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Structure of Strontium Thiocyanate Trihydrate, Sr(SCN)₂·3H₂O, at 295 and 125 K

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Abstract. Sr(SCN)₂·3H₂O, $M_r = 257.82$, monoclinic, $P2_1/n$. At $T = 295$ K: $a = 9.501$ (1), $b = 7.140$ (1), $c = 13.470$ (2) Å, $\beta = 94.27$ (1)°, $V = 911.3$ (2) Å³, $Z = 4$, $D_x = 1.879$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 61.4$ cm⁻¹, $F(000) = 504$, final $R = 0.029$ for 1458 independent reflections; at $T = 125$ K: $a = 9.452$ (2), $b = 7.103$ (2), $c = 13.373$ (3) Å, $\beta = 94.51$ (2)°, $V = 895.1$ (4) Å³, $Z = 4$, $D_x = 1.913$ g cm⁻³, $\mu = 62.9$ cm⁻¹, final $R = 0.031$ for 1511 independent reflections. The structure contains SrSN₄(H₂O)₃ polyhedra which are linked by the SCN groups into chains of composition Sr(SCN)₂·3H₂O. The water molecules form exclusively O—H···S type hydrogen bonds which are all oriented approximately perpendicular to the acceptor SCN groups.

Introduction. Combined structural and vibrational spectroscopic studies have shown that hydrogen bonds between H₂O molecules as donors and S atoms as acceptors depend in strength not only on the donor–acceptor distance (O···S) but also on the chemical nature of the acceptor S atom (Mikenda, Mereiter & Preisinger, 1989). This means that O—H···S bonds of comparable bond distances may differ considerably in strength for different kinds of S acceptor atoms. Thiocyanates were found to form rather weak O—H···S bonds, but further experimental data were desirable. The present work was carried out in order to find compounds suitable for corre-

lations between structure and spectroscopy. Low-temperature data were required to that end.

Experimental. The title compound was obtained by the reaction Sr(ClO₄)₂ + 2KSCN → Sr(SCN)₂ + 2KClO₄ in aqueous solution, removal of the KClO₄ precipitate, and evaporation crystallization at room temperature. A prismatic crystal of size 0.11 × 0.20 × 0.50 mm was selected. A Philips PW 1100 diffractometer with graphite-monochromated Mo $K\alpha$ radiation was used. Lattice parameters were determined from least-squares fit of 33 reflections with $10 < \theta < 28^\circ$. Data collection at $T = 295$ K was carried out with $\omega/2\theta$ scans, scan width $(1 + 0.33\tan\theta)^\circ$, scan speed 4° min^{-1} . Three standard reflections (400, 040, 008) were monitored every 60 min and showed a continuous intensity loss of up to 6%. 4124 reflections with $2 \leq \theta \leq 27^\circ$, $-17 \leq h \leq 17$, $0 \leq k \leq 9$, $-17 \leq l \leq 17$ were measured, corrected for Lorentz–polarization, decay and absorption effects (Gaussian integration, minimum and maximum transmission factors 0.29 and 0.54), and averaged ($R_{\text{int}} = 0.045$ based on F) to 1991 unique reflections, 1458 of which with $F_o > 6\sigma(F_o)$ were subsequently used. Data collection at 125 K was performed with a Leybold Heraeus NCD2 nitrogen-gas-stream cooler. Crystal, measurement conditions and data processing methods were the same as at 295 K. The standard reflections remained

stable within $\pm 1.3\%$. 4043 reflections were measured, averaged to 1946 unique reflections ($R_{\text{int}} = 0.038$), 1511 of which with $F_o > 6\sigma(F_o)$ were used.

