7)	3.293 (6)	175.9 (4)	(d)
xx	0.927 (6)	2.830 (7)	3.588 (4)	139.8 (5)	(d)
xx	0.927 (6)	2.861 (8)	3.594 (6)	137.0 (5)	(d)
x	0.971 (5)	2.359 (5)	3.330 (1)	178.8 (5)	(e)
x	0.969 (6)	2.550 (6)	3.513 (1)	172.3 (5)	(e)
x	0.978 (5)	2.311 (5)	3.284 (1)	173.2 (4)	(e)
x	0.973 (5)	2.294 (5)	3.264 (1)	175.2 (4)	(e)
x	0.975 (5)	2.359 (5)	3.334 (1)	179.8 (4)	(e)
x	0.957 (5)	2.441 (5)	3.391 (1)	171.8 (4)	(e)
x	0.975 (5)	2.262 (6)	3.214 (5)	165.2 (4)	(f)
xxx	1.000 (11)	1.919 (14)	2.860 (11)	155.6 (9)	(g)

References: (a) This work; (b) Lisensky & Levy (1978); (c) Manojlović-Muir (1975); (d) Mereiter, Preisinger & Guth (1979); (e) Preisinger, Mereiter, Baumgartner, Heger, Mikenda & Steidl (1980); (f) Van Roey & Kerr (1981a); (g) Van Roey & Kerr (1981b).

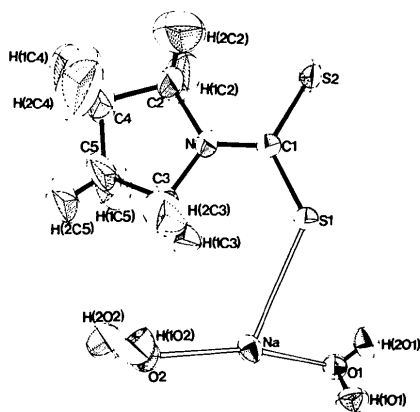


Fig. 1. The asymmetric unit viewed along the normal to the plane defined by S(1), S(2), C(1) and N. The thermal ellipsoids are drawn with 50% probability.

0.92 (5). Supposing that the O—H...S bond is linear and that the O—H distance is unaffected by the hydrogen bonding one should expect the equation $y = 1.0x + 0.963$ (0.963 from Table 4). The rather good correlation (almost within one σ) between the two equations suggests that the O—H...S hydrogen bonds are too weak to significantly affect the O—H distances.

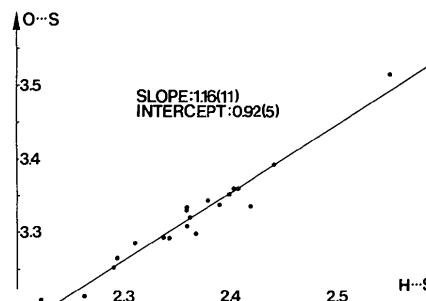


Fig. 2. Observed hydrogen bonds: O...S (Å) plotted against H...S (Å). Only those bonds marked with no or one x in Table 4 were used.

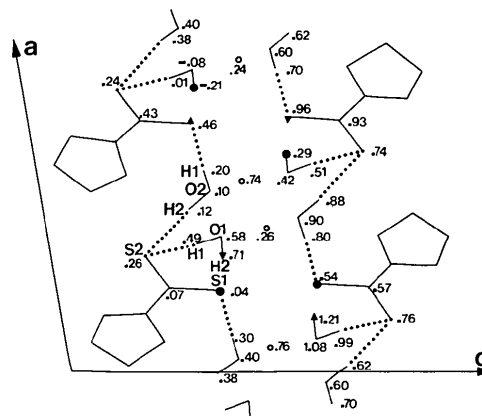


Fig. 3. The hydrogen-bond system: dotted lines indicate the H...S bond, the large dot a H...S connexion downwards and the arrow a H...S connexion upwards.

