BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (4), 1209—1210 (1979)

The X-Ray Structure Determination of Heptaethylene Glycol-$Sr(SCN)_2$

Hideyo OHMOTO, Yasushi KAI, Noritake YASUOKA,† Nobutami KASAI,*
Shozo YANAGIDA, and Mitsuo OKAHARA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565

(Received September 12, 1978)

Synopsis. The crystal structure of heptaethylene glycol-$Sr(SCN)_2$ has been determined by X-ray diffraction. The Sr ion is coordinated by eight oxygen atoms arising from the heptaethylene glycol moiety and a nitrogen atom from one of SCN groups. The coordination polyhedron is irregular, Sr–O distances ranging from 2.56 to 2.73 Å.

It is well known that macrocyclic ethers interact with alkali and alkaline earth metal ions to give complexes, some structures of which have been determined by X-ray crystallography.[1-3] On the other hand, linear poly(oxyethylene) (POE) derivatives also have a chelating ability to metal cations.[4] The structures of various glymes with $HgCl_2$ and $CdCl_2$ have been investigated by Iwamoto[5,6] in connection with structural studies of polyethylene glycol–$HgCl_2$ complexes.[7,8] Recently, POE deraviatives with the appropriate number of oxyethylene units have been found to form complexes with alkali and alkaline earth metal thiocyanates.[9] In order to investigate the chlating behavior of POE, X-ray diffraction studies have been made and here the structure of heptaethylene glycol–$Sr(SCN)_2$ is presented.

The crystals, colorless and transparent prisms, were obtained by recrystallization from an acetone solution.

Crystal Data: $(C_{14}H_{30}O_8)\cdot Sr(SCN)_2$, *F.W.*=530.2, monoclinic, space group $P2_1/c$, a=11.368(3), b=14.311(2), c=17.665(6) Å, β=122.13(2)°, V=2434(2) Å^3, D_m=1.45 g cm^{-3} (flotation in dichloromethane–carbon tetrachloride), D_c=1.45 g cm^{-3} for Z=4, μ(Mo $K\alpha$)=23.6 cm^{-1}.

Intensity data were measured on a Rigaku diffractometer with graphite monochromatized Mo $K\alpha$ radiation employing the ω scan technique. The integrated intensity was determined by scanning the peak at a rate of 2°/min along the ω axis. A total of 5313 reflections were obtained, of which 3151 reflections were $F_o > 3\sigma(F_o)$. Lorentz and polarization corrections were made, but no absorption correction was applied, which might limit the accuracy of the present structure determination.

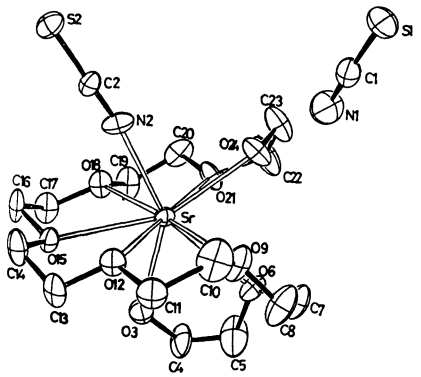

Fig. 1. An ORTEP drawing of the $Sr(SCN)_2$–EO7 molecule together with the numbering scheme.

The structure was solved by the heavy atom method, and refined by the block-diagonal least-squares method with HBLS V[10] program. The atomic scattering factors used in all the computations were taken from the International Tables of X-Ray Crystallography.[11] The refinement was converged to a rather high R value of 0.113 for 3151 reflections and this will be discussed later.

An *ORTEP* drawing of the complex molecule is shown in Fig. 1, together with the numbering system. The bond lengths and bond angles are listed in Table 1.††

Coordination Geometry: Eight oxygen atoms from heptaethylene glycol (EO7) and one nitrogen atom from a SCN anion are coordinated to the Sr ion. The coordination polyhedron is irregular. It is difficult to express the polyhedron in simple terms, although a nine

