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Transition Metal Complexes of "Crown" Ethers

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Complexes have been prepared of 18-crown-6 with hydrated halides of manganese(II), cobalt(II) and nickel(II) from acetone solutions. With both manganese and nickel hydrated complexes are obtained which appear to undergo changes from square planar or octahedral to tetrahedral on heating. With cobalt a variety of complexes with varying amounts of water and acetone of crystallisation, are obtained. With the fifteen membered rings, benzo-15-crown-5 and dibromobenzo-15-crown-5, complexes with $CoCl_2$ and $MnBr_2$ appear to contain tetrahedrally coordinated metal.

Introduction

Since Pedersen's discovery [1] that crown ethers will form complexes with alkali metal salts, there have been many reports of complexes with non-transition metals. Some transition metal complexes [2, 3] have been reported but not large numbers. We report the preparation and characterisation of some complexes of the bivalent transition metal ions Mn^{2+}, Co^{2+} and Ni^{2+}.

Experimental

Preparation of the Compounds

Complexes of benzo-15-crown-5

$(CoCl_2)_2$(benzo-15-crown)-5-acetone $CoCl_2·6H_2O$ and benzo-15-crown-5 were refluxed together in methanol. The supernatant liquor was poured from the resultant blue oil, and acetone was added. The sides of the beaker were scratched and a blue crystalline powder came down. *Anal.* Calc. for $(CoCl_2)_2$ (benzo-15-crown-5)·acetone: C, 34.7, H, 4.4, Co, 20.1. Found: C, 34.7, H, 4.7, Co, 20.7%.

This compound was identical to that previously prepared from acetone solution [3].

$(MnBr_2)_2$(benzo-15-crown-5)·1½acetone·H_2O $MnBr_2·6H_2O$ and benzo-15-crown-5 (2:1, M:L) were each dissolved in acetone. On mixing the two solutions a pale yellow crystalline precipitate appeared. *Anal.* Calc. for $(MnBr_2)_2$ (benzo-15-crown-5)·1½acetone·H_2O: C, 27.3, H, 3.8, Br, 39.3. Found C, 27.5, H, 3.7, Br, 39.3%.

Complex of Dibromobenzo-15-crown-5

$(CoCl_2)_3$(4,5-dibromobenzo-15-crown-5)·acetone·$2H_2O$ $CoCl_2·6H_2O$ and dibromobenzo-15-crown-5 (2:1, M:L) were each dissolved in acetone and the solutions mixed. After several days a blue oil separated out. This oil solidified to a blue powder on the addition of ether. *Anal.* Calc. for $(CoCl_2)_3$ (4,5-dibromobenzo-15-crown-5)·acetone·$2H_2O$: C, 22.3, H, 3.1. Found: C, 21.5, H, 3,0%.

Complexes of 18-crown-6

$(NiCl_2)_3$(18-crown-6)·$13H_2O$ $NiCl_2·6H_2O$ and 18-crown-6 (2:1, M:L) were mixed in a methanol/acetone mixture (1:1). After several days a green oil appeared, which solidified to a green powder on the addition of ether. *Anal.* Calc. for $(NiCl_2)_3$(18-crown-6)·$13H_2O$: C, 16.2, H, 5.7, Cl, 24.0. Found: C, 16.8, H, 5.7, Cl, 23.3%.

$NiBr_2$(18-crown-6)·$4H_2O$ $NiBr_2·3H_2O$ and 18-crown-6 were mixed in acetone solution (2:1, M:L) and a yellow green precipitate came down. *Anal.* Calc. for $NiBr_2$ (18-crown-6)·$4H_2O$: C, 24.2, H, 5.8, Br, 28.8. Found: C, 24.1, H, 5.95, Br, 29.2%.

NiI_2(18-crown-6)$_2$·$8H_2O$ NiI_2 and 18-crown-6 (M:L, 2:1) were each dissolved in acetone, on mixing the solutions a yellow–green product was obtained. *Anal.* Calc. for NiI_2 (18-crown-6)$_2$·$8H_2O$: C, 29.3, H, 6.5, I, 25.8. C, 29.7, H, 6.5, I, 26.1%.

$(MnCl_2)_2$(18-crown-6)·$8H_2O$ $MnCl_2·6H_2O$ and 18 crown-6 mixed in methanol (M:L, 2:1) on the addition of ether a pale pink precipitate was obtained. *Anal.* Calc. for $(MnCl_2)_2$(18-crown-6)·$8H_2O$: C, 21.8, H, 6.1, Cl, 21.5. Found: C, 22.0, H, 6.2, Cl, 21.6%.

