Pure & Appl. Chem., Vol. 60, No. 4, pp. 467–472, 1988.
Printed in Great Britain.

Conception and birth of new receptor chemistry from dibenzo-18-crown-6

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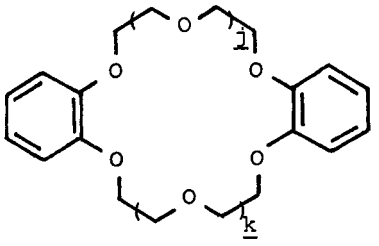
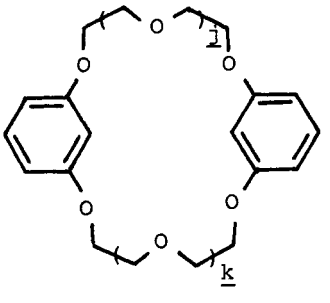
Abstract - The ability of dibenzo-3n-crown-n ethers (n = 6-12) to form stable adducts in solution with a range of neutral and cationic transition metal complexes is discussed. The concept of second sphere coordination can be enlarged to one of molecular recognition involving the whole gamut of non-covalent bonding interactions. It is described how this research led logically to molecular receptors for the bipyridinium herbicides Diquat and Paraquat. In particular, dibenzo-30-crown-10 forms a highly selective 1:1 complex with Diquat whereas, a constitutional isomer, bispara-phenylene-34-crown-10, is a good molecular receptor for Paraquat.

INTRODUCTION

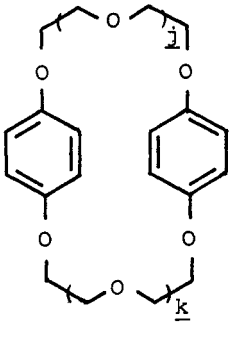
Dibenzo-18-crown-6 [DB18C6] was the first-born amongst the family of macrocyclic polyethers described by Pedersen (ref. 1) in his seminal paper published 20 years ago. The ability of this simple molecule to form complexes with alkali and alkaline earth metal cations and with (substituted) ammonium ions is now part of the folklore and legend surrounding the discovery (ref. 2) and early life of this compound. In this account, two new areas of receptor chemistry, where dibenzo-3n-crown-n ethers [DB3nCn] and their constitutionally-isomeric bismetaphenylene [BMP(3n+2)Cn] and bisparaphenylene [BPP(3n+4)Cn] crown ethers have played an important role in the conception and development phases, will be highlighted. The first will deal with the second sphere coordination (ref. 3) of transition metal complexes (ref. 4,5); the second will relate to the complexation of the bipyridinium herbicides, Diquat $[DQT]^{2+}$ and Paraquat $[PQT]^{2+}$.



DB3nCn
(n=6-12/j=k=1-4)



BMP(3n+2)Cn
(n=6-12/j=k=1-4)



BPP(3n+4)Cn
(n=6-12/j=k=1-4)

SECOND SPHERE COORDINATION

The first crystalline adducts to be isolated between DB18C6 and neutral monoammine transition metal complexes involved (ref. 6) $[W(CO)_5(NH_3)]$ and [trans-$Pt(PR_3)Cl_2(NH_3)$] (R = Me or Et). In all cases, the adducts exhibited 1:1 stoichiometry. The tungsten derivative was characterised by IR and NMR spectroscopies. The platinum (R = Me) derivative was characterised by X-ray

crystallography (Fig. 1). The catechol rings of the DB18C6 in

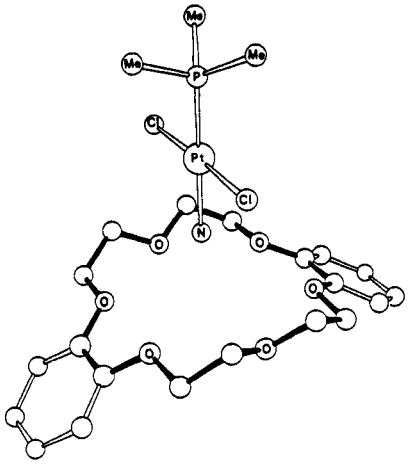
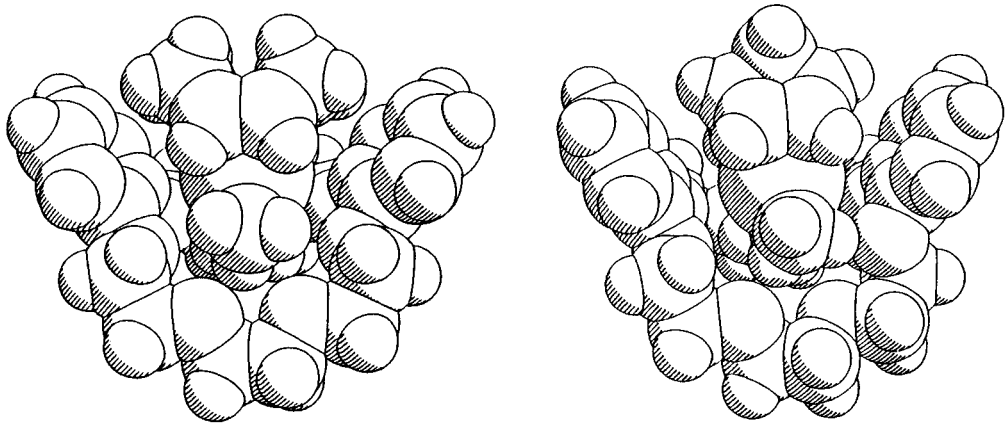


