

Reaction of K_2PtCl_4 with Some Macrocyclic Ligands

DEEB MARJI* and KHAMIS ABBAS

Chemistry Department
Yarmouk University, Irbid, Jordan

The reaction of K_2PtCl_4 with B15 C5, DB18C6, DB24C8, Kryptofix 5 and Kryptofix (2, 1, 1) in aqueous solution resulted in stable complexes. In these complexes, the potassium ion complexes with the oxygen ethers in the cavity of the crown, while the phenyl or quinoline group coordinates with the platinum metal. Characterization of the complexes has been accomplished using elemental analysis, IR and UV-visible spectroscopy.

INTRODUCTION

Interest in electrically-neutral complexing agents such as macrocyclic polyethers (crown-ethers) has increased continuously since the original work of Pedersen.^{1–3} Their affinity towards metal cations^{4, 5}, neutral molecules⁶ and even anions⁷ has led to intensive efforts to understand the factors that affect the thermodynamical and kinetic stability of the resulting complexes.^{8, 9} The stability of crown complexes depends on several factors including the relative size of the cation and the macrocyclic cavity, the number and nature of binding sites, the acid-base character of metal ions, the counter anion and the solvent.

The use of crown-ethers was mainly concentrated on alkali, alkaline earth metals and on lanthanides. However, little work has been done on the complexation of transition metals with crown ethers.^{10–14} The stability constants of the complexes of some divalent cations with crown ethers were very low ($\log K_f$ 2.02–3.62). In this sense cations and crowns do not behave according to electrostatic attraction only. The transition metal ions favour the complexation with aza-crowns and thia-crowns much more than with the crown-ethers. This is probably due to the polarized nature of these cations and their low affinity towards oxygen ligands.¹⁵ The complexation reactions occur through electrostatic attraction between the positively charged metal ions and crown-ethers.

It was of interest to us to investigate the reactions of K_2PtCl_4 with benzo-15-crown-5 (B15C5), dibenzo-18-crown-6 (DB18C6), dibenzo-24-crown-8 (DB24C8), kryptofix-5 and kryptofix-(2,1,1) (Fig. 1), very stable complexes in which the platinum coordinates with the ligands through the phenyl ring or the nitrogen atom.

EXPERIMENTAL

Materials: Benzo-15-crown-5, dibenzo-18-crown-6, dibenzo-24-crown-8, kryptofix-5 and kryptofix-(2,1,1) all purchased from Merck were used without further purification. K_2PtCl_4 (Fluka) was of highest purity. Deionized water was used throughout. Ethanol was of reagent grade.

Elemental Analyses: These were carried out by M.H.W. Laboratories, P.O. Box 15853, Phoenix, Arizona 85018, U.S.A.

Physical Measurements: UV-visible spectra were recorded with a Unicam UV-visible Spectrophotometer V4.15. KBr disc IR spectra were taken on a Perkin-Elmer FTIR spectrophotometer 2000.

Synthesis of Complexes

I. *Reactions of K_2PtCl_4 with kryptofix-5 and kryptofix-(2,1,1):* 1 mmol of each of the ligands and K_2PtCl_4 was dissolved in 10 mL H_2O . Two drops of 1 M H_2SO_4 were added and the solution was refluxed for 30 min, during which the colour of the solution disappeared and a precipitate formed. After cooling, desired precipitate was collected, washed with ethanol and diethyl ether.

II. *Reactions of K_2PtCl_4 with benzo-crown ethers:* A solution of 3 mmol K_2PtCl_4 was dissolved in 10 mL H_2O , then 3 mmol of the appropriate benzo-crown ether dissolved in 10 mL of the mixed solvent $H_2O-C_2H_5OH$ was added. The solution was then heated to boiling temperature at which the colour of the solution disappeared and a dark brown to black precipitate was formed. The precipitate was collected and washed several times with ethanol and diethyl ether.