Table 1. The bond lengths (l/Å) and bond angles (φ/°) in the complex molecule

Sr-O(N) bond		in SCN anion		C-C bond		C-O bond		C-C-O angle		C-O-C angle	
Sr-O(3)	2.56(2)	N(1)-C(1)	1.13(3)	C(4) -C(5)	1.31(5)	O(3) -C(4)	1.41(3)	O(3) -C(4) -O(5)	115(3)	C(5) -O(6) -C(7)	116(2)
Sr-O(6)	2.73(2)	C(1)-S(1)	1.61(2)	C(7) -C(8)	1.42(4)	C(5) -O(6)	1.43(4)	C(4) -C(5) -O(6)	123(3)	C(8) -O(9) -C(10)	120(2)
Sr-O(9)	2.68(2)	N(2)-C(2)	1.15(3)	C(10)-C(11)	1.49(4)	O(6) -C(7)	1.38(3)	O(6) -C(7) -C(8)	117(3)	C(11)-O(12)-C(13)	113(2)
Sr-O(12)	2.72(2)	C(2)-S(2)	1.66(2)	C(13)-C(14)	1.48(4)	C(8) -O(9)	1.36(3)	C(7) -C(8) -O(9)	116(3)	C(14)-O(15)-C(16)	113(2)
Sr-O(15)	2.69(2)	N(1)-C(1)-S(1)	178(2)	C(16)-C(17)	1.50(3)	O(9) -C(10)	1.41(3)	O(9) -C(10)-C(11)	109(2)	C(17)-O(13)-C(19)	110(2)
Sr-O(18)	2.71(2)	N(2)-C(2)-S(2)	179(2)	C(19)-C(20)	1.50(4)	C(11)-O(12)	1.42(3)	C(10)-C(11)-O(12)	109(2)	C(20)-O(21)-C(22)	115(2)
Sr-O(21)	2.66(2)			C(22)-C(23)	1.41(5)	C(12)-C(13)	1.38(3)	O(12)-C(13)-C(14)	108(2)		
Sr-O(24)	2.56(2)					C(14)-O(15)	1.46(3)	C(13)-C(14)-O(15)	108(2)		
Sr-N(2)	2.57(2)					O(15)-C(16)	1.43(3)	O(15)-C(16)-C(17)	109(2)		
						C(17)-O(18)	1.42(3)	C(16)-C(17)-O(18)	107(2)		
						O(18)-C(19)	1.43(3)	O(18)-C(19)-C(20)	107(2)		
						C(20)-O(21)	1.39(3)	C(19)-C(20)-O(21)	109(2)		
						O(21)-C(22)	1.39(4)	O(21)-C(22)-C(23)	116(3)		
						C(23)-O(24)	1.40(4)	C(22)-C(23)-O(24)	111(3)		

† Present address: Institute for Protein Research, Osaka University, Yamadakami, Suita, Osaka 565.

†† The complete F_o-F_c data and the tables of atomic parameters are kept at the Chemical Society of Japan. Document No. 7915.

Table 2. The torsion angles (φ/°) in the heptaethylene glycol chain

O(3) -C(4) -C(5) -O(6)	-15	C(4) -C(5) -O(6) -C(7)	140	C(5) -O(6) -C(7) -C(8)	-107
O(6) -C(7) -C(8) -O(9)	-35	C(7) -C(8) -O(9) -C(10)	179	C(8) -O(9) -C(10)-C(11)	-103
O(9) -C(10)-C(11)-O(12)	-58	C(10)-C(11)-O(12)-C(13)	178	C(11)-O(12)-C(13)-C(14)	168
O(12)-C(13)-C(14)-O(15)	60	C(13)-C(14)-O(15)-C(16)	177	C(14)-O(15)-C(16)-C(17)	-173
O(15)-C(16)-C(17)-O(18)	-60	C(16)-C(17)-O(18)-C(19)	-178	C(17)-O(18)-C(19)-C(20)	173
O(18)-C(19)-C(20)-O(21)	54	C(19)-C(20)-O(21)-C(22)	175	C(20)-O(21)-C(22)-C(23)	115
O(21)-C(22)-C(23)-O(24)	41				

coordinated distorted tricapped trigonal prisms or eight coordinated bicapped trigonal prism have been reported.[12,13] The Sr–O bond lengths range from 2.56 to 2.73 Å. The Sr–O(3) and Sr–O(24) distances are rather short, possibly attributable to the two oxygen atoms at both ends of the EO7 chain being more basic.

