Volume 23
Number 17
August 15, 1984

Inorganic Chemistry

Communications

Multinuclear Magnetic Resonance Studies of Macrocyclic Complexation in Room-Temperature Molten Salts

Sir:

Binary salt mixtures that are liquid at room temperatures have a wide gamut of practical and theoretical applications. The best known and best explored medium is a mixture of aluminum(III) chloride and *n*-butylpyridinium chloride ((B-P)Cl),[1-5] which is liquid near room temperature in the composition range 45–67 mol % of $AlCl_3$.

In a previous publication[6] we have shown that in the "basic" (<50 mol % $AlCl_3$) and in the "acidic" (>50 mol % of $AlCl_3$) mixtures lithium chloride is sufficiently soluble to yield a ^7Li NMR signal and that the chemical shifts of ^7Li differ by approximately 2.5 ppm. Considering the relatively narrow range of ^7Li chemical shifts,[7] the results clearly indicate a very different environment of the Li^+ ion in the two media. This conclusion is also supported by the fact that the two lines are very different in width, the first being approximately 1 Hz and the second approximately 20 Hz. It seemed reasonable to conclude that LiCl forms two types of mixed chloro complexes with $AlCl_3$.

The main objective of this study was to see if the dissolved alkali-metal cations are sufficiently reactive to form macrocyclic complexes in the absence of a molecular solvent and, if so, how the properties of such complexes are affected by the ionic medium of the melt. To our knowledge macrocyclic complexes of the alkali-metal ions have not been previously investigated in molten salt media.

NMR measurements were performed on a Bruker WH-180 spectrometer at a field strength of 42.3 kG. Chemical shifts were referenced to external aqueous 0.015 M LiCl, 0.01 M NaCl, and 0.01 M CsBr solutions for ^7Li, ^{23}Na, and ^{133}Cs measurements, respectively.

The addition of crown ethers 12-crown-4 (12C4), 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), and 18-crown-6 (18C6) to basic melts, containing 1 mol % of LiCl, resulted in significant shifts of the ^7Li resonance, indicating the formation of the corresponding crown ether complex. In all cases the exchange was fast and only one, population-averaged, signal was observed; the signals shifted upfield with increasing ligand concentrations. For cryptands C211, C221, and C222, (diazapolyoxa macrobicyclic polyethers[8]) the exchange was

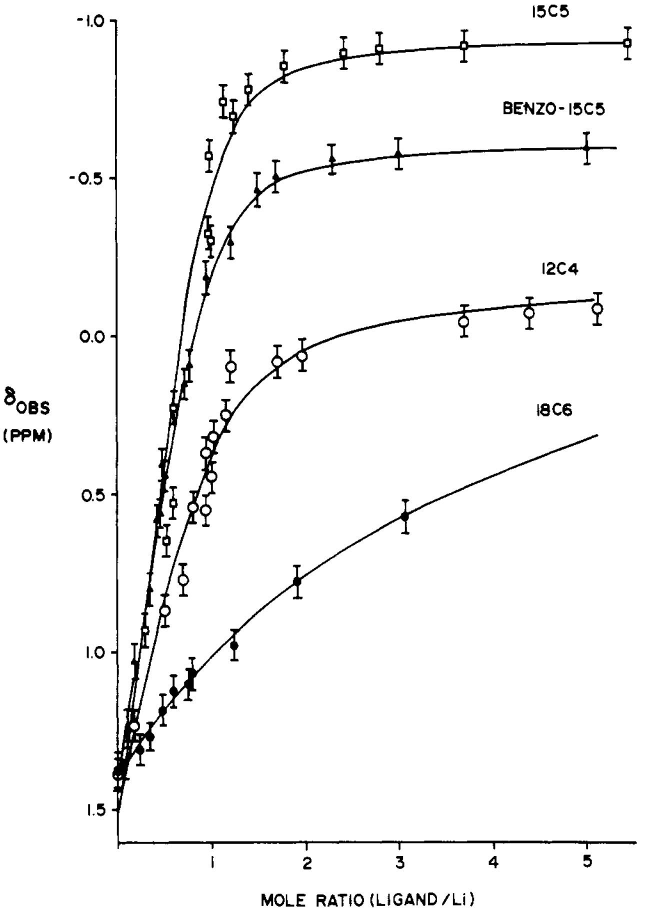


Figure 1. Lithium-7 chemical shifts vs. ligand-to-lithium mole ratio in basic (0.8:1) $AlCl_3$–(BP)Cl melts for four crown ether–Li^+ complexes. Uncertainties in the experimental chemical shifts are indicated by error bars. Solid lines are the computer-generated curves.