RESULTS AND DISCUSSION

The reactions of K_2PtCl_4 with nitrogen containing ligands have been subjected to thorough investigation and characterization by different techniques. As far as we know, no attempts have been made to study the reactions of K_2PtCl_4 with crown-ethers and aza-crown-ethers. The present study shows that the reactions of K_2PtCl_4 with different macrocyclic ligands resulted in the formation of stable complexes with different stoichiometry. Elemental analysis shown in Table-1 confirms the suggested formulas. The very limited solubility of the resulting complexes prevents us from measuring the conductivity and recording the NMR-spectra.

TABLE-1
ELEMENTAL ANALYSIS OF THE COMPLEXES

S.No.	Complex	Analysis: Calculated (found) %			
		C	H	N	Cl
1.	$C_{28}H_{46}O_{14}KPt_2Cl_3$ (B15C5) $_2KPt_2Cl_3(OH)_2 \cdot 2H_2O$	29.43 (28.63)	4.03 (4.04)	— —	9.33 (10.23)
2.	$C_{20}H_{24}O_6KPtCl$ (DB18C6) $KPtCl(OH)_2$	36.17 (36.09)	3.92 (4.01)	— —	5.35 (5.78)
3.	$C_{24}H_{36}O_{11}KPt_2Cl_3$ (DB24C8) $KPt_2Cl_3(OH)_2 \cdot H_2O$	27.81 (27.64)	3.48 (3.47)	— —	10.28 (9.73)
4.	$C_{26}H_{34}O_7N_2KPt_2Cl_5$ (Kryptofix-5) $KPt_2Cl_5 \cdot 2H_2O$	28.57 (27.80)	3.11 (3.15)	2.56 (2.63)	16.25 (15.38)
5.	$C_{14}H_{34}O_5N_2K_2Pt_2Cl_4$ (Kryptofix-(2,1,1)) $Pt_2Cl_4(OH)_2 \cdot 2H_2O$	17.36 (18.25)	3.51 (3.65)	2.89 (2.83)	14.67 (13.80)

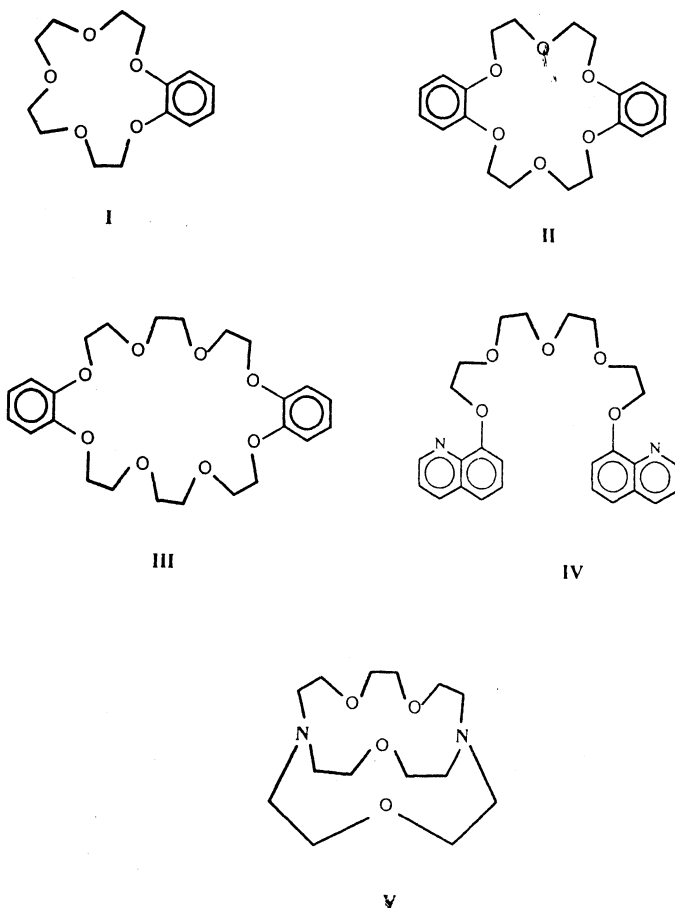
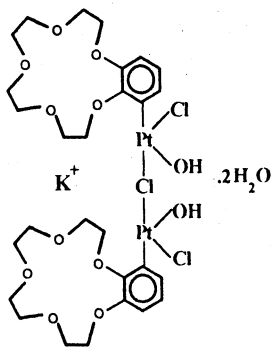


