# The Crystal and Molecular Structure of Strontium Bis(thiocyanate)-Hexaethylene Glycol (1/1)

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The molecular structure of strontium bis(thiocyanate)–hexaethylene glycol(1/1) has been determined from single crystal X-ray diffraction data(3121 observed reflections): triclinic, space group $P\bar{1}$, $a=12.086(4)$, $b=8.732(2)$, $c=10.628(2)$ Å, $\alpha=80.88(2)$, $\beta=101.99(3)$, $\gamma=100.55(2)°$, $D_m=1.48$, $D_c=1.48$ g cm$^{-3}$ for $Z=2$. The central Sr ion is coordinated by seven O atoms from the hexaethylene glycol moiety and two N atoms from the SCN groups; the Sr–O distances range from 2.603(5) to 2.750(5), while the Sr–N distances are 2.628(8) and 2.634(8) Å. The hexaethylne glycol moiety assumes a $GT_2\bar{G}T_2GT_2\bar{G}T_2GTG_2$ conformation.

In connection with the studies of the metal-ion complexation of non-cyclic poly(oxyethylene) derivatives by Yanagida, Okahara, and their co-workers,[1] X-ray diffraction studies have been made of strontium bis(thiocyanate)–heptaethylene glycol(1/1) and –hexaethylene glycol(1/1) (EO7–$Sr(SCN)_2$ and EO6–$Sr(SCN)_2$) in order to examine the chelating behavior of heptaethylene glycol(EO7) and hexaethylene glycol (EO6) to the strontium. An account of the structure of the former, EO7–$Sr(SCN)_2$, has been reported.[2] This paper will deal with the structure of the latter, EO6–$Sr(SCN)_2$.

## Experimental

Colorless, transparent, and prismatic crystals were recrystallized from acetone-hexane. A crystal with approximate dimensions of 0.5 mm × 0.2 mm × 0.1 mm was used for the X-ray experiments. The unit-cell parameters and diffraction intensities were measured on a Rigaku automated, four-circle diffractometer. Zr-filtered Mo $K\alpha$ radiation was used.

*Crystal Data.* $(C_{12}H_{26}O_7)\cdot Sr(SCN)_2$, *F.W.* 478.02, triclinic, space group $P\bar{1}$, $a=12.086(4)$, $b=8.732(2)$, $c=10.628(2)$ Å, $\alpha=80.88(2)$, $\beta=101.99(3)$, $\gamma=100.55(2)°$, $V=1070(1)$ Å$^3$, $D_m=1.48$, $D_c=1.48$ g cm$^{-3}$ for $Z=2$, $\mu$(Mo $K\alpha$)$=28.6$ cm$^{-1}$. The intensity data were measured by the $\theta$-$2\theta$ scan technique at a $2\theta$ rate of 2° min$^{-1}$. The scan width was $\Delta(2\theta)=(2.4+0.7\tan\theta)°$. Backgrounds were measured for 7.5 s at both ends of a scan. A total of 3957 reflections ($2\theta<50°$) were measured, of which 3121 ($|F_o|>3\sigma(F_o)$) were non-zero reflections. Usual Lorentz and polarization corrections were applied, but no absorption correction was made [max($\mu R$)$=0.8$].

## Structure Solution and Refinement

The structure was solved by the heavy-atom method. The positions of the Sr and S atoms were determined from the Patterson function. The subsequent Fourier map revealed the remaining non-hydrogen atoms.

The structure was refined anisotropically by the block-diagonal least-squares procedure (*HBLS*-V).[3] The difference Fourier map calculated at the stage with $R=0.085$ revealed the positions of 26 H atoms, those atoms were included in the subsequent cycles and refined isotropically. The final $R$ was 0.061 for non-zero reflections ($R_w=0.069$). The weighting schemes used in the final cycle were $w=\{\sigma_{cs}(F_o)+a|F_o|+b|F_o|^2\}^{-1}$, where $a=0.0223$ and $b=0.0008$, for $|F_o|>0$ and $w=0.0508$ for $|F_o|=0$. The final atomic parameters are summarized in Table 1.†††

The atomic scattering factors used were taken from the International Tables for X-Ray Crystallography, Vol. IV.[4] Computations were done on an ACOS Series 77 NEAC System 900 computer at Osaka University.

