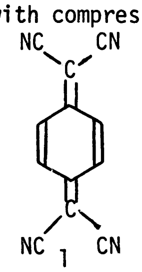
CHEMISTRY LETTERS, pp. 111-112, 1979. Published by the Chemical Society of Japan

SYNTHESES AND ELECTRICAL PROPERTIES OF ALKALI-METAL-TCNQ-CROWN ETHER COMPLEXES

Takashi NOGAMI, Minoru MORINAGA, Yasuhiro KANDA, and Hiroshi MIKAWA
Department of Applied Chemistry, Faculty of Engineering, Osaka University,
Yamadakami, Suita, Osaka 565

Complexes of crown ethers (2,3,4,5,6) and cryptand (7) with alkali-metal-TCNQ salts (8,9,10,11) were isolated in expectation of interesting electrical, magnetic, structural and optical properties. The electrical resistivities, dielectric constant, and dielectric loss of several complexes were measured.

Many inorganic salts have been known to complex with crown ethers.[1] However, no report has appeared which aims at the studies of the electrical, magnetic, and optical properties. Furthermore, the isolations of the complexes of crown ethers with organic anion salts have been scanty. The high conductive complexes of 7,7,8,8-tetracyanoquinodimethane (TCNQ,1) have been extensively studied, and many interesting properties have been clarified.[2] We prepared the complexes of 15-crown-5 (2), 18-crown-6 (3), dibenzo-18-crown-6 (4), dicyclohexyl-18-crown-6 (5), dibenzo-24-crown-8 (6), and cryptand [2,2,2] (7) with alkali-metal-TCNQ salts[3] (M^+TCNQ^-), i.e., $M^+=Na^+$(8), $M^+=K^+$ (9), $M^+=Rb^+$(10), and $M^+=Cs^+$(11), and measured their electrical resistivities, dielectric constant, and dielectric loss with compressed samples (see Tables 1 and 2).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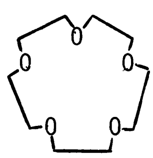
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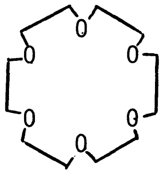
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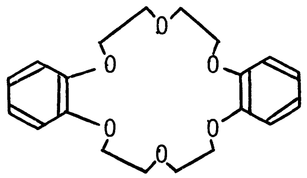
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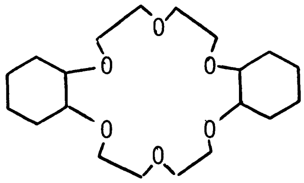
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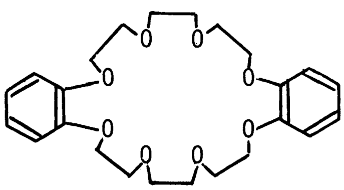
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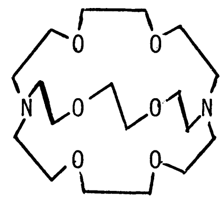
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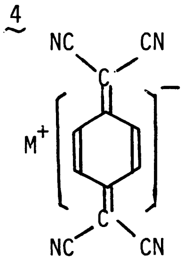
8: $M^+ = Na^+$
9: $M^+ = K^+$
10: $M^+ = Rb^+$
11: $M^+ = Cs^+$

8,9,10,11

Alkali-metal-TCNQ salts with excess molar ratios of crown ethers or cryptand were dissolved in methanol, warmed for 10 min at 60°C, and cooled overnight at -15°C. Filtration of the precipitate gave simple salts ((crown ether)$_m$(M^+TCNQ^-)$_n$) as blue crystals in the cases of 2,3,5,6, and 7, and green ones in the cases of 4 and 6. Equimolar amounts of simple salts and neutal TCNQ in methanol gave complex salts (crown ether·M^+TCNQ^-·TCNQ) after keeping it overnight at -15°C. These complexes gave good analytical agreements.

The electrical resistivities (ρ), dielectric constant at 1 kHz (ε), and dielectric loss at 1 kHz (tan δ) with compressed samples[4] were measured at room temperature, which are shown in Table 2 (accuracy: within 4 %). Simple salts were found to be almost insulators. However, the complex salt 3-10-1 was 10^5 times more conductive than the corresponding simple salts 3-10.

Table 1. Alkali-metal-TCNQ-Crown Ether Complexes.

complexes	mp (°C)	composition*
simple salts		
2-8	150	1:1
2-9	210	2:1
2-10	202-203	2:1
3-8	151-153	1:1
3-9	213-216	1:1
3-10	208-210	1:1
3-11	200-202	3:2
4-8	214-216	1:1
4-9	202-204	1:1
4-10	173-177	2:1
4-11	155-156	2:1
5-8	173-174	1:1
5-9	189-192	1:1
5-10	190-192	1:1
6-11	137-138	1:1
7-8	160-161	1:1
7-9	137	1:1
7-10	146-148	1:1
7-11	151-153	1:1
complex salts		
2-9-1	uncertain	2:1:1
2-10-1	260	2:1:1
3-10-1	235	1:1:1
4-9-1	224-225	1:1:1
7-9-1	206-207	1:1:1

* Simple salts; crown ether:M^+TCNQ^-
Complex salts; crown ether:M^+TCNQ^-:TCNQ

Table 2. Electrical resistivities (ρ), dielectric constant at 1 kHz (ε), and dielectric loss at 1 kHz ($\tan\delta$) with compressed samples at room temperature.

complexes	ρ (Ωcm)	ε	$\tan\delta$
2-9	8.5×10^{11}	3.3	0.017
2-10	1.3×10^{9}	5.9	0.41
3-10	6.9×10^{9}	4.1	0.17
4-8	insulator	3.1	0.0027
4-9	insulator	2.8	0.0032
4-10	2.0×10^{9}	4.4	0.27
4-11	1.1×10^{11}	4.3	0.020
5-10	2.8×10^{11}	3.0	0.098
6-11	insulator	3.6	0.0043
7-9	1.3×10^{10}	7.5	0.22
7-11	2.4×10^{10}	5.0	0.15
3-10-1	1.2×10^{4}	-	-

References

1) C. J. Pederson, J. Am. Chem. Soc., 89, 2495, 7017 (1967).
2) For example, "Low-Dimensional Cooperative Phenomena", ed. by H. J. Keller, Plenum Press, New York and London (1974); "Chemistry and Physics of One-Dimensional Metals", ed. by H. J. Keller, Plenum Press, New York and London (1977).
3) L. R. Melby, R. J. Harder, W. R. Hertler, M. Mahler, R. E. Benson, and W. E. Mochel, J. Am. Chem. Soc., 84, 3374 (1962).
4) Samples were ground into powder in an agate bowl, and compressed at 2200 kg/cm^2. The pellet thus obtained has a diameter of 13 mm, and thickness of about 800~900 μm. Silver paste was painted onto the both surfaces of the pellet as electrodes (electrode area: about 50 mm^2).

(Received November 11, 1978)