Spectrochemistry of Solutions. Part 7.[1] Raman Studies of the Effects of Cationic Complexing Agents on Ion Association in Liquid-ammonia Solutions of Alkali-metal Salts

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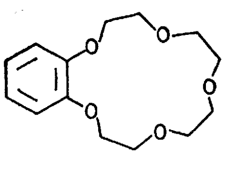
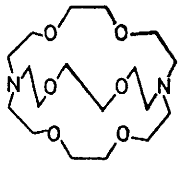
The Raman spectra of sodium and potassium salts of $[NO_3]^-$, $[NO_2]^-$, $[NCO]^-$, $[NCS]^-$, $[N_3]^-$, and $[CN]^-$ in liquid ammonia in the presence of an equimolar amount of the cryptand C222 show a set of single bands characteristic of the free solvated anion. The presence of the ether benzo-15-crown-5 had comparatively little effect on the spectra of sodium and potassium cyanides, which displayed bands characteristic of ion-associated species. The effects of cation-complexing agents on ion association in liquid-ammonia solutions are briefly discussed.

RECENT Raman-spectroscopic studies of 1 : 1 electrolytes have provided direct evidence that a variety of species coexist in equilibrium in liquid-ammonia solutions.[1,2] The assignment of bands to individual species was attempted on the basis of changes in relative band intensity as the temperature or salt concentration changed. In most spectra one band was characterized as due to the ' free ' anion, and the others as due to ion-associated species whose nature was unknown.

By sequestering the cation with a large organic ligand, we expected that the solution equilibria would be drastically altered, and hoped to obtain confirmation of the assignment of the free-anion bands. The ligands used in these experiments were benzo-15-crown-5 and the cryptand C222. Cyclic polyethers have been used previously[3,4] to characterize ion-paired species using this principle. The cavity size of the present ligands is most favourable for the Na^+ cation.



Benzo-15-crown-5



C222

EXPERIMENTAL AND RESULTS

The cryptand was used as received. The crown ether[5] was recrystallized three times from light petroleum, and its purity was checked by t.l.c. All the salts were recrystallized from liquid ammonia before use, using methods similar to those previously described.[6] Solutions containing cryptand were prepared on a semimicro-scale and sealed in thin-walled Pyrex tubing (internal diameter, 2 mm). Ammonia was frozen on to an equimolar mixture of salt and cryptand at *ca.* 77 K to stop the formation of gas pockets which might transfer the solid along the tube. Solutions containing the crown ether were prepared as before.[6] Concentrations were determined on a w/w basis and are expressed as R = (number of moles of solvent)/(number of moles of solute).

Cryptand Mixtures.—The Raman spectra of the anions showed fewer bands in the presence of cryptand than had been observed previously in the absence of cation-complexing agent. In some cases a band narrowing was also observed.

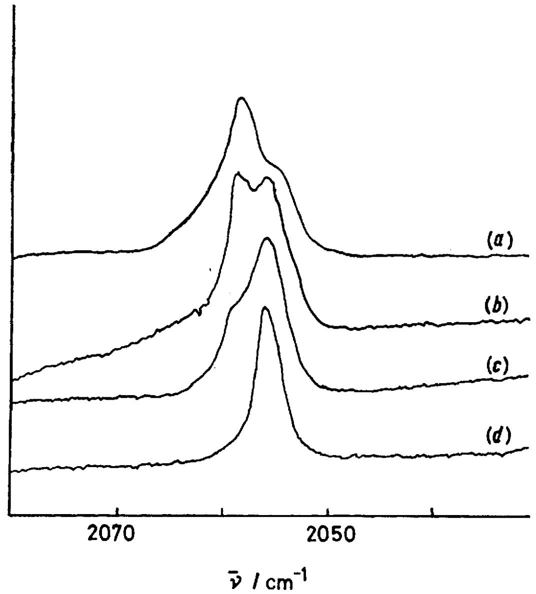


FIGURE 1 Raman spectra between 2 030 and 2 080 cm^{-1} of liquid-ammonia solutions, at 298 K, of (*a*) K[CN] (*R* 183), (*b*) K[CN] (*R* 140) + one equivalent of the crown ether, (*c*) K[CN] (*R* 186) + two equivalents of the crown ether, and (*d*) K[CN] (*R* 92) + one equivalent of the cryptand