Fig. 1. Skeletal representation of the X-ray crystal stucture of [trans-Pt(PMe$_3$)Cl$_2$(NH$_3$).DB18C6]

[trans-Pt(PMe$_3$)Cl$_2$(NH$_3$).DB18C6] are directed away from the complex and the six oxygen atoms form three bifurcated hydrogen bonds to the NH$_3$ ligand. Dynamic ^{1}H NMR spectroscopy revealed that the 1:1 adduct is also present in CD_2Cl_2 solution, albeit a much weaker adduct than those involving cationic monoammine transition metal complexes.

In order to allow the organic ligand in a transition metal complex to interact with a second sphere ligand, the size of the macrocyclic ring had to be increased. For this reason, the DB3nCn ethers (n = 7-12) were synthesised and their abilities to form 1:1 adducts with the cationic rhodium (I) complexes [Rh(cod)(NH$_3$)$_2$]$^+$ (cod = 1,5-cyclooctadiene) and [Rh(nbd)(NH$_3$)$_2$]$^+$ (nbd = norbornadiene) were investigated (ref. 7,8) in CD_2Cl_2 solution by ^{1}H NMR spectroscopy. Significant upfield shifts were observed for the protons on the cod and nbd ligands, especially when the second sphere ligands are DB21C7 and DB24C8: these observations suggest that the catechol rings in the molecular receptors arrange themselves within close proximity of the cod and nbd ligands. This conclusion was confirmed by a series of X-ray crystal structure determinations performed on four 1:1 adducts crystallised from halocarbon solutions. In all cases, the second sphere ligands adopt V-shaped conformations that wrap themselves around the rhodium complexes. Space-filling representations of the [Rh(cod)(NH$_3$)$_2$.DB21C7]$^+$ and [Rh(nbd)(NH$_3$)$_2$.DB24C8]$^+$ adducts are shown in Fig. 2.

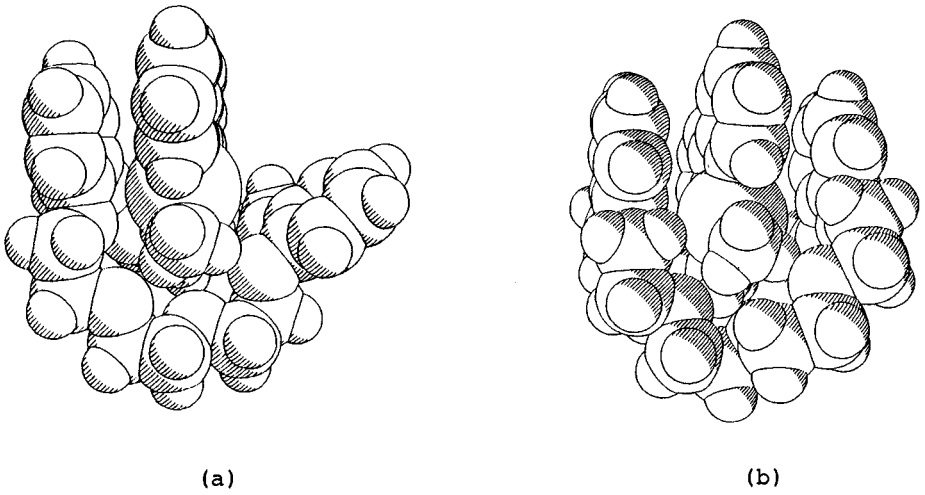


(a) (b)

Fig. 2. Space-filling representations of the X-ray crystal structures of (a) [Rh(cod)(NH$_3$)$_2$.DB21C7]$^+$ and (b) [Rh(nbd)(NH$_3$)$_2$.DB24C8]$^+$.