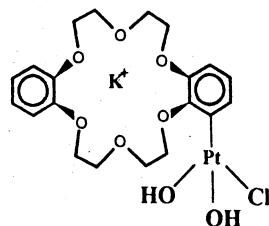
Fig. 1 Structure of Macrocyclic Ligands
 I. Benzo-15-Crown-5 II. Dibenzo-18-crown-6
 III. Dibenzo-24-crown-8 IV. Kryptofix 5
 V. Kryptofix (2, 1, 1).

However, infrared spectroscopy is a valuable technique used to indicate the complexation of crown ethers. The oxygen donor atoms are bonded to carbon by ether linkage which absorbs in the range $1150\text{--}1000\text{ cm}^{-1}$ for aliphatic ethers and in the range $1300\text{--}1200\text{ cm}^{-1}$ for aromatic ethers. The complexation between the crown ether and metal cations will decrease the stretching frequency of $R\text{--}O\text{--}R$ and $Ar\text{--}O\text{--}R$ compared to that of the free ligand. In addition, the complexation will cause splitting and changes in the intensities of some bands. The change in $C\text{--}O$ stretching vibration is due to unequal participation of the oxygen donor atoms in the complexation process. In addition to the ether linkage the $C\text{--}N$ bond in kryptofix ligands and the phenyl groups are expected to be affected by complexation which shifts their vibrational to lower values. This effect is also taken as an indication of the complexation between metal cations and crown-

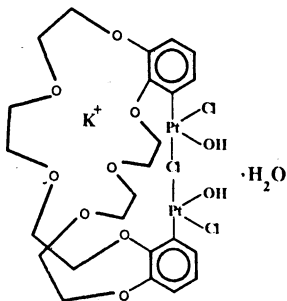
ethers. The assignment of some IR bands for the free ligands and their complexes is included in Table-2.



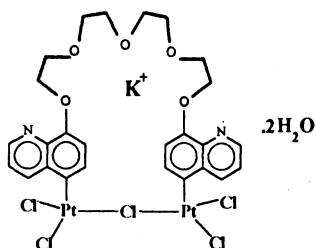
Ia



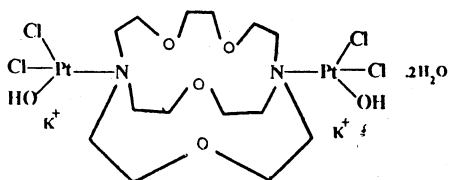
IIa



IIIa



IVa



Ia. Benzo-15-Crown-5-complex IIa. Dibenzo-18-crown-6-complex
 IIIa. Dibenzo-24-crown-8-complex IVa. Kryptofix 5-complex
 Va. Kryptofix (2, 1, 1)-complex.