Table I. Formation Constants of Li^+ Macrocyclic Complexes

	$\log K_f$			
crown ether	melt	pyridine[a]	methanol[a]	acetone[a]
12C4	1.87 ± 0.12	0.70 ± 0.05	~0	1.62 ± 0.03
15C5	2.39 ± 0.17	2.48 ± 0.06	1.23 ± 0.06	3.59 ± 0.08
benzo-15C5	2.33 ± 0.05			
18C6	0.59 ± 0.12	0.62 ± 0.07	~0	1.50 ± 0.02

[a] Reference 11.

---

(1) Hussey, C. L.; King, L. A.; Wilkes, J. S. *J. Electroanal. Chem.* **1979**, *102*, 321.
(2) Singh, P.; Rajeshuar, K.; DuBow, J.; Job, R. *J. Am. Chem. Soc.* **1980**, *102*, 4676.
(3) Laher, T. M.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 4079.
(4) Pickup, P. G.; Osteryoung, R. A. *J. Electrochem. Soc.* **1983**, *130*, 1965.
(5) Gale, R. J.; Motyl, K. M.; Job, R. *Inorg. Chem.* **1983**, *22*, 130.
(6) Taulelle, F.; Popov, A. I. *Polyhedron* **1983**, *2*, 889.
(7) Cahen, Y. M.; Handy, P. R.; Roach, E. T.; Popov, A. I. *J. Phys. Chem.* **1975**, *79*, 80.

0020-1669/84/1323-2557$01.50/0 © 1984 American Chemical Society

slow, and solutions containing an excess of the lithium ion showed two ^{7}Li signals. These results are very similar to the ones we had previously obtained with lithium cryptates in nonaqueous solutions.[9]

Plots of observed ^{7}Li chemical shifts vs. (ligand)/(Li^+) mole ratio are shown in Figure 1. Formation constants and limiting chemical shifts for the complexed lithium ion were calculated from these data by using previously described techniques.[10] The results are shown in Table I. Values of some formation constants, obtained previously in nonaqueous solutions, are given for comparison.[11]

It is interesting to note that the stabilities of the complexes in the melt and in nonaqueous solvents follow the order 15C5 > 12C4 > 18C6. The fact that 18C6 forms the weakest complex is not surprising in view of the large disparity between the ionic diameter and the size of the cavity. It is surprising, however, that 15C5 forms more stable complexes than 12C4 since, according to the literature, its cavity size is considerably larger than the Li^+ ion.[12]

It seems reasonable to expect that the lithium ion enclosed in the two-dimensional cavity of a crown ether also remains bonded to one or even two chloride ions. Crystal structure studies on crown ether complexes abound with examples where the complexed cation has either one or two anions as near neighbors. For example, in the LiNCS·12C4 complex, the Li^+ ion is coordinated to the NCS^- counterion,[13] and in the $LiNO_3$·B14C4 complex, it is coordinated to the nitrate ion,[14] while in the $Mg(NCS)_2$·B15C5 complex, the cation is coordinated to two anions, one above and one below the macrocyclic plane.[15] The likelihood of a Li^+–Cl^- bond is much less for the C211 complex, where Li^+ is enclosed in a three-dimensional cavity. Studies on the nature and the structures of macrocyclic complexes of lithium in molten salts are being continued in our laboratory.

Initial studies by ^{23}Na and ^{133}Cs NMR on sodium chloride and cesium chloride in the melts showed that the two salts are essentially insoluble in the basic media. However, CsCl is soluble in acidic melts to the extent of approximately 0.25 mol %. The ^{133}Cs chemical shift remains essentially constant between 50 and 60 mol % of $AlCl_3$ but then changes rapidly and shifts upfield some 20 ppm in the 67 mol % mixture. It is quite obvious that the immediate environment of the Cs^+ ion undergoes a substantial change somewhere between 60 and 67 mol % of $AlCl_3$. One possible explanation would be that, with melt compositions in excess of 60 mol % $AlCl_3$, the interaction of Cs^+ with $Al_2Cl_7^-$ begins to predominate over that with $AlCl_4^-$.

Addition of crown ethers to the CsCl solution in acidic melts changed very little the ^{133}Cs resonance, indicating only a minor change in the cationic environment. It is interesting to note, however, that the addition of 18C6 to a CsCl suspension in a basic melt (45 mol % $AlCl_3$) resulted in a ^{133}Cs signal some 50 ppm upfield from the ^{133}Cs resonance in a 60% $AlCl_3$–(BP)Cl melt. This behavior is very similar to the one described by Pedersen,[16] where $KMnO_4$ was solubilized in benzene by the addition of dicyclohexano-18C6.

Preliminary studies have shown that NaCl is soluble in the acidic melt. In a 51 mol % $AlCl_3$ melt a rather broad line (approximately 100 Hz) appeared about 6 ppm upfield from the reference. There is a slight (approximately 2 ppm) upfield shift when the melt composition is changed from 60 to 67 mol % of $AlCl_3$. The addition of B15C5 to NaCl solution in a 51 mol % melt results in a very large broadening of the signal, which indicates the formation of the B15C5·Na^+ complex.