Although the most important intermolecular binding forces between the cationic rhodium complexes and the DB3nCn ethers (n = 7-12) are associated with hydrogen bonds involving the ammine ligands and the oxygen atoms in the polyether chains, there are also numerous metal-oxygen and metal-carbon contacts at around van der Waals distances which may provide weak additional binding of a Coulombic and dispersive nature. These interactions are probably responsible for the ordering of the molecular superstructures in which the DB3nCn ethers (n = 7-10) undergo considerable conformational changes in order to form adducts with the cationic rhodium complexes.

It is known (ref. 9) that the incorporation of π-acceptor co-ligands such as 2,2-bipyridyl (bipy) into the first coordination sphere of an ammine complex will enhance the hydrogen bonding potential of ammine ligands on a transition metal. Hence, we investigated (ref. 10, 11) the abilities of the DB3nCn ethers (n = 6-12) to form 1:1 adducts in hydrocarbon and halocarbon solvents with the square-planar platinum (II) complex $[Pt(bipy)(NH_3)_2][PF_6]_2$. We noticed that CD_2Cl_2 solutions of the 1:1 adducts (particularly for the DB3nCn ethers where n = 7-11) assume a deep yellow colour immediately they are prepared for ^1H NMR spectroscopy. Single crystals suitable for X-ray crystal structure analysis were obtained for the 1:1 adducts with DB24C8 and DB30C10. Space-filling representations of the $[Pt(bipy)(NH_3)_2.DB24C8]^{2+}$ and $[Pt(bipy)(NH_3)_2.DB30C10]^{2+}$ adducts are shown in Fig. 3. Once again, the



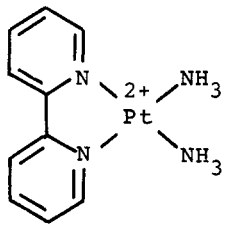
(a) (b)

Fig. 3. Space-filling representations of the X-ray crystal structures of (a) $[Pt(bipy)(NH_3)_2.DB24C8]^+$ and (b) $[Pt(bipy)(NH_3)_2.DB30C10]^{2+}$.

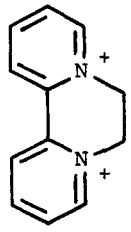
ammine ligands are directed towards the polyether chains forming hydrogen bonds with some of their oxygen atoms. In the case of DB24C8, the receptor is V-shaped whilst in the case of DB30C10 it is U-shaped. The parallel arrangement and close contact (3.48-3.52 Å) between the π-electron deficient bipy ligand and one or both of the π-electron rich catechol units in DB24C8 and DB30C10 respectively, suggest the existence in these adducts of a π-π charge-transfer interaction. Indeed, in acetonitrile solution, a broad electronic transfer absorption band centred on 350 nm is present and no doubt accounts for the deep yellow colour of these adducts. Analysis of the concentration dependence of their charge-transfer absorptions was used to derive association constants (K_a) and free energies of binding ($\Delta G°$). The values of K_a = 66000, 191000, and 69000 M^{-1}, corresponding to $-\Delta G° = 6.6$, 7.2, and 6.6 kcal mol^{-1} respectively for n = 9, 10, and 11 in the DB3nCn ethers, reveal that DB30C10 forms the most stable 1:1 adduct in acetonitrile solution. This conclusion was supported by the results of ^1H NMR spectroscopic investigations in CD_2Cl_2 solutions where substantial upfield shifts were observed for both the aromatic protons in the complex and in the DB3nCn ethers. This research has raised the question of the relative importance of hydrogen bonding, electrostatic interactions, dispersion forces, and charge-transfer interactions in the stabilisation of adducts between transition metal complexes and second sphere ligands.

COMPLEXATION OF DIQUAT AND PARAQUAT

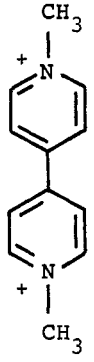
Also, because of the obvious constitutional similarities between $[Pt(bipy)(NH_3)_2]^{2+}$ and $[DQT]^{2+}$, it has led (ref. 5) to an investigation of the complexation by DB3nCn ethers and by the related molecular receptors, BMP(3n+2)Cn and BPP(3n+4)Cn, of the bipyridinium herbicides, $[DQT]^{2+}$ and $[PQT]^{2+}$.