$(MnBr_2)_2$(18-crown-6)·$8H_2O$ $MnBr_2$ and 18-crown-6 were mixed in acetone solution (M:L, 2:1)

and a pink crystalline precipitate appeared. *Anal.* Calc. for $(MnBr_2)_2$(18-crown-6)$\cdot8H_2O$: C, 17.0, H, 4.78, Br, 38.1. Found: C, 17.2, H, 4.8, Br, 37.9%.

$(CoCl_2)_2$(18-crown-6)$\cdot$acetone$\cdot8H_2O$ $CoCl_2\cdot6H_2O$ and 18-crown-6 (M:L, 2:1) were each dissolved in acetone. A blue precipitate formed when the solutions were mixed. *Anal.* Calc. for $(CoCl_2)_2$(18-crown-6)$\cdot$acetone$\cdot8H_2O$: C, 24.5, H, 5.8, Co, 17.2. Found: C, 23.7, H, 6.0, Co, 17.2%.

Complexes of $CoBr_2$ with 18-crown-6 A variety of compounds was obtained from this preparation. The whole procedure has been carried out several times and compounds of identical spectral properties were obtained in each preparation. Where duplicate analyses are reported these are for different preparations.

$CoBr_2$ and 18-crown-6 (M:L, 2:1) were mixed in acetone solution. After about 30 minutes blue crystals appeared (I). These were filtered off, using a pleated filter paper and rapidly transferred to a stoppered flask. I analysed for $(CoBr_2)_2$(18-crown-6)$\cdot$acetone$\cdot6H_2O$. Calc: C, 20.75, H, 4.9. Found: C, 20.8, H, 4.8%. If I were filtered using a filter pump or left in moisture, the blue crystals rapidly turned pale pink (II) and finally to purple powder (III).

At this stage there appeared to be no further change and the purple powder was formed when crystals of I were left in air. III analysed as $(CoBr_2)_2$(18-crown-6)$\cdot$½acetone$\cdot8H_2O$. Calc: C, 18.5, H, 5.0, Co, 12.5. Found: C, 18.5, 18.5, H, 5.0, 5.0, Co, 12.5%. If the pink crystals II were carefully warmed these turned deep blue (IV), there was then no further change, and IV was not identical to I. IV approximated to $(CoBr_2)_2\cdot$¾acetone$\cdot7H_2O$ Calc: C, 19.6, H, 4.9, Co, 13.5. Found: C, 19.8, 19.3, H, 4.9, 4.9, Co, 12.8%.

From the filtrate from I or if $CoBr_2\cdot6H_2O$ and 18-crown-6 are mixed in a 1:1 molar proportions then large pink crystals are obtained, V, of $CoBr_2$(18-crown-6)$\cdot8H_2O$. Calc: C, 23.0, H, 6.3, Co, 9.4. Found: C, 22.7, 22.8, H, 6.3, 6.1, Co, 9.3%.

Spectra

Infrared spectra were measured using a Perkin-Elmer 457 recording spectrophotometer as nujol mulls between potassium bromide plates. Reflectance spectra were measured on a Unicam SP700 recording spectrophotometer fitted with the SP735 reflectance attachment.

Results

Results of Spectroscopic Measurements

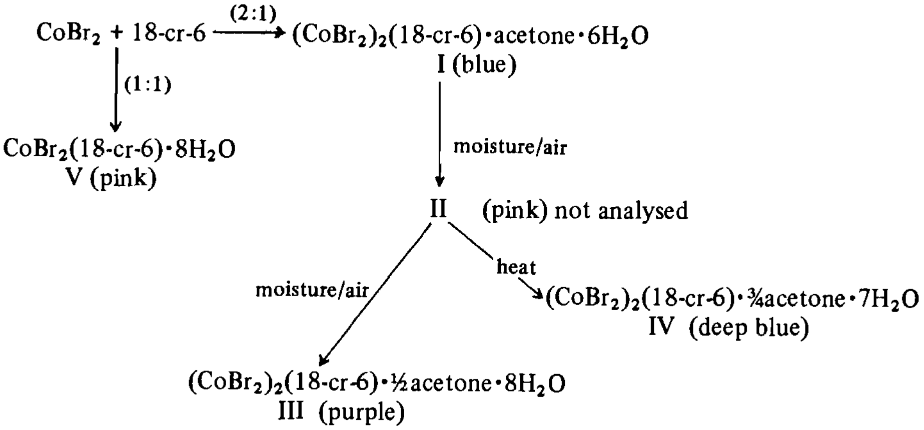
15-membered ring compounds

The infrared spectra of the transition metal-15-membered ring complexes of benzo-15-crown-5 and of dibromo benzo-15-crown-5, are different from those of [3, 4] their complexes with Groups IA and IIA metal ions and of [5] Tl(benzo-15-crown-5)$_2$SCN (Fig. 1). All three compounds show bands in their infrared spectra between 1690–1640 cm^{-1} which may be assigned to acetone.