The spectrum of potassium cyanide [Figure 1(*a*)] clearly exhibits two components. The spectrum of the K[CN]–C222 mixture [Figure 1(*d*)] contains only a single band at *ca.* 2 057 cm^{-1}. The Na[CN]–C222 mixture also showed a single band at *ca.* 2 056 cm^{-1}, whereas in the absence of cryptand at least three other bands were also reported.[2] The spectrum of the Na[NCO]–C222 mixture showed a single ν(CN) band at *ca.* 2146 cm^{-1}. The spectrum of sodium cyanate alone in liquid ammonia has an additional band at *ca.* 2 156 cm^{-1}. The spectrum of sodium nitrite showed at least four bands in the ν_2 region, including one

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[1] Part 6, P. Gans, *Pure Appl. Chem.*, 1977, **49**, 99.

[2] P. Gans, J. B. Gill, and M. Griffin, *J. Amer. Chem. Soc.*, 1976, **98**, 4661.

[3] M. M. A. Loupy and J. Corset, *Compt. rend.*, 1974, **C279**, 713.

[4] U. Takashi, T. E. H. Esch, and J. Smid, *J. Amer. Chem. Soc.*, 1971, **93**, 6760.

[5] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1967, **89**, 7017.

[6] P. Gans and J. B. Gill, *J.C.S. Dalton*, 1976, 779.

at *ca.* 795 cm^{-1}. In the presence of the cryptand only the latter remained.

Both the ν_1 and $2\nu_2$ bands of sodium azide showed reduced complexity in the presence of the cryptand, with bands common to the two spectra at *ca.* 1 321 and 1 246 cm^{-1}. With sodium nitrate the cryptand caused a band at *ca.* 720 cm^{-1} to disappear, and the band at *ca.* 710 cm^{-1} to decrease by *ca.* 40% in half-width. A similar decrease occurs in the spectra of $Na[NO_3]$ alone, at low concentration or temperature.[7] It was not possible to examine the ν_3 nitrate band because of interference from cryptand bands.

There is also some interference from the ligand's vibrations in the spectra of its mixtures with potassium thiocyanate [Figure 2(*b*)]. The $\nu(CS)$ band at *ca.* 736 cm^{-1} is partly overlapped by a cryptand band at *ca.* 750 cm^{-1}, and another weak feature at *ca.* 730 cm^{-1} may also be due to the ligand. In the $\nu(CN)$ region the alkali-metal thiocyanates give broad, slightly asymmetric, bands whose structure does not correlate well with the structure of the $\nu(CS)$ bands, and presumably consists of a number of unresolved peaks. In the thiocyanate–cryptand mixtures the $\nu(CN)$ region is similar to that of the thiocyanates, with an additional feature consisting of a long tail on the low-frequency side.

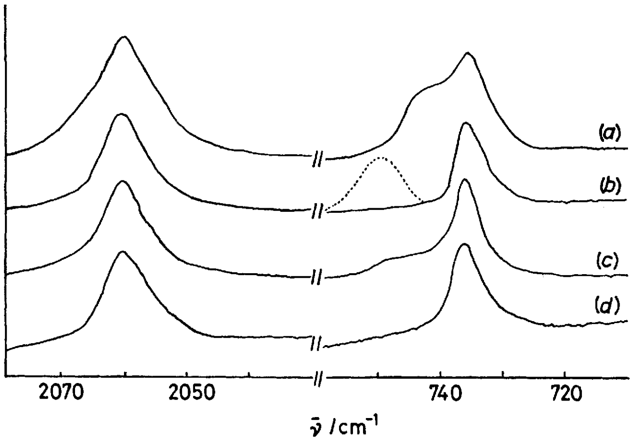

FIGURE 2 Raman spectra in the 710—760 and 2 030—2 080 cm^{-1} regions of liquid-ammonia solutions, at 298 K, of (*a*) K[NCS] (*R* 91), (*b*) K[NCS] (*R* 79) + one equivalent of the cryptand, (*c*) Na[NCS] (*R* 86), and (*d*) Na[NCS] (*R* 80) + one equivalent of the cryptand. The broken section of curve (*b*) corresponds to a ligand vibration

The spectrum of K[NCS]–C222 contained a strong, polarized, Raman shift at *ca.* 264 cm^{-1} which is probably attributable to a metal-in-cage vibration. Most sodium salt–C222 mixtures had a weak Raman shift at *ca.* 275 cm^{-1} which may be similarly assigned.

