3180 © 1992 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 65, 3180—3182 (1992) [Vol. 65, No. 11

The Crystal Structure of Tetraethylene Glycol Complex of Sodium Tetraphenylborate

Takahiro UEDA† and Nobuo NAKAMURA*
Department of Chemistry, Faculty of Science,
Osaka University, Toyonaka 560
(Received May 12, 1992)

Synopsis. The crystal of 2, 2′-[oxybis(ethyleneoxy)] diethanol (tetraethylene glycol or TEG) complex of sodium tetraphenylborate, $[Na(C_8H_{18}O_5)]B(C_6H_5)_4$, is triclinic, $P\bar{1}$, with the unit cell dimensions: a=1.1730 (2), b=1.3212 (3), c=1.1408 (2) nm, α=108.83 (1), β=112.40 (1), and γ=67.42° (2), Z=2. This compound contains binucear metal complex ion, $[Na(C_8H_{18}O_5)]_2^{2+}$ The sodium ion is coordinated highly asymmetrically by six oxygens in two TEG.

The mechanism of the electric conduction in the polyelectrolytes of polyethylene glycol (PEG) with NaI and other inorganic salts[1)] has not been clearly understood yet because of the lack of the precise structure data of these complex compounds. We performed recently the structural studies of PEG–NaI and tetraethylene glycol (TEG)–NaI complexes by means of the proton, ^{13}C, and ^{23}Na NMR and proposed probable model structures for these substances.[2)] However there remain some problems about the nature of the coordination bond between Na$^+$ and the ligands, with respect to the distances, the stability of the complex structure, etc., because the single crystal X-ray diffraction studies cannot be applied to these complexes. Now we succeeded to prepare single crystals of TEG–NaBPh$_4$ complex, which may have similar structure to TEG–NaI complex, and carried out the single crystal X-ray diffraction experiment. Here we present the results which will be of use for future works on the similar type of complex electrolytes.

Experimental

The single crystals of $[Na(TEG)]B(C_6H_5)_4$ were obtained by recrystallization from aqueous solution by the slow evaporation of the solvent. A specimen with an approximate size of 0.2×0.2×0.3 mm was used for the diffraction experiment. Both the determination of the cell constants and the collection of the intensity data were carried out by a full-automated four-circle diffractometer (Rigaku Co., Ltd., model AFC-5R) using the Mo $K\alpha$ radiation with graphite monochrometer at the X-ray Diffraction Service of the Department of Chemistry. The ω–2θ scan technique was employed at a scan rate of 8° min^{-1} in ω and with a take-off angle of 6.0° in 2θ. The number of reflections were 3158, which are collected in the range of $3° < 2\theta < 60.2°$ and corrected for Lorentz and polarization effects.

Structure Determination and Refinement. The lattice parameters were refined by least-squares fit of 25 reflections in the range $20° \leqq 2\theta \leqq 30°$. The structure was solved by direct methods program package TEXSAN.[3),4)] The non-hydrogen atoms were refined with anisotropic temperature factors. The final cycle of full-matrix least-squares refinement was based on 2966 observed reflections and 390 variable parameters and converged with unweighted and weighted refinement factors of R=0.046 and R_w=0.047, respectively. Positional parameters of non-hydrogen atoms are listed in Table 1. The complete lists of the structure factors, atomic coordinates, and

Table 1. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (×10^{-2}/nm^2); $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\times\cos\gamma+B_{23}bc\times\cos\alpha+B_{13}ac\times\cos\beta)$