Diffuse reflectance spectra in the visible region show bands typical of tetrahedral cobalt [8] and manganese [9]. In addition the cobalt complexes show weak bands in the visible region.

18-Membered complexes

The infrared spectra of the transition metal complexes of 18-crown-6 fall into three types: (a) those showing large splitting in the bands centred



Scheme I.

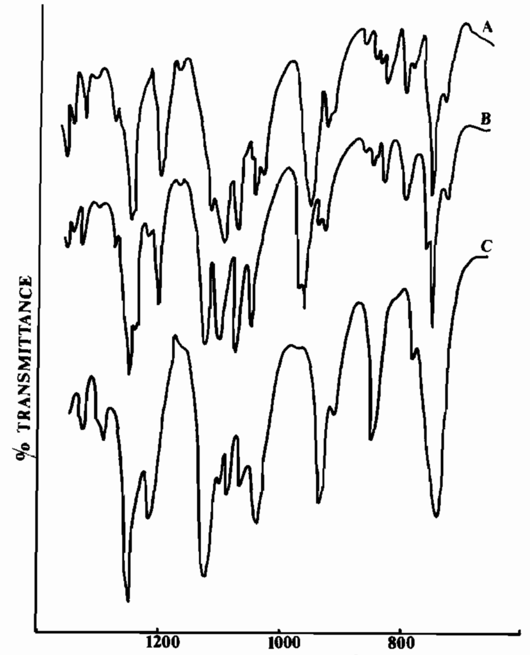


Figure 1. Infrared spectra of: A, $(MnBr_2)_2$(benzo-15-crown-5)$\cdot$1½acetone$\cdot H_2O$; B, $(CoCl_2)_2$(benzo-15-crown-5)$\cdot$acetone; C, TlSCN(benzo-15-crown-5)$_2\cdot 2H_2O$.

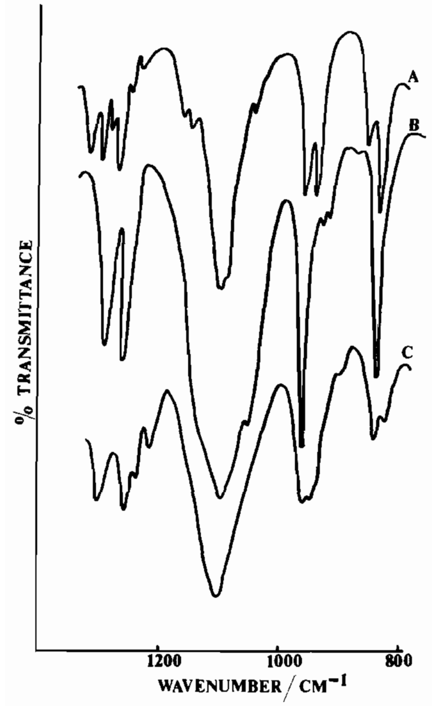


Figure 2. Infrared spectra of: A, $(NiCl_2)_3$(18-crown-6)$\cdot 13H_2O$: B, $TlClO_4$(18-crown-6); C, $(CoCl_2)_2$(18-crown-6)$\cdot$acetone$\cdot 8H_2O$.

around 1050 and 840 cm^{-1}, (b) spectra showing little splitting in these regions and (c) spectra showing slight splittings in these regions (Fig. 2).

