Inorganica Chimica Acta, 142 (1988) 27 -28

Preparation and Characterization of Complexes Between Dibenzo-18-crown-6 and some Potassium Mercurate(II) Salts

K. F. MOK

Department of Chemistry, National University of Singapore, Kent Ridge 0511, Singapore

(Received August 14, 1987)

It is well known that crown ethers form relatively stable complexes with Group I alkali metal and Group II alkaline earth metal salts. In particular, dibenzo-18-crown-6 (DB18C6) complexes with simple potassium salts are amongst the most stable of these [1, 2]. However, there have been relatively few publications of complexes formed between this crown ether and double salts of potassium [3, 4]. We wish to report the preparation and characterization of complexes between dibenzo-18-crown-6 and dipotassium tetracyanomercurate(II), dipotassium tetraiodomercurate(II) and dipotassium tetrathiocyanatomercurate(II) salts

Experimental

A solution of 1 mmol of dipotassium tetracyanomercurate(II) in a minimum amount of aqueous ethanol (1:1) was added with stirring to a solution of 2 mmol of dibenzo-18-crown-6 in 30 ml of ethanol–chloroform mixture (1:1) The mixture was heated on a steam-bath until most of the solvents had evaporated off. The solid product was filtered off and recrystallized from ethanol. Preparation of the other two complexes followed the same procedure but using dipotassium tetraiodomercurate(II) and dipotassium tetrathiocyanatomercurate(II) respectively $[DB18C6-K]_2[Hg(CN)_4]\cdot 2H_2O$, melting point (m.p.) 213–215 °C. *Anal.* Found: C, 46.4; H, 4.2; N, 4.7; K, 7.0. Calc.: C, 46.4; H, 4.6; N, 4.9; K, 6.9%. $[DB18C6-K]_2[HgI_4]$, m.p. 190–195 °C. *Anal.* Found: C, 33.7; H, 3.6; I, 35.1; K, 5.2. Calc.: C, 33.5; H, 3.4; I, 35.4; K, 5.4%. $[DB18C6-K]_2[Hg(SCN)_4]\cdot C_2H_5OH$, m.p. 192–193 °C. *Anal.* Found: C, 43.9; H, 4.2; N, 4.1; S, 10.2; K, 6.2. Calc.: C, 43.3; H, 4.3; N, 4.4; S, 10.0; K, 6.2%.

Infrared spectra were obtained using CsI discs on a Perkin-Elmer 598 spectrometer and proton NMR spectra were run on a Perkin-Elmer R32 spectrometer.

Results and Discussion

Absorption bands of the free crown ether ligand and the three complexes in the 4000 to 250 cm^{-1} infrared region are given in Table I. The $-C{\equiv}N$ group in the tetracyanide complex absorbs only weakly at 2140 cm^{-1} while that in the tetrathiocyanate complex absorbs strongly at 2130, 2110 and 2060 cm^{-1}, the multiple band observed is probably due to the non-equivalence of the thiocyanate

TABLE I. Infrared Absorption Bands (cm^{-1}) in the 4000 to 250 cm^{-1} Range

DB18C6	3600–3400(w,vb), 3075(w), 2960(m), 2940(m), 2895(m), 1600(s), 1510(vs,b), 1496(m,sh), 1480(w), 1458(s), 1420(vw), 1395(vw), 1370(w), 1345(w,sh), 1334(m), 1296(m), 1256(vs), 1232(vs), 1220(s,sh), 1134(vs,b), 1082(w), 1064(s), 1052(s), 1030(w), 998(s), 938(s), 918(vw), 845(w), 824(w), 780(m), 754(s), 745(s), 734(m,sh), 602(w,b), 500(w).
Tetracyanide complex	3580–3460(w,vb), 3085(vw), 2945(m), 2890(m), 2840(w), 2140(w), 1630(w,b), 1600(s), 1514(vs), 1510(vs), 1487(w), 1460(s), 1434(w), 1402(vw), 1388(w), 1364(s), 1330(s), 1296(m), 1256(vs), 1218(vs), 1128(vs,b), 1100(m), 1090(w), 1064(s), 1054(s,sh), 960(vs), 948(vs), 922(w), 906(w), 854(m), 786(m), 752(vs), 604(m), 462(w), 342(w), 322(w), 230(w).
Tetraiodide complex	3075(vw), 3045(vw), 2950(w), 2935(w), 2915(w), 2885(w), 2835(w), 1598(m), 1506(vs,b), 1472(w,sh), 1456(s), 1432(vw), 1400(vw), 1389(vw), 1360(m), 1328(m), 1306(w,sh), 1288(m,sh), 1250(vs,b), 1214(s), 1166(s,sh), 1128(vs,b), 1094(w), 1082(vw), 1060(vs), 1050(m,sh), 960(vs), 944(vs), 928(vw,sh), 916(w), 904(w), 860(w), 854(w), 784(m), 756(s), 742(s), 732(m,sh), 698(w), 630(vw), 600(m), 526(w), 466(w), 336(w).
Tetrathiocyanate	3590–3520(vw,vb), 3090(vw), 3075(vw), 2945(w), 2910(w), 2885(w), 2840(vw), 2130(s), 2110(vs), 2060(s), 1600(m), 1510(vs,b), 1480(w,sh), 1460(s), 1434(w), 1400(w), 1386(w), 1360(m), 1328(m), 1288(m), 1252(vs,b), 1218(vs), 1170(w,sh), 1128(vs,b), 1102(w), 1090(w), 1064(s), 1054(s,sh), 960(s), 946(vs), 916(w,sh), 856(w), 786(m), 752(s), 742(s,sh) 700(w), 604(m), 470(w).