Conformations of EO7 Chain: The C–C bond distances found in the EO7 chain are rather short, the mean value being 1.45 Å. The C(4)–C(5) distance of 1.31 Å is abnormally short. The thermal ellipsoids of the atoms are large, and the largest directions are approximately normal to the O(3)–C(4)–C(5)–O(6) plane. Moreover, the torsion angle is −15°, a value which cannot be considered real. It is most probable that partial disorder is present in this part of the chain. Consider a plane made by passing through the Sr, O(3), O(6) atoms and the midpoint between C(4) and C(5). If C(4) lies above the plane, then C(5) must lie below the plane as shown in Fig. 2(a), or *vice versa* (Fig. 2(b)). There may be no energy difference between the two conformations if other conditions are similar. It is most probable that partial disorder, caused by the two conformations is present in the crystal. Some residual peaks were found in the difference map, but attempts to locate the disordered atoms were not successful; possibly real situation is more complex. This may also explain the rather high observed *R* value. Such apparent bond shortening due to thermal libration and partial disorder has also been discussed by Dunitz, *et al.*[2]

The torsion angles in the EO7 chain are listed in Table 2, and in the central part a TGT–T$\bar{G}$T–TGT conformation is observed. This may be the most stable conformation, a conformation also found in the TGM·$HgCl_2$ complex. Both ends of the chain assume a different conformation, since the TGT–T$\bar{G}$T–TGT conformation results in a helical form of an EO7 chain.

Hydrogen Bonding: Two hydrogen atoms at both ends of the EO7 chain possibly serve as donors to form hydrogen bonding. The N(1) atom in a free SCN group

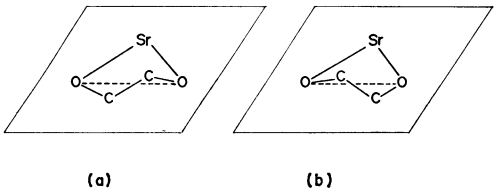

Fig. 2. Two plausible conformations of the $-O-CH_2-CH_2-O$ group.

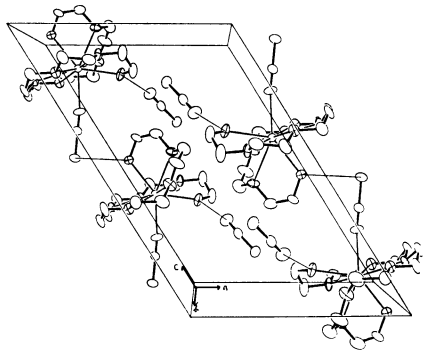

Fig. 3. An ORTEP drawing of the contents of a unit cell.

is located at a distance of 2.73 Å from O(24). Another SCN group is coordinated to the Sr atom *via* N(2) as described above, and S(2) is bonded to the O(3) atom in a neighbouring molecule, the hydrogen bond distance being 3.26 Å. The crystal structure is shown in Fig. 3.

References

1) M. R. Truter, *Struct. Bonding (Berlin)*, **16**, 71 (1973).
2) J. D. Dunitz, M. Dobler, P. Seiler, and R. P. Phizackery, *Acta Crystallogr., Sect. B*, **30**, 2733, 2741, 2746, 2748 (1974).
3) M. R. Truter, "Metal-ligand Interactions in Organic Chemistry and Biochemistry," ed by P. Pullman and M. Goldblum, D. Reidel Publishing Company, Dordrecht-Holland (1977), p. 317.
4) S. Yanagida and M. Okahara, *Kagaku Zokan*, **74**, 149 (1978).
5) R. Iwamoto, *Bull. Chem. Soc. Jpn.*, **46**, 1114, 1118, 1123 (1973).
6) R. Iwamoto and H. Wakano, *J. Am. Chem. Soc.*, **98**, 4777 (1976).
7) R. Iwamoto, Y. Saito, H. Ishihara, and H. Tadokoro, *J. Polym. Sci., Part A-2*, **1968**, 1509
8) M. Yokoyama, H. Ishihara, R. Iwamoto, and H. Tadokoro, *Macromolecules*, **2**, 184 (1969).
9) S. Yanagida, K. Takahashi, and M. Okahara, *Bull. Chem. Soc. Jpn.*, **51**, 3111 (1978).
10) T. Ashida, "The Universal Crystallographic Computing System-Osaka," The Computation Center, Osaka University (1973), pp. 55—60.
11) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp. 71—73.
12) B. Briggman and Å. Oskarsson, *Acta Crystallogr., Sect. B*, **33**, 1900 (1977).
13) A. F. Wells, "Structural Inorganic Chemistry," Clarendon Press, Oxford (1975), pp. 556, 562.