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Na	0.4712(1)	0.1513(1)	0.0288(1)	3.95(6)	C(7)	0.8276(2)	0.2498(2)	0.9233(3)	3.1(1)
O(1)	0.2574(2)	0.1646(2)	0.0075(2)	4.6(1)	C(8)	0.8722(3)	0.1621(2)	0.9874(3)	3.5(1)
O(2)	0.3969(2)	0.2937(2)	0.1958(2)	5.5(1)	C(9)	0.9172(3)	0.1763(3)	1.1213(3)	4.3(2)
O(3)	0.6064(2)	0.2653(2)	0.1225(2)	6.5(2)	C(10)	0.9177(3)	0.2804(3)	1.1975(3)	4.6(2)
O(4)	0.3827(2)	−0.0098(2)	−0.1534(2)	3.9(1)	C(11)	0.8766(3)	0.3694(2)	1.1390(3)	4.7(2)
O(5)	0.4831(2)	0.1425(2)	−0.1675(2)	5.6(1)	C(12)	0.8334(3)	0.3539(2)	1.0055(3)	4.2(2)
C(25)	0.2133(3)	0.2321(3)	0.1154(3)	5.8(2)	C(13)	0.8014(3)	0.1056(2)	0.6923(2)	3.1(1)
C(26)	0.2601(3)	0.3316(3)	0.1630(4)	6.6(2)	C(14)	0.7305(3)	0.0381(2)	0.6833(3)	4.3(2)
C(27)	0.4578(4)	0.3796(3)	0.2388(4)	7.9(3)	C(15)	0.7544(3)	−0.0732(3)	0.6212(3)	5.0(2)
C(28)	0.5940(4)	0.3290(3)	0.2438(4)	7.4(2)	C(16)	0.8529(3)	−0.1233(2)	0.5665(3)	4.9(2)
C(29)	0.2190(3)	0.0655(3)	−0.0488(3)	5.0(2)	C(17)	0.9274(3)	−0.0623(3)	0.5748(3)	5.0(2)
C(30)	0.2467(3)	0.0186(3)	−0.1750(3)	4.9(2)	C(18)	0.9015(3)	0.0505(2)	0.6366(3)	4.0(2)
C(31)	0.4141(3)	−0.0177(3)	−0.2671(3)	4.9(2)	C(19)	0.6093(3)	0.2918(2)	0.7287(3)	3.2(1)
C(32)	0.4034(3)	0.0939(3)	−0.2814(3)	5.4(2)	C(20)	0.5311(3)	0.2723(3)	0.6007(3)	4.4(2)
C(1)	0.8311(3)	0.3038(2)	0.7178(3)	3.3(1)	C(21)	0.3973(3)	0.3155(3)	0.5652(3)	5.1(2)
C(2)	0.9590(3)	0.3036(3)	0.7753(3)	5.0(2)	C(22)	0.3362(3)	0.3791(3)	0.6581(4)	5.6(2)
C(3)	1.0196(3)	0.3504(3)	0.7328(4)	5.8(2)	C(23)	0.4083(3)	0.4004(3)	0.7849(3)	5.1(2)
C(4)	0.9528(3)	0.4012(3)	0.6292(3)	5.4(2)	C(24)	0.5419(3)	0.3577(2)	0.8184(3)	3.9(2)
C(5)	0.8272(3)	0.4033(3)	0.5693(3)	5.3(2)	B	0.7675(3)	0.2383(3)	0.7659(3)	3.1(2)
C(6)	0.7676(3)	0.3560(3)	0.6131(3)	4.3(2)					

---

† Present address: National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305.

anisotropic thermal parameters including the hydrogens, and bond distances, and angles have deposited as Document No. 9043 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

The structure of the complex in the unit cell is shown in Fig. 1, and the dimeric structure of cation is shown in Fig. 2. Selected bond distances and torsional angles are given in Table 2.

The cation is binuclear metal complex ion formed by two $[Na(C_8H_{18}O_5)]^+$. The sodium ion is six-coordinated by five ether oxygens O(1)—O(5) of one TEG and O(4′) of the other TEG. The bond distances Na-O(1), Na-O(2), Na-O(3), and Na-O(5) are comparable to the Na-O bond distances in some other complexes such as [Na(benzo-15-crown-5)]I[5] and $[Ca(TEG)](C_6H_2N_3O_7)_2$.[6] O(4) and O(4′) are coordinated to two Na^+ simultaniously and play the role of bridges to connect two $[Na(C_8H_{18}O_5)]^+$. The bond lengths Na–O(4) and Na–O(4′) are significantly longer than other Na–O distances. The ligand molecules are highly strained due probably to the compact dimeric structure of the overall cation. For example, the dihedral angle C(30)-O(4)-C(31)-C(32), 83.5(3)°, is largely deviated from the stable angle, ca. 180°.[7] This unique conformation leads to an increase of the energy of the ligand by about 5 kJ mol^{-1} as compared with state of the stable trans conformation.[8] We consider that the binuclear metal complex is highly stable to overcome the strain energy produced in the TEG molecule.

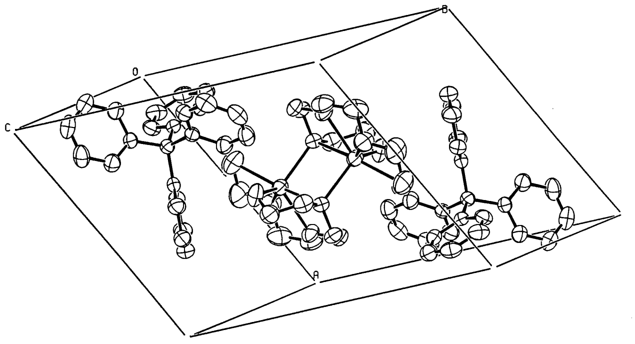

Fig. 1. The structure of binucler complex [Na(TEG)-$B(C_6H_5)_4]_2$ in the unit cell.

The boron atom in $B(C_6H_5)_4^-$ is bonded tetrahedrally by four phenyl groups in slightly distorted manner. The conformation of the phenyl groups are arranged so as to minimize the mutual repulsion energy between each other.