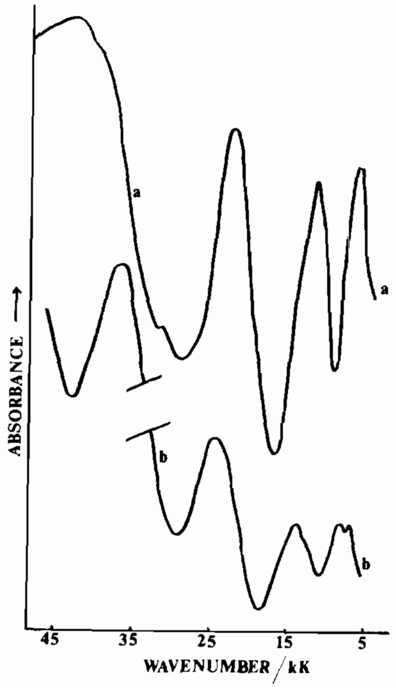


Figure 3. Diffuse reflectance spectra of: a, $(NiCl_2)_3$(18-crown-6)$\cdot 13H_2O$; b, $NiBr_2$(18-crown-6)$\cdot 4H_2O$.

Manganese complexes. Complexes of the type $(MnX_2)_2$(18-crown-6)$\cdot 8H_2O$ are obtained. The infrared spectra of these compounds are of type (a), showing large splittings (Fig. 2).

Solvent bands are evident in the infrared spectra at 1630, 1645 cm^{-1} and 1625 and 1640 cm^{-1} of the chloride and the bromide respectively. In addition broad bands are shown in the region 3200–3500 cm^{-1} and in the 600 cm^{-1} region. No bands appear in these regions in the anhydrous KSCN complex [8]. Both the chloride and bromide compounds are pale pink and thus appear to contain octahedral manganese [7, 9]. The diffuse reflectance spectra show a series of weak bands in the visible region in the chloride complex, more distinct bands in the bromide at 19,000, 24,800, 27,200, 28,500 and 31,000 and in addition a very strong sharp band at 39,000 cm^{-1}. When the solid $(MnBr_2)_2$(18-crown-6)$\cdot 8H_2O$ is gently heated it turns to a cream colour. The bands in the visible region change and the band at 39,000 cm^{-1} disappears while a new band at 30,000 cm^{-1} is shown. The infrared spectrum also shows changes.

Nickel complexes. Complexes of 18-crown-6 with the chloride, bromide and iodide of nickel have been prepared. The green chloride compound analyses for $(NiCl_2)_3$(18-crown-6)$\cdot 13H_2O$. The infrared spectrum is very split and almost identical to that of the $MnCl_2$ and $MnBr_2$ complexes. The visible spectrum of the solid shows bands at 23,200, 12,500 (sh 14,000) and a split bands at 7,200 and 6,900 cm^{-1} (Fig. 3).

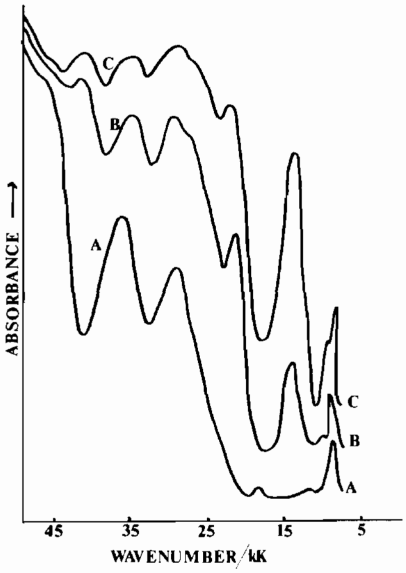


Figure 4. Diffuse reflectance spectrum of solid $NiI_2(18\text{-crown-6})_2\cdot 8H_2O$: A, cold; B, warm; C, heated until colour changed to red.

The yellowish green bromide has the formula $(NiBr_2)(18\text{-crown-6})\cdot 4H_2O$. Bands in the visible region are at 24,400 cm^{-1}; 13,500 weak and 7,800 weak (Fig. 4). The iodide complex $NiI_2(18\text{-crown-6})_2\cdot 8H_2O$ has bands at 26,800 and 7,900 (weak) cm^{-1} (Fig. 4). When the iodide complex is rubbed on filter paper or gently heated it turns red. The colour change is reversible. The change is accompanied by the appearance of new bands in the visible region (Fig. 4). The infrared spectra of both the bromide and iodide compounds are unsplit and thus different from that of the chloride. The iodide shows bands which can be assigned to uncomplexed ether [8].

Cobalt complexes. The situation regarding cobalt complexes is much more complicated owing to a variety of complexes with varying amounts of solvent.

$(CoCl_2)_2(18\text{-crown-6})\cdot \frac{1}{2}acetone\cdot 7H_2O$ (blue)

The infrared spectrum shows the presence of solvent molecules and is slightly split. The diffuse reflectance spectrum (Fig. 5) shows the presence of tetrahedral cobalt.