Acknowledgment. The authors gratefully acknowledge the support of this work by NSF Grant CHE-8010808.

Department of Chemistry
Michigan State University
East Lansing, Michigan 48824

Rick R. Rhinebarger
John W. Rovang
Alexander I. Popov*

Received February 15, 1984

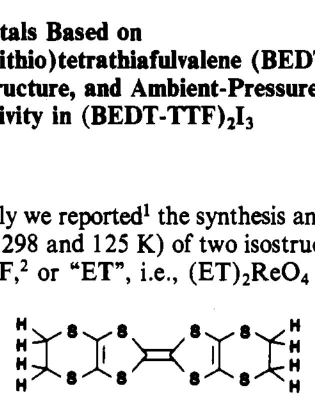
---

(8) Dietrich, B.; Lehn, J.-M.; Sauvage, J. P. *Tetrahedron Lett.* **1969**, 2885.
(9) Cahen, Y. M.; Dye, J. L.; Popov, A. I. *J. Phys. Chem.* **1975**, *79*, 1289.
(10) Bodner, R. L.; Greenberg, M. S.; Popov, A. I. *Spectrosc. Lett.* **1972**, *5*, 489.
(11) Smetana, A. J.; Popov, A. I. *J. Solution Chem.* **1980**, *9*, 183.
(12) Pedersen, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 386.
(13) Groth, P. *Acta Chem. Scand., Ser. A* **1981**, *A35*, 463.
(14) Holt, E. M.; Malpass, G. D.; Ghirardelli, R. G.; Palmer, R. A.; Rubin, B. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 394.
(15) Owen, J. D. *J. Chem. Soc., Dalton Trans.* **1978**, 1418.
(16) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 2495.

Synthetic Metals Based on Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF): Synthesis, Structure, and Ambient-Pressure Superconductivity in $(BEDT\text{-}TTF)_2I_3$

Sir:

Very recently we reported[1] the synthesis and detailed crystal structures (at 298 and 125 K) of two isostructural derivatives of BEDT-TTF,[2] or "ET", i.e., $(ET)_2ReO_4$ and $(ET)_2BrO_4$.



BEDT-TTF
(ET)

These materials comprise a new *structural*[1] class of electrical conductors of which $(ET)_2ReO_4$ was, until very recently, reportedly the only S-based organic superconductor[3] ($T_c \simeq 2.0$ K) when under an applied pressure of $\simeq$4 kbar. It was suggested that $(ET)_2X$ systems having this structural type, i.e., a predominance of shorter *inter*chain vs. intrachain (stacking) S–S interaction distances (the former less than the van der Waals S-atom radius sum of 3.6 Å), might hold the promise of a rich variety of electrical properties including potentially new superconductors.[1] On the basis of two consecutive reports[4,5] it appears that $(ET)_2I_3$ is a member of this new structural class, but more importantly, that this salt is the first *ambient-pressure* S-based organic *super*conductor (four-probe resistivity measurements, $T_c \simeq 1.4$–1.5 K).[4] To date, the only ambient-pressure organic superconductor has been *Se*-based $(TMTSF)_2ClO_4$,[7] ($T_c \simeq 1.2$ K). However, numerous crystalline phases of $(ET)_2I_3$ have been reported[5,6] with electrical

---

(1) Williams, J. M.; Beno, M. A.; Wang, H. H.; Reed, P. E.; Azevedo, L. J.; Schirber, J. E. *Inorg. Chem.* **1984**, *23*, 1790.
(2) BEDT-TTF or "ET" is bis(ethylenedithio)tetrathiafulvalene, $C_{10}S_8H_8$.
(3) Parkin, S. S. P.; Engler, E. M.; Schumaker, R. R.; Lagier, R.; Lee, V. Y.; Scott, J. C.; Greene, R. L. *Phys. Rev. Lett.* **1983**, *50*, 270.
(4) Yagubskii, E. B.; Shchegolev, I. F.; Laukhin, V. N.; Kononovich, P. A.; Kartsovnik, M. V.; Zvarykina, A. V.; Buravov, L. I. *Zh. Eksp. Teor. Fiz., Pis'ma Red.* **1984**, *39*, 12.
(5) Kaminskii, V. F.; Prokhorova, T. G.; Shibaeva, R. P.; Yagubskii, E. B. *Zh. Eksp. Teor. Fiz., Pis'ma Red.* **1984**, *39*, 15. The reported crystal data are as follows: $a = 6.609$ (1), $b = 9.083$ (1), $c = 15.267$ (2) Å; $\alpha = 85.63$ (2), $\beta = 95.62$ (2), $\gamma = 70.22$ (2)°; $V_c = 852.2$ Å^3; $Z = 1$. While no positional or refinement parameters are reported in this reference, the structural projections and associated description convince us that the distorted-hexagon phase and the superconducting[4] needle or flake phases have the same structure.