## Results and Discussion

The molecular structure as drawn by the *ORTEP* program[5] is shown in Fig. 1. The interatomic dis-

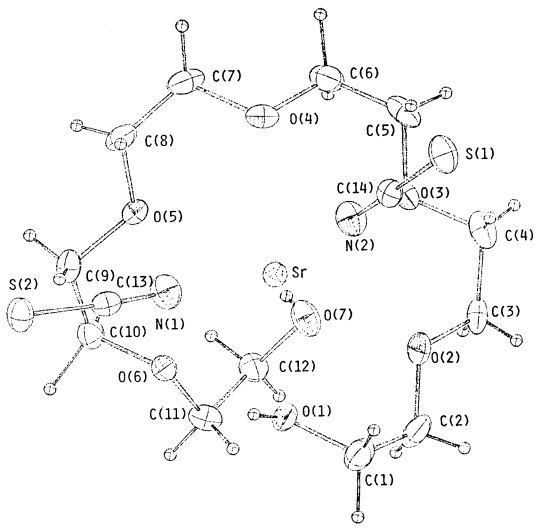


Fig. 1. A prespective view[5] of EO6–$Sr(SCN)_2$ molecule with the numbering scheme of non-hydrogen atoms.
Non-hydrogen atoms are expressed as thermal ellipsoids at 50% probability level and hydrogen atoms as spheres with the radius of 0.1 Å.

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††† Lists of the observed and calculated structure factors and anisotropic thermal parameters are kept at the Chemical Society of Japan (Document No. 8219).

TABLE 1. FRACTIONAL ATOMIC COORDINATES, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Non-hydrogen atoms with equivalent temperature factors.

| Atom | $x$ | $y$ | $z$ | $B_{eq}$[6]/Å$^2$ |
|---|---|---|---|---|
| Sr | 0.25433(7) | 0.24284(9) | 0.18693(7) | 3.36 |
| S (1) | 0.1495(3) | −0.3421(3) | 0.4327(3) | 5.58 |
| S (2) | 0.3557(3) | −0.0048(3) | −0.1954(3) | 5.19 |
| O (1) | 0.4722(5) | 0.2261(7) | 0.2461(5) | 4.3 |
| O (2) | 0.3633(5) | 0.2392(7) | 0.4371(5) | 5.2 |
| O (3) | 0.1319(5) | 0.2512(6) | 0.3690(5) | 4.3 |
| O (4) | 0.0245(5) | 0.1966(7) | 0.1201(6) | 4.8 |
| O (5) | 0.1490(5) | 0.3573(7) | −0.0558(5) | 4.2 |
| O (6) | 0.3667(5) | 0.4812(6) | 0.0341(5) | 3.6 |
| O (7) | 0.2810(6) | 0.5304(7) | 0.2402(6) | 5.5 |
| N (1) | 0.3059(7) | 0.0802(9) | 0.0251(8) | 5.5 |
| N (2) | 0.2087(7) | −0.0477(8) | 0.2978(8) | 5.5 |
| C (1) | 0.5292(8) | 0.2002(12) | 0.3753(9) | 5.7 |
| C (2) | 0.4816(8) | 0.2798(13) | 0.4562(9) | 6.3 |
| C (3) | 0.3042(9) | 0.2992(10) | 0.5176(8) | 4.8 |
| C (4) | 0.1859(9) | 0.2146(10) | 0.5026(9) | 5.5 |
| C (5) | 0.0172(8) | 0.1715(12) | 0.3424(10) | 6.0 |
| C (6) | −0.0389(8) | 0.2299(12) | 0.2092(10) | 5.9 |
| C (7) | −0.0310(8) | 0.2340(11) | −0.0119(10) | 5.7 |
| C (8) | 0.0535(8) | 0.2412(11) | −0.0966(9) | 5.4 |
| C (9) | 0.2244(8) | 0.4105(10) | −0.1454(8) | 4.7 |
| C (10) | 0.3092(8) | 0.5407(10) | −0.0934(8) | 4.5 |
| C (11) | 0.4228(7) | 0.6062(10) | 0.1103(9) | 4.7 |
| C (12) | 0.3388(8) | 0.6626(10) | 0.1688(8) | 4.6 |
| C (13) | 0.3300(7) | 0.0432(9) | −0.0646(8) | 3.8 |
| C (14) | 0.1851(7) | −0.1676(9) | 0.3543(8) | 3.8 |

