Reactions of some Transition Metal Salts with N-phenylaza 15-crown-5* (L)

DHEEB MARJI** and JAMIL ABRAHIM

Chemistry Department, Yarmouk University, Irbid, Jordan

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There is currently much interest in the complexing properties of the macrocyclic polyethers (crown ethers). Their selective metal binding properties [1] make them useful ligands in the study of the coordination chemistry of metallic ions for synthetic and analytical purposes [2]. The use of crown ethers has been particularly concentrated on the complexation of alkali, alkaline earth metals and lanthanides [1–5]. However, little work has been undertaken on transition metal/crown ether complexes. Several complexes of transition metal cations with different crown ethers had been prepared [6–8]. As almost all complexes were prepared from solution, the solvent could be a part of the complex. Sometimes the presence of solvent prevents complexation. Therefore in the present study a new method was utilized which involves reaction between the appropriate metal salt and N-phenylaza 15-crown-5 without using any solvent. Reactions between $Fe(NO_3)_3$, $CuBr_2$, $Co(NO_3)_2$, $Hg(NO_3)_2$ and $NiCl_2$ and the crown ether (L) were investigated. Except with $NiCl_2$, very stable complexes were formed as indicated by the visible absorption and infrared spectra.

Experimental

All the reactions were undertaken using small quantities to demonstrate the feasibility of this method. This was achieved by first introducing a small amount of the crown ether in a narrow diameter tube followed by a small quantity of the hydrated metal salt. Then the contents were heated electrically to a temperature of ~160 °C at which point the reaction occurs as indicated by the new color produced. While heating bubbles of water vapor were evolved, this might suggest that the reaction occurs between the crown ether and the anhydrous metal salt. It is therefore possible to use this method to prepare films of transition metal crown ether complexes. The visible absorption spectra of methanolic solutions of the complexes produced were recorded using SP8-100 spectrophotometer. Infrared spectra of thin films of the complexes were recorded on a Beckmann DK-2 recording spectrophotometer.

Results and Discussion

Except for the nickel salt, the reaction of the metal salts with N-phenylaza 15-crown-5 resulted in formation of stable coordinated complexes. The complexation of metal cations can be observed by IR and visible absorption spectroscopy. Figure 1 shows the visible absorption spectra of the different complexes. As shown, ferric nitrate complex shows an absorption peak at 13 514 cm^{-1} which accounts for the green color observed. The spectrum of $Hg(NO_3)_2$–crown ether shows an absorption maximum at 15 500 cm^{-1} and a shoulder at 16 722 cm^{-1}. The spectrum of $Co(NO_3)_2$–crown ether shows one broad band centered at 18 730 cm^{-1}. For $CuBr_2$–crown ether, the spectrum shows several absorption peaks at: 16 892 cm^{-1}, shoulder at 18 018 cm^{-1}, 20 833 cm^{-1}, 21 739 cm^{-1} and 22 727 cm^{-1}. IR spectra of films of the complexes were recorded and compared with those of the free ligand. Remarkable differences can be observed between the IR spectra of the crown ether and those of their complexes. The greatest differences are observed in the region 1000–1350 cm^{-1}. This is assigned to the CH_2 rocking band and the C–C and C–O stretching bands. Upon complexation the bands were shifted to lower frequencies and an increase in the intensities was observed.

The results above provide strong evidence for complexation between metal salts and N-phenylaza 15-crown-5. If certain assumptions concerning the coordination number are made, comparison (based on electronic spectra) between these complexes and other known complexes with different ligands such as

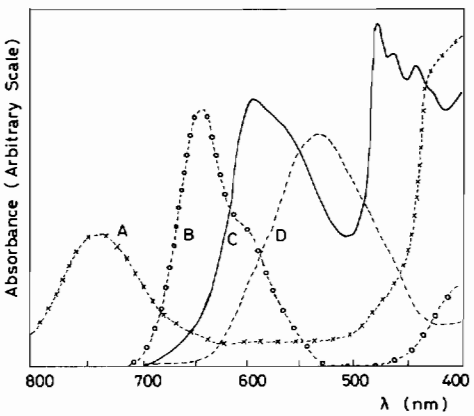

Fig. 1. Absorption spectra of some transition metal complexes with N-phenylaza 15-crown-5 in methanol. A(- -X) $Fe(NO_3)_3$; (B(- -O) $Hg(NO_3)_2$; C(—) $CuBr_2$; D(- - -) $Co(NO_3)_2$.

*IUPAC name is N-phenyl-13-aza-1,4,7,10-tetraoxacyclopentadecan.

**Author to whom correspondence should be addressed.

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ethylenediammine is possible. This ligand (crown ether) has the same strength and is probably in the same place in the spectrochemical series. Inspite of that, the geometry of these complexes cannot be predicted and more information is needed for their characterization. However, this study has been undertaken to demonstrate a new method for preparation of transition metal–crown ether complexes. Further investigations are in progress.

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References

1 J. J. Christensen, D. J. Eatough and R. M. Izzat, *Chem. Rev.*, *74*, 351 (1974).
2 I. M. Kotthoff, *Anal. Chem.*, *51*, IR (1979).
3 C. J. Pedersen, *J. Am. Chem. Soc.*, *89*, 7017 (1967).
4 C. J. Pedersen, *J. Am. Chem. Soc.*, *92*, 391 (1970).
5 C. J. Pedersen and H. K. Frensdorff, *Angew. Chem.*, *11*, 16 (1972).
6 D. Vos, J. Daalen, A, Knegt, Th. Heyningen and L. Otto, *J. Inorg. Nucl. Chem.*, *37*, 1319 (1975).
7 A. C. Su and J. F. Weiher, *Inorg. Chem.*, *7*, 176 (1968).
8 J. Abrahim and D. Marji, *Inorg. Chim. Acta*, *101*, L23 (1985).