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Crown-ether Complexes with some Transition Metals

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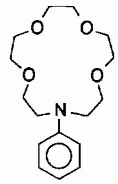
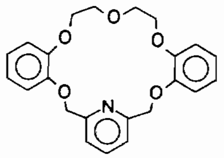
Interest in electrically-neutral ion-complexing agents such as macrocyclic polyethers (crown-ethers) has increased continually since the original work of Pedersen [1–3]. Their selective metal binding properties [4] make them useful ligands for the study of the coordination chemistry of metallic ions for synthetic processes and for analytical purposes [5]. The use of crown-ethers was mainly concentrated on alkali, alkaline earth metals and on lanthanides [1–5]. However, little work has been done on transition metals/crown-ether complexes [6, 7]. In their study, Vos *et al.* [6] showed the formation of stable solid complexes of Cu^{2+}, and Ni^{2+} with 18-crown-6. The aim of our study is to synthesize some complexes of crown ethers with Fe^{3+} and Cu^{2+} cations. Very stable complexes with different metal/crown ratio were formed.



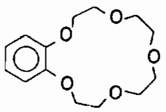
L_1

N-Phenylaza-15-Crown-5



L_2

Dibenzopyridino-15-Crown-5



L_3

Benzo-15-Crown-5

Experimental

A solution of 3 mmol of ligand(s) (Merck, purum) in methanol was added to a solution of 5 mmol of metal salt. The resulting mixture was stirred at about 40 °C for half an hour and the solvent was partially evaporated. The polycrystalline complex was filtered, washed with ether and dried under vacuum. Some of the complexes were precipitated by addition of ether to the methanolic solution; the yield in most cases was larger than 50%. The elemental analyses are reported in Table I. Infrared spectra were recorded on a Beckmann DK-2 recording spectrophotometer using KBr discs; melting points were determined without correction.

Results and Discussion

Reactions of $FeCl_3$ and $CuBr_2$ with crown-ethers resulted in the formation of stable complexes with different metal to crown ratios. The complexation of the cations Fe^{3+} and Cu^{2+} cations can be observed by IR spectroscopy. The composition of the complexes was confirmed by elemental analysis and supported by conductivity measurements.

The infrared spectra of the complexes were recorded and compared with those of the free ligands. Figure 1 displays a portion in the 1600–600 cm^{-1} region of the IR spectra of ligand L_1 and its Fe^{3+} complex. The region due to the CH_2 rocking modes

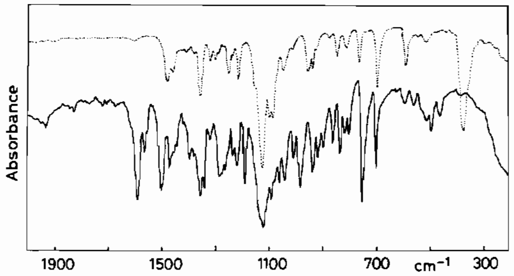


Fig. 1. Part of the IR spectra of N-phenyl-aza-15-Crown-5 (——) and its $FeCl_3$ complex (.......).

TABLE I. Elemental Analysis Data.

Compound	m.p. (°C)	Analysis					
		Found (%)			Calc. (%)		
		C	H	N	C	H	N
$FeCl_3 \cdot L_1$	130	40.90	5.64	3.18	40.40	5.70	3.10
$FeCl_3 \cdot L_2$	155	45.96	4.64	2.40	46.16	4.58	2.44
$FeCl_3 \cdot L_3$	135	37.30	5.20		37.60	5.05	
$2CuBr_2 \cdot L_1$	170	24.95	3.31	1.79	25.89	3.34	1.88
$CuBr_2 \cdot (L_2)_2$	179	53.55	5.04	2.89	24.69	4.90	2.80

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centred at 980 cm^{-1} in the free ligand is shifted to lower frequencies in the complexes. The asymmetric COC stretching band centred at 1120 cm^{-1} in the free ligand is also shifted to lower frequencies in the complexes.

The 1600–600 cm^{-1} region of the IR spectra of ligand L_2 and its Cu^{2+} complex were also compared. The CH_2 modes in the 1200–1300 cm^{-1} region, which is a broad doublet, are shifted to lower frequencies and become a sharp singlet which increases in intensity. In addition the broad COC band between 1100–1200 cm^{-1} also shows an increase in intensity.

Molar conductivities at 25 °C of 10^{-3} M solution in anhydrous methanol were measured. $FeCl_3 \cdot L_1$, $FeCl_3 \cdot L_2$ and $FeCl_3 \cdot L_3$ complexes exhibit molar conductivities of 152, 182 and 98 ohm^{-1} cm^2 mol^{-1}, respectively. This indicates a 1:2 complex for the first two compounds and 1:1 for the third one. On the other hand, $CuBr_2 \cdot L_1$ and $CuBr_2 \cdot L_2$ exhibit molar conductivities of 160, 175 ohm^{-1} cm^2 mol^{-1}, respectively, which indicates 1:1 complexes. These results indicate that different types of crown-ether transition metal complexes can be prepared, and the compositions of these complexes depend on the ligand and transition metal used.

As indicated by the IR spectra, N-phenylaze-15-crown-5 showed a stronger coordination ability among the crown-ethers used. This probably suggests that the lone pair of the nitrogen atom plays a role in the coordination. The complexing ability of this ligand with Lewis acids is noteworthy.

Acknowledgement

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