(b) Hydrogen atoms with isotropic temperature factors.

| Atom | $x$ | $y$ | $z$ | $B$/Å$^2$ |
|---|---|---|---|---|
| H (1) | 0.477(8) | 0.163(11) | 0.198(9) | 5(3) |
| H (2) | 0.616(9) | 0.248(12) | 0.390(10) | 6(3) |
| H (3) | 0.507(8) | 0.094(11) | 0.394(9) | 6(3) |
| H (4) | 0.508(9) | 0.261(13) | 0.539(11) | 7(3) |
| H (5) | 0.497(12) | 0.403(17) | 0.427(14) | 12(5) |
| H (6) | 0.313(6) | 0.410(9) | 0.496(7) | 2.2(17) |
| H (7) | 0.341(10) | 0.290(13) | 0.588(11) | 8(4) |
| H (8) | 0.183(7) | 0.102(10) | 0.514(9) | 4(3) |
| H (9) | 0.142(9) | 0.262(12) | 0.544(10) | 6(3) |
| H (10) | −0.014(7) | 0.188(9) | 0.403(8) | 3.2(19) |
| H (11) | 0.024(9) | 0.053(12) | 0.356(10) | 7(3) |
| H (12) | −0.031(13) | 0.343(17) | 0.212(14) | 13(5) |
| H (13) | −0.125(9) | 0.157(12) | 0.181(10) | 7(3) |
| H (14) | −0.053(7) | 0.338(10) | −0.016(8) | 4(2) |
| H (15) | −0.105(10) | 0.161(13) | −0.033(11) | 8(4) |
| H (16) | 0.030(9) | 0.288(13) | −0.172(11) | 7(3) |
| H (17) | 0.079(8) | 0.126(11) | −0.093(9) | 5(3) |
| H (18) | 0.176(8) | 0.438(11) | −0.217(9) | 5(3) |
| H (19) | 0.258(9) | 0.302(12) | −0.153(10) | 6(3) |
| H (20) | 0.262(8) | 0.617(11) | −0.087(9) | 6(3) |
| H (21) | 0.389(11) | 0.569(15) | −0.142(12) | 9(4) |
| H (22) | 0.468(10) | 0.695(13) | 0.064(11) | 8(4) |
| H (23) | 0.478(8) | 0.546(11) | 0.165(9) | 5(3) |
| H (24) | 0.286(9) | 0.708(12) | 0.092(10) | 7(3) |
| H (25) | 0.371(8) | 0.736(11) | 0.216(9) | 5(3) |
| H (26) | 0.244(9) | 0.564(12) | 0.202(10) | 6(3) |