The hydrogen-bond system is depicted in Fig. 3. Along **b** ligands one unit length apart are connected by H₂O(1) so that spiral-shaped chains —S(2)...H(101)—O(1)—H(201)...S(2)— are formed. Along these chains are connected by H₂O(2).

The C—H distances vary in the range 1.04 (2)—1.17 (2) Å.* The large range of distances is most probably due to systematic errors caused by the conformational reorientation of the pyrrolidine ring at room temperature as discussed in the X-ray study.

The closest intramolecular S...H contacts are S(1)...H(1C3) and S(2)...H(2C2) with distances 2.85 (1) and 2.84 (2) Å, respectively. These values are about 0.15 Å smaller than their van der Waals contact distances (Bondi, 1964) suggesting strong intramolecular H...S interactions.

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* See previous footnote.

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Di- μ -nitrosyl-*trans*-bis[bis(acetylacetonato)ruthenium](*Ru*–*Ru*)

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Abstract. [$\text{Ru}(\text{CH}_3\text{COCHCOCH}_3)_2(\mu\text{-NO})_2$], triclinic, $P\bar{1}$, $a = 10.853(3)$, $b = 12.115(3)$, $c = 9.931(3)$ Å, $\alpha = 89.29(2)$, $\beta = 97.17(2)$, $\gamma = 82.91(2)^\circ$, $D_c = 1.70$, $D_m = 1.70$ Mg m $^{-3}$, $Z = 2$, Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), $\mu = 1.20$ mm $^{-1}$, 3107 reflections with $I > 3\sigma(I)$, $R = 0.040$, $R_w = 0.069$. Two *cis*-[Ru(acac) $_2$] (acac = acetylacetonato) fragments are connected by a double $\mu\text{-N(O)}$ bridge so that each Ru is octahedrally coordinated by four O and two N atoms. The Ru($\mu\text{-NO})_2$ Ru unit is planar and the [Ru(acac) $_2$] fragments are *trans* to one another, giving effective D_2 symmetry to the dimer. The Ru–O distances average 2.031 (24) Å, Ru–N 1.918 (3) Å. The latter distance is indicative of delocalized π -bonding over the Ru($\mu\text{-NO})_2$ Ru unit. The Ru–Ru distance is 2.614 (1) Å, the shortest distance yet reported for an apparently single Ru–Ru bond.

Introduction. One of us recently obtained an oligomeric ruthenium nitrosyl of empirical formula [Ru(acac) $_2(\text{NO})$] $_n$ (acac = acetylacetonato, $n = 2$ or 4) apparently containing bridging nitrosyl groups (Mukaiida, Nomura & Ishimori, 1975). Because of the

stability of the {RuNO} 6 unit bridging nitrosyls are very rare in ruthenium chemistry (Bottomley, 1978), being so far confined to two trimeric clusters, [Ru $_3(\text{CO})_{10}(\mu\text{-NO})_2$] (Norton, Collman, Dolcetti & Robinson, 1972) and [Ru $_3(\text{CO})_7\{\text{PO}(\text{CH}_3)_3\}_3(\mu\text{-H})(\mu\text{-NO})$] (Johnson, Raithby & Zuccaro, 1980). In view of the unusual nature of [Ru(acac) $_2(\text{NO})$] $_n$ we have investigated it crystallographically and shown it to be [$\text{Ru}(\text{acac})_2(\mu\text{-NO})_2$], this formulation being one of those previously suggested (Mukaiida *et al.*, 1975).

Examination of Weissenberg and precession photographs revealed no systematic absences or symmetry elements. Successful refinement was accomplished in $P\bar{1}$. The crystal used for the intensity determination was 0.58 \times 0.42 \times 0.33 mm. Intensities of 3345 independent reflections ($2\theta < 45^\circ$) were measured using graphite-monochromatized Mo $K\alpha$ radiation on a Picker FACS-1 diffractometer, of which 3107 were considered to be observed [$I > 3\sigma(I)$]. These were corrected for absorption (transmission factors ranged from 0.52 to 0.68). Initial atomic coordinates for ruthenium were obtained using the *MULTAN* procedure (Main, Woolfson & Germain, 1971) and the