The structure was solved (direct methods) and refined with the program *SHELX76* (Sheldrick, 1976) in space group $P2_1/n$. Corrections for extinction, neutral-atom scattering functions, anisotropic temperature factors for non-H atoms, and one common isotropic term for H atoms were applied. H atoms were refined as parts of rigid H₂O molecules only with the 125 K data [O—H = 0.8 Å for X-ray scattering centres, O—H = 0.96 Å for nuclear H positions, and H—O—H = 108° for both; cf. Mikenda, Mereiter & Preisinger (1989)]. The positions obtained were transferred to the 295 K structure and not varied further. Final residuals: $R = 0.029$, $wR = 0.035$ and $S = 1.88$ for $w = 1/[\sigma^2(F_o) + 0.0004F_o^2]$, 1458 reflections and 93 variable parameters for the structure at 295 K; $R = 0.031$, $wR = 0.036$ and $S = 1.57$ for $w = 1/[\sigma^2(F_o) + 0.0004F_o^2]$, 1511 reflections and 102 variable parameters for the structure at 125 K. Final difference maps showed no peaks higher than 1.0 or less than $-1.1 \text{ e } \text{\AA}^{-3}$, with all main features near Sr. All $\Delta/\sigma < 0.01$. Geometric calculations and drawings were performed with the programs *PARST* (Nardelli, 1982) and *ORTEPII* (Johnson, 1976).*

Discussion. Final atomic parameters are listed in Table 1, bond lengths and angles in Tables 2 and 3. Thermal effects on the structure of Sr(SCN)₂·3H₂O on stepping from 295 to 125 K are statistically significant but mostly moderate in size: thermal vibration parameters decrease by a factor 0.4, lattice constants a , b and c become smaller by 0.5–0.7%, non-H atoms change their position in the unit cell by 0.010–0.060 Å, bonds to Sr and hydrogen bonds become shorter on average by 0.012 (13) and 0.025 (9) Å, respectively (maximum change 0.041 Å), and the bonds within the SCN groups virtually increase their lengths by 0.011 (9) Å, on average. As to bond lengths and angles the subsequent discussion will be restricted to the 125 K data.

The structure contains discrete continuous zigzag chains of composition Sr(SCN)₂·3H₂O. They extend at $x \approx \frac{1}{2}$, $z = 0$ and $x \approx 0$, $z \approx \frac{1}{2}$ parallel to b and are mutually linked by hydrogen bonds only. The chains are built up from one kind of edge-sharing SrSN₄(H₂O)₃ polyhedron, from two kinds of SCN groups – each of them N-bonded to two Sr atoms and one of them S-bonded to one Sr atom – and

Table 1. Atomic coordinates and equivalent isotropic temperature factors (\AA^2)

For each atom each first line for 295 K, each second line for 125 K, for H atoms only 125 K data. H atoms were refined as parts of rigid H₂O molecules with OH = 0.96 Å and HOH = 108° for the nuclear positions given here. E.s.d.'s of the H₂O rotation angles average 4.1°. One common $B_{\text{iso}} = 3.6$ (6) \AA^2 for all H atoms at 125 K.

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B_{eq}
Sr	0.39088 (3)	0.25292 (5)	0.04884 (2)	1.88 (1)
	0.38937 (3)	0.25275 (5)	0.04916 (2)	0.73 (1)
S(1)	0.60443 (13)	-0.20665 (16)	0.30099 (7)	3.11 (3)
	0.60715 (10)	-0.21241 (14)	0.30217 (7)	1.19 (2)
C(1)	0.5794 (4)	-0.1023 (5)	0.1916 (3)	2.19 (8)
	0.5815 (4)	-0.1062 (5)	0.1925 (3)	0.97 (8)
N(1)	0.5600 (4)	-0.0334 (4)	0.1144 (2)	2.68 (8)
	0.5616 (3)	-0.0330 (4)	0.1143 (2)	1.08 (7)
S(2)	0.16820 (11)	0.89926 (15)	0.06487 (8)	3.13 (3)
	0.16770 (10)	0.90254 (13)	0.06577 (8)	1.21 (2)
C(2)	0.2829 (4)	0.7364 (5)	0.0427 (3)	2.17 (8)
	0.2831 (4)	0.7375 (5)	0.0422 (3)	0.95 (8)
N(2)	0.3654 (4)	0.6239 (5)	0.0269 (3)	2.87 (8)
	0.3672 (3)	0.6242 (4)	0.0258 (2)	1.13 (7)
O(1)	0.5473 (3)	0.3661 (5)	0.2010 (2)	4.21 (10)
	0.5460 (3)	0.3618 (4)	0.2031 (2)	1.66 (7)
O(2)	0.2423 (4)	0.3144 (6)	0.1908 (3)	5.31 (12)
	0.2395 (3)	0.3219 (5)	0.1906 (2)	2.11 (8)
O(3)	0.1632 (4)	0.3163 (5)	-0.0581 (3)	4.57 (12)
	0.1606 (3)	0.3180 (5)	-0.0588 (2)	1.96 (8)
H(1)	0.5507	0.4855	0.2322	
H(2)	0.6405	0.3118	0.2061	
H(3)	0.1403	0.2937	0.1918	
H(4)	0.2801	0.3263	0.2587	
H(5)	0.1417	0.4366	-0.0915	
H(6)	0.0802	0.2376	-0.0741	

