# Second-Sphere Coordination

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The design and synthesis of artificial receptors, able to recognize and bind transition metal complexes, is an area of growing interest in supramolecular chemistry. Macrocyclic hosts such as crown ethers, cyclodextrins, and cyclophanes have been employed to generate second-sphere adducts with numerous transition metal complexes as a result of noncovalent bonding interactions, such as hydrogen bonding, π-π stacking, and hydrophobic interactions. The effect of second-sphere coordination on the chemical, electrochemical, and photochemical properties of the adducts, as well as on their geometries in solution and in the solid state, has been investigated; these investigations have demonstrated the potential of second-sphere coordination in modulating the behavior of transition metal complexes by designed external intervention.

Transition metals are able to coordinate reversibly, as well as – in some instances – irreversibly, organic and inorganic ligands. The resulting complexes possess defined structural properties that are induced by the coordination geometry of the metal center. Thus, matching appropriate transition metals with designed ligands provides the possibility of engineering not only molecular but also supramolecular architectures, leading to an area of research that has been christened metallosupramolecular chemistry[1]. Indeed, the potential of metal coordination as a synthetic paradigm has been already demonstrated[2] with the construction of molecular assemblies, such as catenanes, knots, rotaxanes, macrocycles, and molecular squares, as well as supramolecular arrays such as double- and triple-helicates, grids, racks, cylindrical ensembles, dendrimers, and infinite two- and three-dimensional networks. In these synthetic processes, transition metals can be employed, either as permanent, or as temporary, building blocks. In the first instance, mono-, oligo- and poly-nuclear molecular assemblies and supramolecular arrays, in which the metal centers are constituent parts of the final thermodynamically-stable architecture are generated. In contrast, transition metals can be employed as templating agents[3] in order to preorganize the ligands around the metal with defined geometries, thus directing subsequent reactions involving the ligands toward particular products, for example [2]catenates[2c,f]. Once the designed structures and superstructures are assembled, the metal templates can be removed; that is, they act as tempo-

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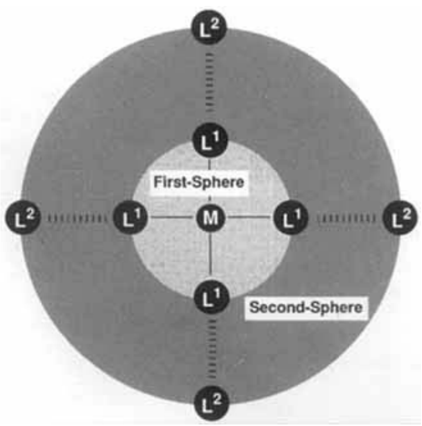
rary building blocks. In addition to their versatility as building units, many of the transition metals are electrochemically- and/or photochemically-active. As a result, metal-based structures and superstructures possessing device-like characteristics – for example the ability to act as a switch, sensor, wire, logic gate, or the ability to harvest and convert light or other forms of energy – can be designed and realized[4].

The majority of transition metal complexes incorporate ligands that are directly linked to the metal center, and constitute (Figure 1) its inner- or first-sphere of coordination. However, further ligands can bind to the first-sphere of the metal complex as a result of noncovalent bonding interactions, affording an outer- or second-sphere of coordination[5]. In other words, second-sphere coordination of transition metals affords complexes of complexes. The second-sphere ligands are often solvent molecules that, by modifying the environment of the complex, can alter substantially its electrochemical, magnetic, and optical properties, as well as its reactivity and geometry in the solid state. In the past, second-sphere coordination has been mainly considered as simply an aspect of solvation. However, the dramatic influence of second-sphere ligands upon the properties of a complex has suggested the possibility of designing appropriate molecular receptors able to bind a metal complex, affording a second-sphere adduct. A number of synthetic macrocyclic receptors have been synthesized since the advent of supramolecular chemistry and some of them have been tested as second-sphere receptors. Indeed, numerous crown ethers, cyclodextrins, calixarenes, and cyclophanes have proved to be efficient second-sphere ligands, both in solution and in the solid state. As a result, a wide number of second-sphere adducts have been generated by exploiting a whole range of noncovalent bonding interactions, such as hydrogen bonding, π-π stacking, and hydrophobic interactions. The synthesis of new second-sphere receptors and the investigation of the effect of their coordination on the second-sphere of numerous transition metals is currently an area of keen interest, with the ultimate goal being to be able to modulate the properties of the adducts by designing appropriate second-sphere ligands.