s, strong; m, medium; w, weak; sh, shoulder; b, broad, v, very.

0020-1693/88/$3.50

groups (see below). On complexation the medium intensity band of the ligand at 2960 cm^{-1} due to CH_2 stretching vibration either disappears or is much reduced in intensity, while the weak shoulder at 1345 cm^{-1} from bending CH_2 modes turns into either a medium intensity band at 1360 cm^{-1} or a strong band at 1364 cm^{-1}. The very intense band of the free ligand at 1232 with a shoulder at 1220 cm^{-1} absorbs at 1214 or 1218 cm^{-1} in the complexes and the strong band at 1134 cm^{-1} is shifted to 1128 cm^{-1} on complexation. These two bands are probably the aromatic carbon–oxygen and aliphatic carbon–oxygen vibrations respectively. Similarly the intense band at 998 cm^{-1} in the ligand is significantly shifted down to 960 cm^{-1} in the complexes while the strong 938 cm^{-1} band is slightly moved up to 944–948 cm^{-1} on complexation. These are either bending or wagging CH bands. A weak to medium intensity band found in the 1094 to 1102 cm^{-1} region in the spectra of the complexes has no equivalence in the free ligand spectrum. The complexes also show some weak bands below 500 cm^{-1} which are absent in the ligand spectrum.

Proton NMR spectra of the crown ether and the complexes in d_6-dimethylsulphoxide consist essentially of a broad band at 6.95 ppm and a very broad doublet centred at 4.05 ppm with a intensity ratio of 1:2. The former may be assigned to the eight aromatic protons per ligand molecule while the doublet to the sixteen protons in the saturated CH_2 groups.

Perhaps the most interesting feature of these complexes is their molecular structure. As expected for such complexes the potassium ion sits in the cavity of the crown ether surrounded by six oxygen atoms. However, the potassium ion is at least seven-coordinated in all three complexes, the extra coordination is achieved in different ways. In the tetracyanomercurate(II) complex one of the end nitrogen atoms of the cyanide groups is coordinated to one of the two $[DB18C6–K]^+$ ions while the other potassium ion has a seventh oxygen from a water molecule coordinated to it [5]. The coordination sphere about the two potassium ions is identical in the tetraiodomercurate(II) complex; the seventh position is occupied by an iodide ion from the tetrahedral $[HgI]_4$ moiety [6]. In the tetrathiocyanatomercurate(II) complex the thiocyanate groups coordinate through the sulphur atom to the mercury ion. Three out of four thiocyanate groups are also coordinated to the potassium ions through the nitrogen atom; two such groups are coordinated to one of the two potassium ions while another group is coordinated to the other potassium. The first potassium is thus eight-coordinated while the other is seven-coordinated. The tendency for potassium in the $[DB18C6–K]^+$ ion to be at least seven-coordinated is thus well illustrated.

References

1 J. J. Christensen, J. D. Eatough and R. M. Izatt, *Chem. Rev., 74,* 351 (1974).

2 J. D. Lamb, R. M. Izatt and J. J. Christensen, in R. M. Izatt and J. J. Christensen (eds.), 'Progress in Macrocyclic Chemistry', Vol. 2, Wiley, New York, 1979, Chap. 2.

3 V. E. Poladyam, A. A. Ermakov, N. P. Sokolova, L. M. Avlasovich, S. F. Pakhol'chuk and K. A. Mukelo, *Zh. Neorg. Khim., 29,* 1192 (1984).

4 Y. P. Fan, Z. Y. Zhang, X. M. Wang, J. Z. Zhang and J. F. Han, *Kexue Tongbao* (foreign language edn.), *30,* 910 (1985).

5 K. F. Mok, V. McKee and W. T. Robinson, *Acta Crystallogr., Sect. C,* in press.

6 K. F. Mok, V. McKee and W. T. Robinson, to be published.