TABLE 2. SELECTED INTERATOMIC DISTANCES AND ANGLES IN EO6-Sr(SCN)$_2$, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

| | | | |
|---|---|---|---|
| Interatomic distances ($l$/Å) | | | |
| Sr-O(1) | 2.603(6) | Sr-N(1) | 2.628(8) |
| Sr-O(2) | 2.709(6) | Sr-N(2) | 2.634(8) |
| Sr-O(3) | 2.686(5) | N(1)-C(13) | 1.160(11) |
| Sr-O(4) | 2.691(6) | N(2)-C(14) | 1.141(11) |
| Sr-O(5) | 2.750(5) | S(1)-C(14) | 1.645(8) |
| Sr-O(6) | 2.762(5) | S(2)-C(13) | 1.618(9) |
| Sr-O(7) | 2.609(6) | | |
| C(1)-O(1) | 1.406(12) | C(11)-O(6) | 1.445(10) |
| C(2)-O(2) | 1.389(12) | C(12)-O(7) | 1.429(11) |
| C(3)-O(2) | 1.431(12) | | |
| C(4)-O(3) | 1.446(12) | | |
| C(5)-O(3) | 1.426(12) | C(1)-C(2) | 1.447(15) |
| C(6)-O(4) | 1.428(12) | C(3)-C(4) | 1.474(14) |
| C(7)-O(4) | 1.438(11) | C(5)-C(6) | 1.491(14) |
| C(8)-O(5) | 1.431(11) | C(7)-C(8) | 1.483(14) |
| C(9)-O(5) | 1.421(10) | C(9)-C(10) | 1.478(12) |
| C(10)-O(6) | 1.451(10) | C(11)-C(12) | 1.485(13) |
| Interatomic angles ($\phi$/°) | | | |
| O(1)-Sr-O(2) | 60.2(2) | O(1)-Sr-N(1) | 71.0(3) |
| O(1)-Sr-O(3) | 121.6(2) | O(1)-Sr-N(2) | 89.9(3) |
| O(1)-Sr-O(4) | 168.1(2) | O(2)-Sr-N(1) | 122.5(3) |
| O(1)-Sr-O(5) | 123.0(2) | O(2)-Sr-N(2) | 73.7(3) |
| O(1)-Sr-O(6) | 71.9(2) | O(3)-Sr-N(1) | 147.9(3) |
| O(1)-Sr-O(7) | 94.0(2) | O(3)-Sr-N(2) | 73.2(2) |
| O(2)-Sr-O(3) | 61.4(2) | O(4)-Sr-N(1) | 100.1(3) |
| O(2)-Sr-O(4) | 122.3(2) | O(4)-Sr-N(2) | 80.3(3) |
| O(2)-Sr-O(5) | 159.4(2) | O(5)-Sr-N(1) | 74.2(3) |
| O(2)-Sr-O(6) | 109.6(2) | O(5)-Sr-N(2) | 124.7(3) |
| O(2)-Sr-O(7) | 73.8(2) | O(6)-Sr-N(1) | 79.7(3) |
| O(3)-Sr-O(4) | 62.0(2) | O(6)-Sr-N(2) | 154.7(2) |
| O(3)-Sr-O(5) | 111.9(2) | O(7)-Sr-N(1) | 140.8(3) |
| O(3)-Sr-O(6) | 131.2(2) | O(7)-Sr-N(2) | 139.8(3) |
| O(3)-Sr-O(7) | 70.9(2) | | |
| O(4)-Sr-O(5) | 59.5(2) | N(1)-Sr-N(2) | 77.9(3) |
| O(4)-Sr-O(6) | 115.2(2) | | |
| O(4)-Sr-O(7) | 97.8(2) | | |
| O(5)-Sr-O(6) | 58.5(2) | | |
| O(5)-Sr-O(7) | 85.6(2) | | |
| O(6)-Sr-O(7) | 61.1(2) | | |
| O(1)-C(1)-C(2) | 109.5(9) | C(2)-O(2)-C(3) | 117.3(8) |
| O(2)-C(2)-C(1) | 110.6(9) | C(4)-O(3)-C(5) | 112.1(7) |
| O(2)-C(3)-C(4) | 108.1(8) | C(6)-O(4)-C(7) | 111.3(7) |
| O(3)-C(4)-C(3) | 107.3(8) | C(8)-O(5)-C(9) | 115.3(7) |
| O(3)-C(5)-C(6) | 109.6(8) | C(10)-O(6)-C(11) | 112.1(6) |
| O(4)-C(6)-C(5) | 107.7(8) | | |
| O(4)-C(7)-C(8) | 107.9(8) | | |
| O(5)-C(8)-C(7) | 107.4(8) | N(1)-C(13)-S(2) | 176.2(8) |
| O(5)-C(9)-C(10) | 107.4(8) | N(2)-C(14)-S(1) | 178.8(8) |
| O(6)-C(10)-C(9) | 107.8(7) | | |
| O(6)-C(11)-C(12) | 110.4(7) | | |
| O(7)-C(12)-C(11) | 108.0(7) | | |