$[Pt(bipy)(NH_3)_2]^{2+}$



$[DQT]^{2+}$



$[PQT]^{2+}$

$[DQT]^{2+}$ is structurally similar to $[Pt(bipy)(NH_3)_2]^{2+}$ in so far as (i) it is a dication and (ii) it contains a 2,2'-bipyridyl residue. Thus, not surprisingly, $[DQT]^{2+}$ is complexed (ref. 12) in both the solution and solid states by the range of DB3nCn ethers (n = 6-12). Spectrophotometric investigations of equimolar mixtures of $[DQT]^{2+}$ as its bis(hexafluorophosphate) and these macrocyclic polyethers in both acetone and acetonitrile revealed the existence of charge-transfer absorption bands centred on 400 nm or thereabouts. These absorption bands can be attributed to intermolecular $\pi-\pi$ charge-transfer between the π-electron rich catechol units of the DB3nCn ethers and the π-electron deficient bipyridinium ring system of $[DQT]^{2+}$. A quantitative treatment of the charge-transfer absorption bands in acetone provided evidence for (i) 1:1 stoichiometry and (ii) the relative stabilities of the 1:1 complexes in solution. The K_a values for the DB3nCn ethers where n = 9, 10, 11, and 12 of 410, 17500, 10800, and 2000 M^{-1}, corresponding to $-\Delta G°$ = 3.6, 5.8, 5.5, and 4.5 kcal mol^{-1}, reveal that the most stable 1:1 complex is formed with DB30C10. Thus, not surprisingly, red crystals of $[DQT.DB30C10][PF_6]_2$ suitable for X-ray crystallography were obtained very easily. Although the crystal structure analysis revealed that there are two independent sets of 1:1 complexes in the unit cell, the gross structural features of the two complexes are very similar. A space-filling representation of one of the $[DQT.DB30C10]^{2+}$ complexes is shown in Fig. 4.

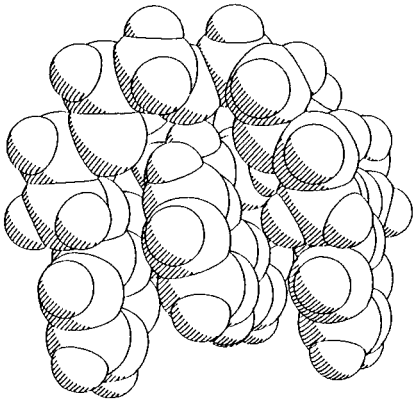
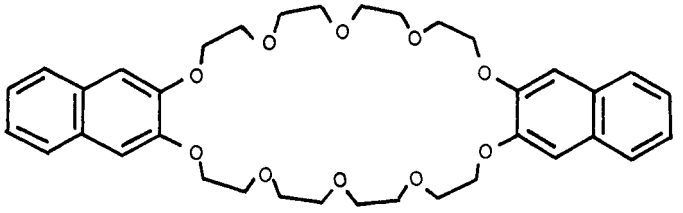


Fig. 4. Space-filling representation of the X-ray crystal structure of $[DQT.DB30C10]^{2+}$

In addition to the parallel alignment of the three aromatic ring systems to accommodate the stabilising intermolecular $\pi-\pi$ charge-transfer interaction, there is further stabilisation of the complex to be gained on account of favourable electrostatic interactions between the phenolic oxygen atoms in DB30C10 and the nitrogen atoms of the bipyridinium ring system of $[DQT]^{2+}$. Moreover, there is some evidence for weak [C-H...O] hydrogen bonding

involving hydrogens on carbons α to the nitrogens in $[DQT]^{2+}$ and some of the oxygen atoms in the polyether chains of DB30C10. ^1H NMR spectroscopy in CD_3COCD_3 demonstrated that the above intermolecular interactions are also responsible for the formation of stable ordered 1:1 complexes with similar gross structural features in solution, at least in the cases where DB30C10, DB33C11, and DB36C12 are the molecular receptors.