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

	$T = 295 \text{ K}$	$T = 125 \text{ K}$
Sr—S(2)	3.312 (1)	3.271 (1)
Sr—N(1)	2.708 (3)	2.703 (3)
Sr—N(1 ⁱⁱ)	2.768 (3)	2.755 (3)
Sr—N(2)	2.674 (3)	2.663 (3)
Sr—N(2 ⁱⁱⁱ)	2.744 (3)	2.726 (3)
Sr—O(1)	2.570 (3)	2.560 (3)
Sr—O(2)	2.498 (4)	2.500 (3)
Sr—O(3)	2.549 (3)	2.546 (3)
S(1)—C(1)	1.653 (4)	1.650 (4)
C(1)—N(1)	1.152 (5)	1.170 (5)
S(1)—N(1)	2.805 (4)	2.820 (4)
S(2)—C(2)	1.636 (4)	1.649 (4)
C(2)—N(2)	1.153 (5)	1.164 (5)
S(2)—N(2)	2.789 (4)	2.812 (4)
S(1)—N(1)—C(1)	178.3 (3)	178.8 (3)
S(2)—N(2)—C(2)	178.9 (4)	178.4 (3)
C(1)—N(1)—Sr	131.9 (3)	132.3 (3)
C(1)—N(1)—Sr ⁱⁱ	116.7 (3)	115.6 (3)
Sr—N(1)—Sr ⁱⁱ	107.4 (1)	107.7 (1)
C(2)—N(2)—Sr	136.6 (3)	135.4 (3)
C(2)—N(2)—Sr ⁱⁱⁱ	116.7 (3)	117.1 (3)
Sr—N(2)—Sr ⁱⁱⁱ	106.7 (1)	107.4 (1)
C(2)—S(2)—Sr ^v	95.3 (2)	95.2 (2)

Symmetry code: none x, y, z ; (i) $x, y - 1, z$; (ii) $1 - x, -y, -z$; (iii) $1 - x, 1 - y, -z$; (iv) $x, 1 + y, z$.

from three independent water molecules which are attached to Sr at terminal positions (Fig. 1). The SrSN₄(H₂O)₃ polyhedron has the shape of a distorted square antiprism (Fig. 2). The strengths of the bonds to the three kinds of ligands are on average 0.15, 0.25 and 0.32 valence units for S, N and O, respectively

* Lists of structure factors, anisotropic thermal parameters, and H-atom parameters at 295 K have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54993 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE0079]

Table 3. *Hydrogen-bond parameters* (\AA , $^\circ$) for $\text{Sr}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$ at 125 K

O...S distances at 295 K are given in square brackets. O—H = 0.96 \AA and H—O—H = 108 $^\circ$ were fixed during refinement (see text and Table 1).