$(CoBr_2)2(18\text{-crown-6})\cdot acetone\cdot 6H_2O$ (blue)

Compound I Scheme I. The infrared spectrum of this compound which is slightly split shows the presence of solvent including a sharp band at 1600 cm^{-1}. The diffuse reflectance spectrum shows very sharp bands in the visible region around 20,000 cm^{-1} in addition to bands from octahedral cobalt.

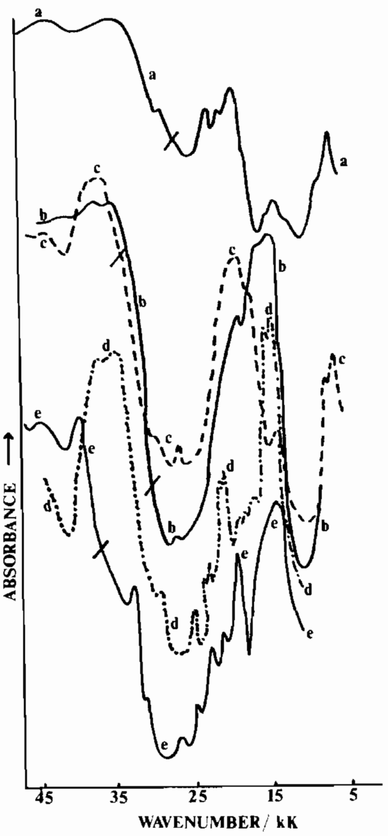


Figure 5. Diffuse reflectance spectra of: a, $CoBr_2(18\text{-crown-6})\cdot 8H_2O$ (pink), V, scheme 1; b, $(CoBr_2)_2(18\text{-crown-6})\cdot \frac{3}{4}$-acetone$\cdot 7H_2O$ (blue), IV, scheme I; c, $(CoBr_2)_2(18\text{-crown-6})\cdot \frac{1}{2}$acetone$\cdot 8H_2O$ (purple), III, scheme I; d, $(CoBr_2)_2(18\text{-crown-6})\cdot$acetone$\cdot 6H_2O$ (blue), I, scheme I; e, $(CoCl_2)_2(18\text{-crown-6})\cdot \frac{1}{2}$acetone$\cdot 7H_2O$.

$(CoBr_2)_2(18\text{-crown-6})\cdot \frac{1}{2}acetone\cdot 8H_2O$ (purple)

Compound III Scheme I. This compound has an infrared spectrum showing split bands like those of the manganese compounds. The diffuse reflectance spectrum shows a broad band centred around 18,700 cm^{-1}.

$(CoBr_2)_2(18\text{-crown-6})\cdot \frac{3}{4}acetone\cdot 7H_2O$ (blue)

Compound IV Scheme I. The infrared spectrum is identical to that of the purple compound III. The visible spectrum (Fig. 5) shows that in addition to the band centred at 18,500 cm^{-1} intense bands around 15,000 appear probably due to the presence of tetrahedral cobalt.

$CoBr_2(18\text{-crown-6})\cdot 8H_2O$ (pink)

Compound V Scheme I. Very weak bands in the visible region at 21,900, 20,500 and 18,800 cm^{-1} (Fig. 5). The infrared spectrum is similar to that of $NiBr_2(18\text{-crown-6})\cdot 4H_2O$ and potassium complexes.

TABLE I. Ionic Radii (Pauling)/Å.

Na^+	K^+	Rb^+	Cs^+	Tl^+	Ca^{2+}	Mn^{2+}	Co^{2+}	Ni^{2+}
0.95	1.33	1.48	1.69	1.40	0.99	0.80	0.74	0.69

Discussion

The infrared spectra of the transition metal 15-membered ring compounds of benzo-15-crown-5 and of dibromo benzo-15-crown-5 are different from those of [3, 4] K(benzo-15-crown-5)$_2$I, Na(benzo-15-crown-5)$_2$BPh$_4$ and from that of [5] Tl(benzo-15-crown-5)$_2$SCN (Fig. 1). The potassium iodide complex has been shown to have a sandwich structure [10]. Because of the similarity of their infrared spectra, this structure has also been postulated for both the sodium tetraphenylborate [4] and the thallium thiocyanate [5] complexes.