Figure 1. Schematic representation of a second-sphere adduct of the transition metal M, where $L^1$ and $L^2$ are first- and second-sphere ligands, respectively



## Crown Ethers as Second-Sphere Ligands

Crown ethers are macrocyclic receptors able to bind ammonium salts as a result of hydrogen bonding interactions between the polyether oxygen atoms incorporated within the macrocycle and the hydrogen atoms attached to the positively-charged nitrogen atom. The ability of the crown ether, 18-crown-6, to bind (Figure 2) primary alkylammonium salts, such as methylammonium perchlorate, was demonstrated[6] unequivocally by X-ray crystallography. The stereoelectronic analogy between primary alkylammonium ions [$R-NH_3^+$] and firstsphere ammine complexes of transition metals [$L_nM-NH_3^{\delta+}$] suggested the possibility of employing crown ethers as second-sphere ligands. An X-ray crystal structure of a second-sphere adduct with 18-crown-6 was obtained[7] by employing the transition metal complex, *trans*-[$Pt(PMe_3)Cl_2(NH_3)$]. A 2:1 stoichiometry results (Figure 2) as a consequence of three-point hydrogen bonding interactions between the polyether oxygen atoms of the crown ether and the ammine ligands of the metal complexes located on opposite faces of the macrocyclic receptor. A similar mode of binding was observed between 18-crown-6 and many other ammine transition metal complexes[5]. In particular, 18-crown-6 and the complex, [$Cu(NH_3)_4H_2O)]^{2+}$, which possesses coaxial *trans*-ammine ligands, form[7b] (Figure 3) infinite polymeric arrays in the solid state, again, as a result of three-point hydrogen bonding interactions. Polymeric arrays are also formed[8] (Figure 4) in the solid state as a result of second-sphere coordination of [$Pt(en)_2][PF_6]_2$, containing ethylene diamine (en) ligands, by 18-crown-6. Hydrogen bonding interactions involving one of the two hydrogen atoms of each $NH_2$ group and four polyether oxygen atoms are responsible for the formation of this adduct. Furthermore, 18-crown-6 is able to discriminate[7b] between copper and cobalt ammine complexes. Addition of one molar equivalent of 18-crown-6 to an ammoniacal solution containing one molar equivalent each of [$Cu(NH_3)_4H_2O)][PF_6]_2$ and [$Co(NH_3)_6][PF_6]_3$ results in the exclusive precipitation of the copper adduct, which can subsequently be isolated by filtration, leaving the cobalt complex in solution. Crown ethers other than 18-crown-6 have been also employed as second-sphere receptors of ammine transition metal complexes. The X-ray crystal structure of the 1:1 adduct formed[9] between dibenzo-21-crown-7 and the cyclooctadiene (cod) rhodium complex [$Rh(cod)(NH_3)_2][PF_6]$ is illustrated in Figure 5. In this case, only one of the two $NH_3$ first-sphere ligands is hydrogen bonded within the cavity of the crown ether while the other interacts with the oxygen atoms of the straddled polyether chain.

Second-sphere adducts of crown ethers and transition metals have also been generated by employing first-sphere ligands other than ammines. Coordination of water molecules to transition metals afford first-sphere complexes [$L_nM-OH_2^{\delta+}$] incorporating aqua ligands, which can sustain hydrogen bonding interactions with second-sphere receptors. As an example, *trans*-[$SnCl_4(H_2O)_2$] forms[10], in the solid state with 15-crown-5, polymeric arrays consisting

Figure 2. Binding of [MeNH$_3$][ClO$_4$] and *trans*-[Pt(PMe$_3$)Cl$_2$(NH$_3$)] by the crown ether 18-brown-6 as a result of three-point hydrogen bonding interactions

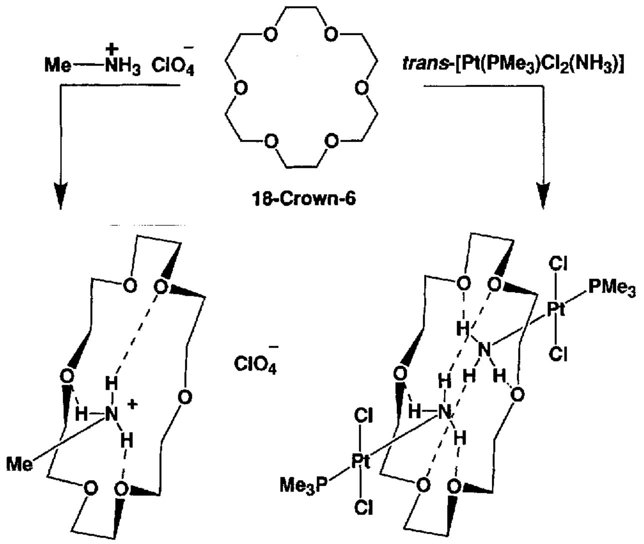


Figure 3. Formation of linear polymeric arrays as a result of second-sphere coordination