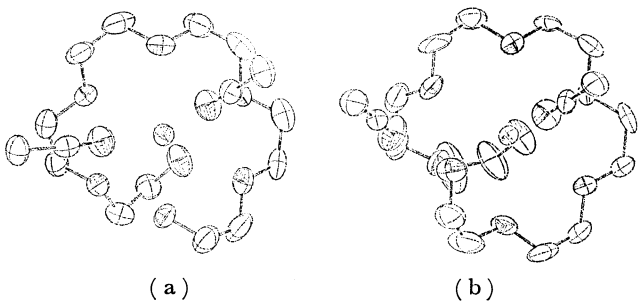


Fig. 2. Molecular structure of EO6-Sr(SCN)$_2$ (a) compared with that of EO7-Sr(SCN)$_2$[2] (b).
A similar conformation is observed at the central portions of the EO6 and EO7 chanis (See also Fig. 3).

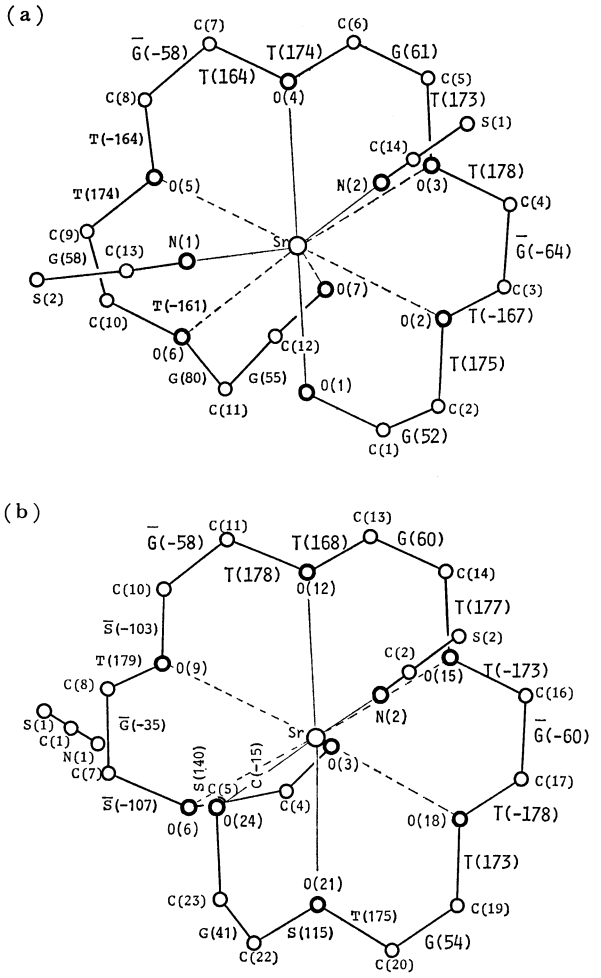


Fig. 3. Conformations and torsion angles($\phi$/°) in oligoethylene glycol part.
(a) EO6-Sr(SCN)$_2$, (b) EO7-Sr(SCN)$_2$.[2] Thick circles represent atoms coordinated to the Sr. Solid and broken lines respectively show the coordination bonds between the Sr and atoms above and below the planes defined by the (a) O(1), O(2), O(3), O(4), and O(5), (b) O(9), O(12), O(18), O(21), and O(24) atoms.

tances and angles are given in Table 2.