Fig. 2 Structure of Complexes

TABLE-2
 INFRARED SPECTRA OF THE MACROCYCLIC LIGANDS
 AND THEIR COMPLEXES^a

Characteristic IR bands (cm^{-1})			
Compound	Ligand	Complex	Assignments
B15C5 and its complex	—	3550–3360(m, br), 1647(w)	H ₂ O & OH
	3070(w), 3030(vw), 2931(s), 2905(s), 2864(s)	3035(vw), 2955(w), 2903(w), 2860(w)	Ar—H & C—H
	1589(s), 1507(vs), 1453(s)	1502(s), 1453(m)	C—C (Ar)
	1255(vs), 1220(vs)	1255(s), 1226(m), 1205(m)	Ar—O—C
	1125(vs), 1074(s), 1034(s)	1120(s), 1080(m), 1042(m)	C—O—C
	DB18C6 and its complex	—	3456(m), 3380(m)
DB18C6 and its complex	3035 (w)	3058(w)	Ar—H
	2950(w), 2910(w), 2860 (w)	2960(s), 2922(s), 2870(m)	C—H
	1594(m), 1506(s), 1449(m)	1594(s), 1506(s), 1449(s)	C—C (Ar)
	1255(vs), 1226(vs),	1250(s), 1220(s)	Ar—O—C
	1125(vs)	1105(s, br), 1020(m)	C—O—C
		3537–3325(w)	H ₂ O & OH
DB24C8 and its complex	2934(m); 2890(m), 2860 (m)	2922(w), 2866(w)	C—H
	1594(s), 1507(vs), 1449(s)	1589(w), 1502(s), 1449(m)	C—C (Ar)
	1250(vs), 1216(vs)	1250 (s), 1212 (m)	Ar—O—C
	1129(vs), 1092(vs), 1057(s)	1125(s) 1047(m)	C—O—C
Kryptofix-5 and its complex	—	3515–3315(m)	H ₂ O & OH
	3039(w)	3049(m)	Ar—H
	2960(w), 2915(m), 2864(s)	2912(m), 2867(m)	C—H
	1608(s), 1565(s), 1497(vs)	1598(m), 1555(m), 1497(w), 1485(m)	C—C (Ar)
	1300(vs)	1303(s)	C—N
	1255(vs), 1220(s), 1210(s)	1269(m), 1212(w)	Ar—O—C
	1130(s, doublet), 1100(vs), 1035(s)	1183(w), 1110(vs), 1028(m)	C—O—C
Kryptofix-(2,1,1) and its complex	—	3450–3250(w, br), 3450– 3325 (w, br)	H ₂ O & OH
	2960(w), 2880(m),	2970(w), 2925(w), 2858(w), C—H	
	1310(s) 1250(s)	1366(m), 1260(m)	C—N
	1184(s), 1065(s)	1100(s), 1023(vs)	C—O—C

^avs, very strong; s, strong; m, medium; w, weak; br, broad.

The data in Table-2 agree with our expectations that the complexation causes a weakening in the strength of the C—O bond and shifts the position to lower frequency from 1125 to 1118 cm^{-1} . In addition, the high intensity doublet at 1255 cm^{-1} due to Ar—O bond splits into multiplet with different intensities. The singlet bond attributed to the phenyl group located at 1585 cm^{-1} with high intensity is replaced by a multiplet with lower intensity indicating the involvement of the phenyl group in the complexation. However, the centre of this multiplet is shifted to higher frequencies which probably indicated a back $\pi \rightarrow \pi^*$ donation from metal to the phenyl group.

Attempts to record the UV-visible absorption spectra of the complexes were carried out qualitatively on very dilute solutions in dimethylformamide. The spectra show a weak absorption in the range 315–320 nm which might be due to MLCT (metal to ligand charge transfer) bands from the *d*-orbitals of the platinum metal to the π^* orbital of the phenyl group.

The difference in the proposed formulas of the complexes depends on the ligand used. While there are two platinum atoms per each formula of the complexes of B15C5, DB24C8, and kryptofix-5 there is only one platinum atom per formula of the complex of DB18C6. However, the complexation of K^+ ion with crown-ethers could have an important role in determining the formulas. This behaviour can be explained as follows. It is well known that K^+ ion with a radius 1.38 Å fits¹⁶ nicely inside the cavity of DB18C6 with a radius¹⁷ of 1.3–1.6 Å, so that the cation is bound very tightly with the unshared electron pairs on the six oxygen atoms.¹⁸ Such a situation is expected to lead to a planar arrangement and the phenyl groups are far away from each other to make a bridge between two platinum atoms *via* chlorine. On the other hand the cavity of B15C5 (0.85–1.1 Å)¹⁷ is too small for the K^+ ion and therefore this ligand can form a 2 : 1 (crown-to-cation) sandwich complex with the potassium ion¹⁹. It is well known that the formation of such a 2 : 1 adduct causes the ligand to flatten out^{20, 21} which facilitates the coordination of phenyl groups with platinum metal with chlorine atom acting as a bridge (Fig-2).