DN30C10

It is interesting that the DB3nCn ethers (DB30C10 in particular) are highly selective in their complexation of $[DQT]^{2+}$ relative to $[PQT]^{2+}$. The search for a $[PQT]^{2+}$ receptor was not an easy one and yet when the answer emerged it was a simple one. The pointer came from a comparison (ref. 14) of the receptor stereochemistry in $[Pt(bipy)(NH_3)_2.DN30C10]^{2+}$ and $[DQT.DN30C10]^{2+}$. ^1H NMR Spectroscopy and X-ray crystallography revealed dramatic differences in the binding of $[Pt(bipy)(NH_3)_2]^{2+}$ and $[DQT]^{2+}$ by dinaphtho-30-crown-10 (DN30C10) with the platinum complex adopting a slewed position, apparently in order to maximise overlap between the π-arene systems in the receptor and in the complex, whereas the organic dication adopts a symmetrical position more consistent with maximisation of Coulombic interactions. CNDO/2 Calculations on free $[DQT]^{2+}$ and free $[PQT]^{2+}$ indicate (ref. 15) that the positive charge density is concentrated more on the carbon atoms ortho and para to the nitrogen atoms than on the latter themselves. The experimental evidence (ref. 12-14) nonetheless demonstrates the propensity for both nitrogen atoms in $[DQT]^{2+}$ to become involved in parallel and collinear arrangements with the aryl oxygen atoms in DB30C10 and DN30C10. It was decided to examine the receptor properties of the BMP(3n+2)Cn ethers towards both $[DQT]^{2+}$ and $[PQT]^{2+}$ since the distance of 4.7 Å between the two aryl oxygen atoms in a resorcinol is almost half-way between the N/N distances of 2.8 and 7.0 Å in $[DQT]^{2+}$ and $[PQT]^{2+}$ respectively. In the event, UV and ^1H NMR spectroscopic studies demonstrated (ref. 16) that BMP32C10, in particular, complexes with both $[DQT]^{2+}$ and $[PQT]^{2+}$. An X-ray crystal structure was obtained for $[DQT.BMP32C10]^{2+}$. A space-filling representation is shown in Fig. 5.

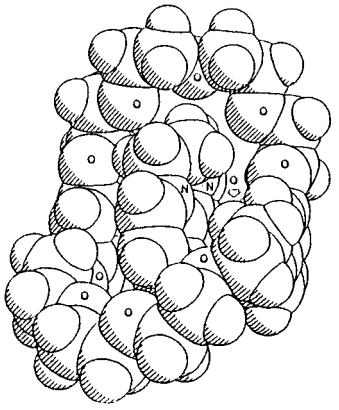


Fig. 5. Space-filling representation of the X-ray crystal structure of $[DQT.BMP32C10]^{2+}$

Encouraged by the observation that BMP32C10 is capable of complexing with $[PQT]^{2+}$ as well as with $[DQT]^{2+}$ by virtue of a combination of electrostatic and charge-transfer interactions, the search for an even better synthetic molecular receptor for $[PQT]^{2+}$ was intensified. This was uncovered amongst the range of BPP(3n+4)Cn ethers incorporating two hydroquinol residues (ref. 17,18). A charge-transfer absorption band is observed centred on 435 nm in the UV spectrum of $[PQT.BPP34C10][PF_6]_2$ in acetone. Quantitative analysis provided evidence for the 1:1 stoichiometry of the complex in solution together with a K_a value of 730 M^{-1} corresponding to $-\Delta G° = 3.90$ kcal mol^{-1}. Decreasing (n = 6-9) or increasing (n = 11 and 12) the macrocyclic ring size leads to an impairment of complexation strengths within the series (n = 6-12) of BPP(3n+4)Cn receptors. These conclusions were supported (ref. 19) by NMR (both ^1H and ^{13}C) and FABMS investigations. The X-ray crystal structure of $[PQT.BPP34C10]^{2+}$ as a space-filling representation

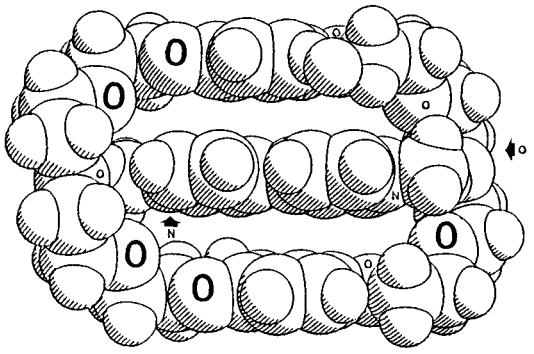


Fig. 6. Space-filling representation of X-ray crystal structure of $[PQT.BPP34C10]^{2+}$

is shown in Fig. 6. The binding of $[PQT]^{2+}$ can be interpreted as reflecting a balance between (i) charge-transfer interactions involving the hydroquinol rings, (ii) electrostatic interactions involving the phenolic oxygen atoms, and (iii) [C-H...O] and van der Waals interactions involving the polyether chains of BPP34C10. The remaining problem is one of selectivity: unfortunately, BPP34C10 forms 1:1 complexes equally well with $[DQT]^{2+}$. The quest to find a highly selective molecular receptor for $[PQT]^{2+}$ continues.

CONCLUDING REMARKS

It is satisfying to reflect on the fact that rather simple molecular receptors based on the first crown ether to be isolated and characterised by Pedersen (ref. 2) can accomplish some quite remarkable feats of molecular complexation. Science is at its most exciting when it is simple.

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