The infrared spectra of the transition metal complexes neither are like those of the 1:1 hydrated sodium benzo-15-crown-5 complex [4a, 11] nor the 1:1 hydrated calcium complex [4b], although there are similarities with the latter [3]. A possible structure would be like that of the calcium complex, the transition metal ion having irregular eight-coordination, comprising of five ether oxygens, one oxygen from acetone, and two bridging halogens to a second tetrahedrally bound transition metal ion. Alternatively, it seems possible that the transition metal ions which have considerably smaller ionic radii than those of the alkali metal (Table I) could go into the hole in the fifteen membered ring [3].

Such a structure would give the transition metal ion in a pentagonal pyramidal structure, with acetone coordinated as the fifth ligand. Thus a second possible structure for these 15 membered ring complexes therefore is one in which the metal is involved in both the anion and the cation, the anion consisting of a tetrahalo species and the cation of a pentagonal pyramidal structure.

Dunitz and co-workers have shown that the conformation of the 18-crown-6 ring in the potassium thiocyanate complex [12] is very regular, giving a very flat octahedron around the potassium. This conformation persists in the rubidium ion [13], with the metal ion displaced by about 1.2Å from the median plane of the ligand; similarly in the Cs [14] complex the Cs ion is displaced further at 1.44Å. The infrared spectra of the KBr [8], KSCN complexes and of thallium complexes of 18-crown-6 [5] are very similar and similar to some of those of the transition metal complexes prepared in this work.

These spectra (type (b), Fig. 2) show little splitting in the bands centred around 1050 and 840 cm^{-1}, and in those between 1300 and 1200 cm^{-1}. It seems very likely therefore that the conformation of the 18-crown-6 ring in compounds in which this spectrum is found is likely to be highly regular.

The infrared spectrum [8] of the solid 18-crown-6 at –60 °C shows splitting of the bands in the region 800–1000 cm^{-1}, and the presence of a band near 1000 cm^{-1} which disappears on coordination. The structure of the solid cyclic ether has been shown [15] to contain three successive non-equivalent OCH$_2$CH$_2$O units. The hydrated NaSCN complex [16] has been shown to contain the crown ether with a highly irregular conformation in which the coordination about the Na$^+$ ion is a distorted pentagonal bipyramid. The smaller size of the transition metal ion (Table I) compared with sodium makes it possible that the polyether could bond as an octahedral ligand, with a similar irregular conformation. Thus there are possibly more types of structure with the more flexible 18 membered ring, than there are with the more rigid 15 membered ring, although different conformers do exist [4] with the latter.

Two blue cobalt complexes, (CoCl$_2$)$_2$(18-crown-6)·½acetone·7H$_2$O, and (CoBr$_2$)$_2$(18-crown-6)·acetone·6H$_2$O contain bands which may be assigned to tetrahedral cobalt, in the diffuse reflectance spectra. The spectra also contain weak bands which are similar to those found in the 15 membered ring complexes.

The infrared spectra of these complexes can be described as "slightly split" (Fig. 2) and it is suggested that the structure of these compounds is similar to those containing the 15 membered ring.

Two of the cobalt complexes (III and IV, Scheme I) show the typical split infrared spectrum. This spectrum is also shown by the MnBr$_2$, MnCl$_2$ and NiCl$_2$ compounds. The cobalt complex III shows the presence of tetrahedral cobalt. The purple complex IV shows the absence of this band but an intense band centred at 18,700 cm^{-1}. It seems possible that these complexes have a metal complexed by the polyether ring in a similar way to the sodium complex. The nickel chloride complex has bands on the visible region which are similar to those of NiCl$_2$ in which the Ni^{2+} ion is surrounded by a distorted octahedron of Cl$^-$ ions in a layered structure [17].

Lastly three of the compounds have infrared spectra which are not split and are like those of the potassium complex, *viz*: CoBr$_2$(18-crown-6)·8H$_2$O, NiBr$_2$-(18-crown-6)·4H$_2$O, and NiI$_2$(18-crown-6)$_2$·8H$_2$O.

The visible spectra appear to be those of very distorted octahedral complexes. On heating the iodide a colour change, apparently to a tetrahedral species [18], is noted.

The complexes formed from crown ethers and transition metal ions are remarkable for the large numbers of solvent molecules included in the solid compounds. The possibility cannot be ruled out that the water molecules are associated with the anions, as in complexes of 12-crown-4 [19]. Without structural data it is not possible to determine absolutely from the infrared spectrum whether or not the crown ether is coordinated. The uranyl complex of 18-crown-6 has been shown to contain the uncomplexed crown ether but in the same conformation as in the potassium complex [20] thus giving the same infrared spectrum.

These compounds are under further investigation.

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