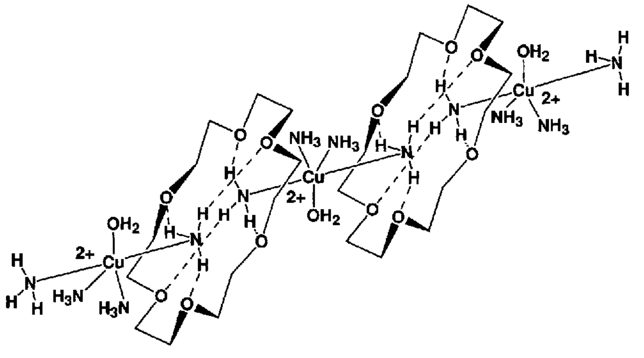
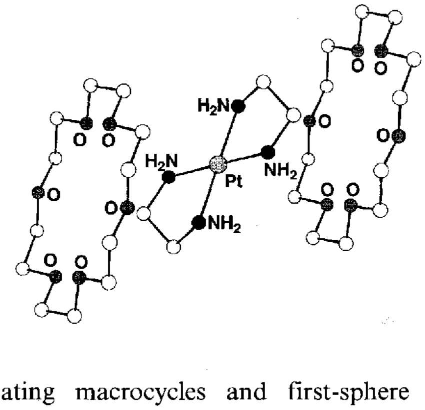


Figure 4. Ball-and-stick representation of the X-ray crystal structure of the second-sphere adduct formed between 18-crown-6 and [Pt(en)$_2$]$^{2+}$



of alternating macrocycles and first-sphere complexes bound by hydrogen bonding interactions between the polyether oxygen atoms and the acidic hydrogen atoms of the aqua ligands.

The acidity of protic first-sphere ligands can be increased by attaching to the same metal, π-acceptor ligands such as 2,2′-bipyridine (bipy), thus enhancing the strength of the hydrogen bonding interactions sustained by the protic first-sphere ligands. Furthermore, it is known[11] that bipyridine is able to sustain π-π stacking interactions with π-electron-rich aromatic units. Thus, the use of 2,2′-bipyridine as a first-sphere ligand provides the possibility of enhancing the stability of second-sphere adducts as a result of π-π stacking interactions, as well as enhanced hydrogen bonding interactions. Indeed, the transition metal complex [Pt(bipy)(NH$_3$)$_2$][PF$_6$]$_2$ forms[12] (Figure 6) stable adducts with the crown ethers dibenzo-3*n*-crown-*n* (*n* = 6–12) both in solution and in the solid state. X-Ray crystallographic analysis of some of these adducts revealed close contact between the π-electron-rich catechol rings and the π-electron-deficient bipyridine unit indicating that a π-π stacking interaction is achieved in addition to the strong hydrogen bonding interactions between the ammine ligands and the polyether oxygen atoms. The stability constants ($K_a$) for these 1:1 adducts in CH$_2$Cl$_2$ solution were obtained by measuring the concentration dependence of the charge transfer band, arising from the π-π stacking interaction: a value as high as 191000 $\text{M}^{-1}$ was measured when dibenzo-30-crown-10 was employed. Replacing the benzene rings incorporated within the crown ether receptor with naphthalene units affords[13] (Figure 7) 1:1 second-sphere adducts with similar geometries. However, in this case, the platinum complex is tilted significantly from its position in the corresponding adduct with dibenzo-30-crown-10, presumably in order to maximize the π-π stacking interaction.