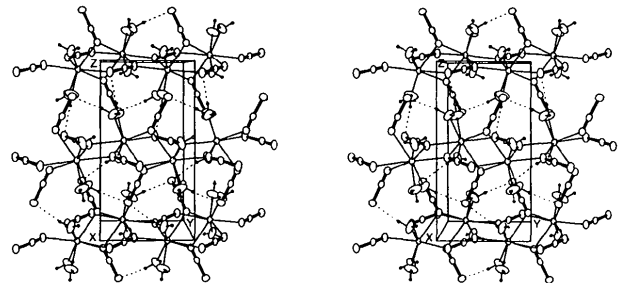
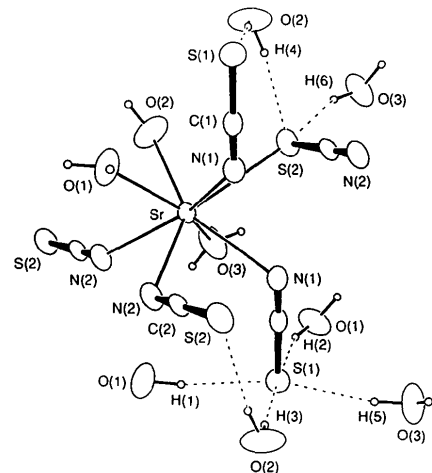
O—H...S	H...S	O...S	[O...S at 295 K]	O—H...S	O...S—C	H...S—C
O(1)—H(1)...S(1 ^a)	2.39 (1)	3.334 (4)	[3.363 (4)]	170 (4)	93.1 (2)	93 (2)
O(1)—H(2)...S(1 ^a)	2.40 (2)	3.327 (4)	[3.352 (4)]	162 (4)	89.1 (2)	90 (2)
O(2)—H(3)...S(1 ^{ab})	2.35 (1)	3.295 (4)	[3.308 (4)]	169 (5)	85.1 (2)	87 (2)
O(2)—H(4)...S(2 ^{bc})	2.42 (2)	3.356 (4)	[3.392 (4)]	164 (5)	86.4 (2)	87 (2)
O(3)—H(5)...S(1 ^c)	2.43 (1)	3.378 (4)	[3.395 (4)]	171 (5)	96.6 (2)	99 (2)
O(3)—H(6)...S(2 ^{cd})	2.56 (2)	3.471 (4)	[3.500 (4)]	159 (5)	106.1 (2)	111 (2)
S(1 ^a)...O(1)...S(1 ^{ab})				90.7 (2)		
S(1 ^{ab})...O(2)...S(2 ^{bc})				99.7 (2)		
S(1 ^c)...O(3)...S(2 ^{cd})				105.3 (2)		

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

(Brown & Altermatt, 1985). The predominance in number and strength of the Sr—N over the Sr—S bonds agrees with the general observation that in essentially ionic compounds SCN groups prefer N-bonding to cations over S-bonding (Norbury, 1975). The bonding situation of the SCN groups in $\text{Sr}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$ resembles that in $\text{Ba}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$ and $\beta\text{-NaSCN} \cdot 2\text{H}_2\text{O}$ (Mereiter & Preisinger, 1982a; Mereiter, Preisinger & Mikenda, 1984).

The water molecules exhibit pyramidal [$\text{H}_2\text{O}(1)$] to approximately planar [$\text{H}_2\text{O}(2)$, $\text{H}_2\text{O}(3)$] three coordination, each forming one relatively strong bond to Sr and two essentially straight O—H...S type hydrogen bonds (Table 3). The bond O(1)—H(1)...S(1) connects atoms of the same $\text{Sr}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$ chain; the remaining five O—H...S bonds crosslink different chains. The O...S distances [mean value 3.360 (60) \AA] and O—H...S angles are fairly close to the average O—H...S bond (Mikenda, Mereiter & Preisinger, 1989), except for O(3)—H(2)...S(2) which is slightly longer. As to their strength these bonds are expected to correspond to relatively weak 3.5 \AA O...S bonds in hydrated alkali salts of XS_4^{2-} , $X = \text{P, As, Sb}$.