In the previous work for TEG–NaI complex,[2] we concluded from the solid-state high-resolution ^{13}C spectrum that the TEG chain assumes *gg* conformation and the terminal OH groups in TEG are not coordinated to the Na ion. In the case of TEG–$NaBPh_4$ complex the TEG chain assumes *tg* conformation except for C(30)-O(4)-C(31)-C(32), in which O(4) is used to form bridging. All of the terminal OH groups contribute to coordination to the Na ion. The differences in these structures may be caused by the difference in the size of

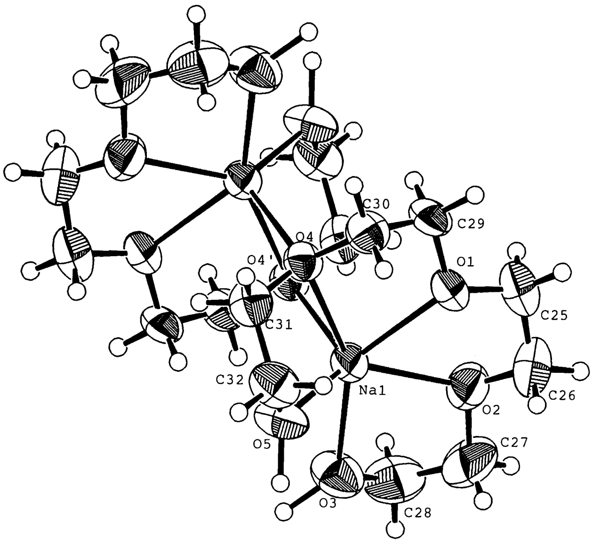

Fig. 2. The dimeric structure of cation $[Na(C_8H_{18}O_5)]_2^{2+}$.

Table 2. Relevant Bond Distances, Angles, and Torsion Angles

Bond distances (Å)		Bond angles (deg.)		Torsion angles[a] (deg.)	
Na-Na	3.667(3)	O(1)-Na-O(2)	69.52(8)	O(1)-C(25)-C(26)-O(2)	−58.4(4)
Na-O(1)	2.368(3)	O(1)-Na-O(3)	137.87(9)	O(1)-C(29)-C(30)-O(4)	62.0(3)
Na-O(2)	2.371(2)	O(1)-Na-O(4)	65.87(7)	O(2)-C(27)-C(28)-O(3)	57.6(5)
Na-O(3)	2.329(3)	O(1)-Na-O(4′)	107.9(1)	O(4)-C(31)-C(32)-O(5)	56.0(4)
Na-O(4)	2.670(2)	O(1)-Na-O(5)	108.67(9)	C(25)-O(1)-C(29)-C(30)	167.5(2)
Na-O(4′)	2.419(2)	O(2)-Na-O(3)	71.5(1)	C(25)-C(26)-O(2)-C(27)	177.5(4)
Na-O(5)	2.259(3)	O(2)-Na-O(4)	134.8(1)	C(26)-O(2)-C(27)-C(28)	−168.6(4)
		O(2)-Na-O(4′)	99.28(9)	C(26)-C(25)-O(1)-C(29)	−179.9(2)
		O(2)-Na-O(5)	136.4(1)	C(30)-O(4)-C(31)-C(32)	83.5(3)
		O(3)-Na-O(4)	153.1(1)	C(29)-C(30)-O(4)-C(31)	−159.2(3)
		O(3)-Na-O(4′)	93.35(9)		
		O(3)-Na-O(5)	89.1(1)		
		O(4)-Na-O(5)	67.60(9)		
		O(4)-Na-O(4′)	87.92(7)		
		O(5)-Na-O(4′)	121.00(9)		

a) For example, A–B–C–D; the sign is positive if when looking from atom B to atom C a clockwise motion of atom A would superimpose it on atom D.

anions.

We would like to thank Mr. S. Ishimaru for his help in preparing the manuscript.

The persent work was partially supported by a Grand-in-Aid for Scientific Research No. 61430006 from the Ministry of Education, Science, and Culture. We are also grateful to Asahi Chemical Industry Co., Ltd. for partial financial support.

References

1) For example, M. B. Armand, J. M. Chabagno, and M. J. Doclot, "Fast Ion Transport in Solids," ed by Vashiha, Mundey, and Shenoy, North-Holland, New York (1979).

2) T. Ueda, H. Ohki, N. Nakamura, and H. Chihara, *Bull. Chem. Soc. Jpn.*, **64**, 2416 (1991).

3) C. J. Gilmore, *J. Appl. Crystallogr.*, **17**, 42 (1984).

4) TEXRAY Structure Analysis Package, Molecular Structure Corporation (1985).

5) M. A. Bush and M. R. Truter, *J. Chem. Soc., Chem. Commun.*, **1970**, 1439.

6) T. P. Singh, R. Reinhardt, and N. S. Poonia, *Indian J. Chem., Sect. A*, **23**, 976 (1984).

7) J. E. Mark and P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1415 (1965).

8) H. Wieser, W. G. Lailaw, P. T. Krueger, and H. Fuhrer, *Spectrochim. Acta, Part A*, **24**,1055 (1968).