Crown-ether Mixtures.—Most of the solutions containing salt–crown ether mixtures fluoresced strongly. The fluorescence was reduced slightly when using 514.5-nm excitation, although sodium perchlorate quenched the fluorescence completely, even when using 488.0-nm excitation. The spectra of the mixtures of crown ether and sodium nitrate, cyanide, or perchlorate showed minimal differences from those of the salt solutions without crown ether, but the fluorescence made the aquisition of good spectra difficult. The spectrum of a 1 : 1 K[CN]–crown ether mixture did, however, show an increase in the relative intensity of the band at *ca.* 2 056 cm^{-1}, as illustrated in Figure 1(*b*). The spectrum of a 1 : 2 K[CN]–crown ether mixture showed an even greater enchancement of this band [Figure 1(*c*)].

DISCUSSION

We have postulated that the unexpected complexity of the Raman spectra of 1 : 1 electrolytes in liquid-ammonia solution is due to the co-existence of various forms of ion pair, and the so-called free ion. In the six systems studied here the spectroscopic effect of added cryptand ligand was to reduce to zero the intensity of all the anion bands except one. We can therefore assign that band to the ' free ' anion. The cryptand C222 is seen to be a good sequestering agent for the sodium and potassium ions in liquid ammonia. By replacing the ammonia molecules in the first co-ordination sphere, the cryptand causes the van der Waals radius of the cation to increase and the predominantly electrostatic cation–anion interactions are effectively reduced to zero. While there is probably still some association between the $[M(cryptand)]^+$ cation and anion, the perturbation of the anion's vibrations by the cation electrostatic field must be too small to be measureable. As regards contact ion-pair formation, the cryptand renders this impossible. Some confirmation of the cation's co-ordination is given by the possible observation of a metal-in-cage vibration.

The assignment of the ' free '-ion band is in agreement with the trend observed in the salt solutions in which the band increases in intensity relative to the other bands with decreasing salt concentration or temperature. Thus, these experiments lend support to our hypothesis concerning the existence of ion association in solutions of 1 : 1 electrolytes, and in particular demonstrate that the ' free ' anions are characterized by a single band at fixed frequency in all the solutions and mixtures. The nature of the ion association is still uncertain, because the cryptand will probably destroy contact and solvent-shared ion pairs equally effectively.

The effects of added crown ether were studied less thoroughly because of the limitations imposed by the ligand's fluorescence, and because the crown ether did not bring about spectacular changes in the spectra. It is clear that the equilibria amongst the free ions and ion-paired species are only slightly modified by the presence of the crown ether. It may be that the ligand adopts a coronal configuration around the cation,[8] and that ion association still takes place above and below the cation in its planar ligand environment. In this case different ion-paired species would be formed and we would have expected this to be reflected in spectral differences. It would be an amazing coincidence if the acceptor nature of the $[M(NH_3)_x]^+$ and $[M(crown\ ether)]^+$ cations was very similar.

A more likely explanation is that the crown ether does not form strong complexes with Na^+ and K^+ in liquid ammonia. Thus, addition of extra ligand to the K[CN]-crown ether mixture caused the ' free ' cyanide-ion concentration to increase, as the equilibrium was displaced

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[7] P. Gans, J. B. Gill, and M. Griffin, unpublished work.

[8] M. R. Truter, *Structure and Bonding*, 1973, **16**, 71.

in favour of the [K(crown ether)]$^+$ complex. The weakness of the crown ether–cation complexes in liquid ammonia relative to other solvents must be attributed both to differences in the medium and to differences in the donor power of the solvent as a ligand.[9]

Although the utility of crown ethers for studies of ion pairing is now well established,[10,11] we are not aware of any previous work of this sort with a cryptand ligand.

We thank Professor A. I. Popov for a generous gift of 500 mg of the cryptand, with which all these experiments were performed.

[7/816 *Received*, 11*th May*, 1977]

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[11] K. H. Pannell and D. Jackson, *J. Amer. Chem. Soc.*, 1976, **98**, 4443.