It is well known that large crown-ethers as DB24C8 and kryptofix-5 with a considerably large flexibility and enough oxygen atoms in their macrocyclic ring are able to twist around a cation of proper size (such as K^+ ion) to form a rigid “warp around” complex both in solution and in crystalline form.^{22–24} It is expected such a situation will bring the phenyl groups in DB24C8 and the quinoline groups in kryptofix-5 at a distance suitable to coordinate with two platinum atoms.

However, the kryptofix-(2,1,1) complexation with K_2PtCl_4 gives a different formula. Since the cavity of the ligand is too small for K^+ , it is expected that K^+ ion complexation with the ligand is negligible and this situation leaves the two nitrogen atom in the ligand to coordinate with two platinum atoms to give the proposed formula as shown in Table-1 (Fig-2).

ACKNOWLEDGEMENTS

Support from Yarmouk University is gratefully acknowledged (project No. 24/97).

REFERENCES

1. C.J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
2. _____, *J. Am. Chem. Soc.*, **92**, 391 (1970).
3. C.J. Pedersen and H.K. Frensdorff, *Angew. Chem.*, **11**, 16 (1972).
4. R.M. Izzat, J.S. Bradshaw, S.A. Nielsen, J. Lamb and J.J. Christensen, *Chem. Rev.*, **85**, 271 (1985).
5. R.M. Izzat, J.S. Bradshaw and J.J. Christensen, *Chem. Rev.*, **91**, 1721 (1990).
6. H.P. Hopkins, D.V. Jahagirdan and F.J. Windler, *J. Phys. Chem.*, **82**, 1254 (1978).
7. R.I. Gelb, J.M. Schwartz and L.J. Zompa, *Inorg. Chem.*, **25**, 1527 (1986).
8. J.D. Lamb, R.M. Lamb, R.M. Izzat and J.J. Christensen, *Progress in Macrocyclic Chemistry*, Vol.1, Wiley, New York (1981).
9. J.D. Lamb, R.M. Izzat and J.J. Christensen, *Progress in Macrocyclic Chemistry*, Vol. 2, Wiley, New York (1981).
10. A.C. Su and J.F. Weiher, *Inorg. Chem.*, **7**, 176 (1968).
11. L.Chen, M. Bos, P.D.J. Crootenhuis, A. Christenhusz, E.H. Hoogendam, D.N. Reinhoudt and W.E. Vander Linder, *Anal. Chim. Acta.*, 117 (1978).
12. J. Abraham and D. Marji, *Inorg. Chim. Acta*, **101**, 23 (1985).
13. D. Marji and J. Abraham, *Inorg. Chim. Acta*, **105**, 3 (1985).
14. H. Parham and M. Shamsipur, *J. Electroanal. Chem.*, **314**, 71 (1991).
15. R.M. Izzat, W. Genge, J. Weiming and N.K. Dally, *Inorg. Chem.*, **29**, 3828 (1990).
16. R.D. Shannon, *Acta Crystallogr.*, **A32**, 751 (1976).
17. H. Frensdorff, *J. Am. Chem. Soc.*, **93**, 600 (1971).
18. G.W. Gokel and H.D. Durst, *Aldrichim. Acta*, **9**, 1 (1976).
19. R.M. Izzat, R.E. Terry, D.P. Nelson, Y. Chan, D.J. Eatough, J.S. Bradshaw, L.D. Hansen and J.J. Christensen, *J. Am. Chem. Soc.*, **98**, 7626 (1976).
20. M.R. Truter, *Struct. Bonding (Berlin)*, **16**, 71 (1973).
21. W.E. Morf, D. Amman, R. Bissig, E. Pretsch and W. Simon, *Progress in Macrocyclic Chemistry*, Vol. 1, Wiley-Interscience, New York (1979).
22. M.A. Bush and M.R. Truter, *J. Chem. Soc., Perkin Trans.*, **II**, 345 (1972).
23. M. Shamsipur, G. Rounaghi and A.I. Popov, *J. Solution Chem.*, **9**, 701 (1980).
24. M.K. Amini and M. Shamsipur, *Inorg. Chim. Acta*, **183**, 65 (1991).

(Received: 20 May 1998; Accepted: 27 August 1998)

AJC-1563