It is well known that SCN groups S-bonded to metal atoms tend to form $M\text{—S—C}$ angles of about 90–100 $^\circ$ (Norbury, 1975; Wells, 1984). The bond angle Sr—S(2)—C(2) = 95.2 (1) $^\circ$ is in this range. However, this rule can now be expanded to hydrogen bonds with thiocyanate S atoms. The clearest example found so far in support of this statement is the atom S(1) in $\text{Sr}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$. Fig. 2 shows that S(1) accepts four O—H...S bonds at approximate right angles to the axis of the SCN group, thus providing it with a square-planar coordination by four H atoms (Fig. 2, Table 3). By analogy, the two O—H...S bonds donated to S(2) also subtend approximate right angles with the acceptor SCN group. Examination of other well refined thiocyanate hydrates shows that this principle is generally valid. Good examples are α - and β -NaSCN $\cdot 2\text{H}_2\text{O}$ [each with four O—H...S bonds, O...S—C = 78–99, H...S—C = 81–101 $^\circ$ (Mereiter, Preisinger & Mikenda, 1984)], $\text{Co}(\text{NCS})_2 \cdot 3\text{H}_2\text{O}$ [two bonds,

Fig. 1. Stereoview of the structure down a^* .Fig. 2. Coordination of Sr and hydrogen bonds in $\text{Sr}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$.

O...S—C = 86–98, H...S—C = 84–98 $^\circ$ (Cano, Garcia-Blanco & Guerrero Laverat, 1976)], $\text{Mg}(\text{NCS})_2 \cdot 4\text{H}_2\text{O}$ [three bonds, O...S—C = 89–112, H...S—C = 90–109 $^\circ$ (Mereiter & Preisinger, 1982b)], and NH_4SCN (two N—H...S bonds, N...S—C = 94–97, H...S—C = 92–95 $^\circ$ (Bats & Coppens, 1977)]. This behaviour of the thiocyanate S atom contrasts with the thiocyanate N atom: in the above mentioned compounds (Na, Co, Mg)—N—C bond angles vary in the range between 105–172 $^\circ$, and the hydrogen bonds donated to N exhibit O(N)...N—C angles

of 100–139°. Referring to the results of two electron deformation density studies on NH₄SCN and NaSCN (Bats & Coppens, 1977; Bats, Coppens & Kvick, 1977), the pronounced bond-direction selectivity of thiocyanate S is attributable to two cooperative effects: (i) by the presence of a larger ring-like region of electron lone-pair density around S lateral to the SCN group, and (ii) by the simultaneous presence of an electron-deficient region protruding from the S atom in the axial direction of the SCN group. Both effects are considered to stem from a thiocyanate S atom which is almost unhybridized and has its electron lone pairs concentrated in 3s and 3pπ orbitals.

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Structure of K₃Na₄H₂[TbW₁₀O₃₆]·20H₂O

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Abstract. Tripotassium tetrasodium dihydrogen decatungstotribate icosahydrate, K₃Na₄H₂[TbW₁₀O₃₆]·20H₂O, *M_r* = 3209, monoclinic, *P*2₁/*n*, *a* = 29.772 (8), *b* = 16.164 (2), *c* = 11.443 (1) Å, β = 96.01 (2)°, *V* = 5476 (2) Å³, *Z* = 4, *D_x* = 3.81 g cm⁻³, λ(Mo Kα) = 0.71069 Å, μ = 230 cm⁻¹, *F*(000) = 5584, *T* = 298 K, *R* = 0.053 for 8398 unique reflections. The *D*_{4d} [TbW₁₀O₃₆]⁹⁻ anion consists of two [W₅O₁₈]⁶⁻ groups chelating to the central Tb³⁺ ion. The Tb³⁺ cation exhibits a tetragonal antiprismatic coordination with Tb—O distances of 2.40–2.44 Å. The average Tb—W distance is 3.83 Å. Two K⁺

cations play a prominent role in linking the two highly negatively charged [W₅O₁₈]⁶⁻ units of the polyanion. While the three K⁺ cations have direct contacts to the polyanion O atoms, forming bridges to the neighboring polyanions, only one O atom of the polyanion is observed in the coordination spheres of the four Na⁺ cations.

Introduction. Heteropolyanions containing lanthanoid atoms have been attracting much interest owing to their fluorescent activity. However, the photoluminescent polyanions whose crystal structures