*Coordination Geometry.* Seven O atoms from the EO6 chain and two N atoms from two SCN anions are coordinated to the Sr ion. In EO7–$Sr(SCN)_2$, the eighth O atom takes part in the coordination instead of the N atom of the second SCN anion. The two Sr–N distances in the present complex are equal, within the limits of experimental error: 2.628(8) and 2.634(8) Å. The seven Sr–O distances are classed into three groups. Both of the terminal O atoms, O(1) and O(7), of the EO6 are rather close to the Sr atom; the Sr–O distances being 2.603(6) and 2.609(7) Å. The Sr–O(2), Sr–O(3), and Sr–O(4) distances are the second longest [2.709(6), 2.686(5) and 2.691(6) Å], while the Sr–O(5) and Sr–O(6) are the longest distances [2.750(5) and 2.762(5) Å].

*Conformations of the EO6 Chain.* The structure of and torsion angles in the EO6 chain are compared in Figs. 2 and 3 respectively with those found in the EO7 chain in EO7–$Sr(SCN)_2$.[2] The EO6 chain assumes a $\mathbf{GT_2\bar{G}T_2GT_2\bar{G}}T_2GTG_2$ conformation About 2/3 of the EO6 chain has a conformation similar to that of the central part of the EO7 chain in EO7–$Sr(SCN)_2$($\mathbf{GT_2\bar{G}T_2GT_2\bar{G}}$). This fact, and the similarity between the corresponding Sr–O distances in the EO6 [2.709(6), 2.686(5) and 2.691(6) Å] and EO7 chains [2.71(2), 2.69(2) and 2.72(2) Å], suggest that some part of the EO6 chain (from O(1) to O(5)) and the corresponding part of the EO7 chain (from O(21) to O(9)) have "rigid structure."

*Crystal Structure.* The crystal structure is drawn in Fig. 4. Close intermolecular distances (less than 3.5 Å) are listed in Table 3; the closest contact is $S(2)(x, y, z)\cdots O(1)(1-x, -y, -z)=3.258(6)$ Å.

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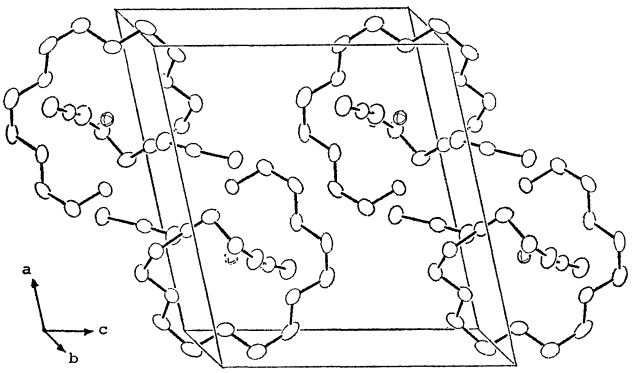


Fig. 4. Crystal structure of EO6–$Sr(SCN)_2$.[5]

Table 3. Short intermolecular atomic contacts($l$/Å) (less than 3.5 Å), with estimated standard deviations in parentheses

| | | |
|---|---|---|
| O(7)···S(1)[a] | 3.267(7) | key: a, $x$, $1+y$, $z$; |
| S(2)···O(1)[b] | 3.258(6) | b, $1-x$, $-y$, $-z$; |
| S(2)···C(1)[b] | 3.393(11) | c, $1-x$, $1-y$, $-z$. |
| O(6)···C(11)[c] | 3.479(10) | |
| O(6)···O(6)[c] | 3.394(10) | |

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