Figure 5. Ball-and-stick representation of the X-ray crystal structure of the 1:1 second-sphere adduct formed between dibenzo-21-crown-7 and [Rh(cod)(NH$_3$)$_2$]$^+$

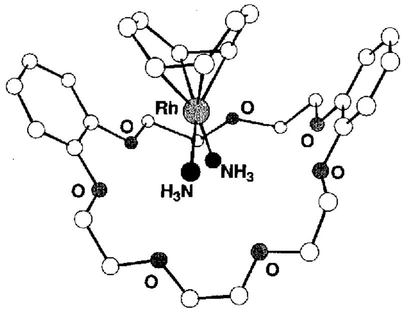


Figure 6. Second-sphere coordination via hydrogen bonding and π-π stacking interactions

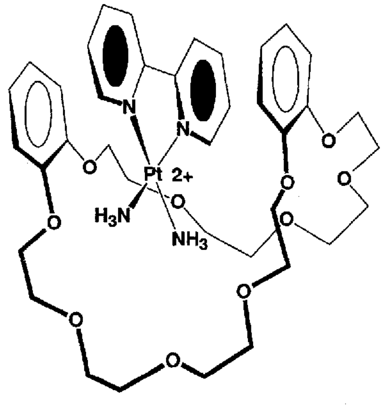
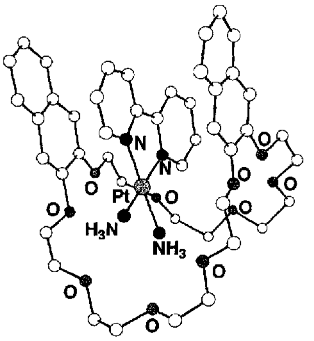


Figure 7. Ball-and-stick representation of the X-ray crystal structure of the 1:1 second-sphere adduct formed between dinaphtho-38-crown-10 and $[Pt(bipy)(NH_3)_2]^{2+}$

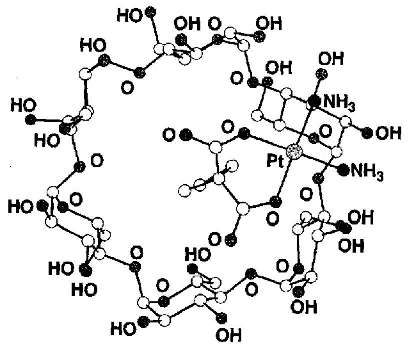


## Cyclodextrins as Second-Sphere Ligands

Cyclodextrins (CD) are oligosaccharides incorporating six or more D-glucopyranose residues α-1,4-linked in a cyclic array. The greek letter prefix, employed in naming these cyclic oligosaccharides, indicates the number of glucose residues – thus, α-, β-, and γ-cyclodextrins incorporate six, seven, and eight glucose residues, respectively. These molecules possess well defined preorganized cavities lined by relatively hydrophobic walls. As a result, cyclodextrins can encapsulate small guests and, indeed, a wide diversity of inclusion compounds have been reported in the literature[14].

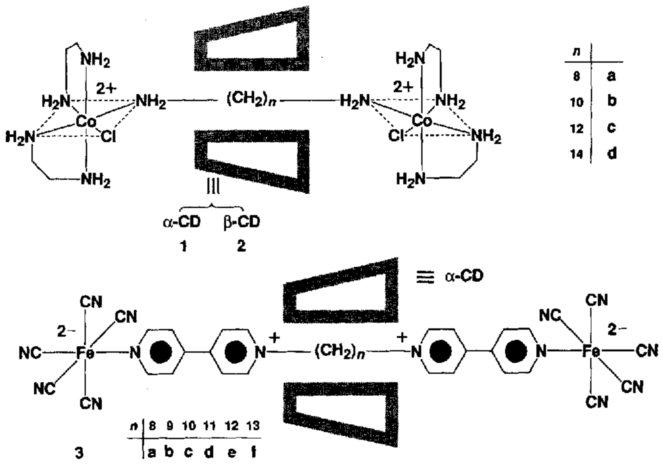
Since the observation[15] that β-CD forms a 1:1 adduct in solution with ferrocene, as a result of the insertion of one of the two cyclopentadienyl rings inside the cavity of the receptor, numerous second-sphere adducts composed of cyclodextrins and transition metal complexes, such as ferrocene derivatives, arene-metal complexes, and oligo-nuclear complexes have been characterized and their properties investigated. An example is illustrated by the X-ray crystal structure shown in Figure 8[16]. In this adduct, $[Pt(1,1\text{-cyclobutanecarboxylate})(NH_3)_2]^{2+}$ is bound by α-CD as a result of the insertion of the cyclobutane ring within the cavity of the cyclodextrin torus. In particular, the involvement of cyclodextrins as hosts in the second-sphere of transition metals has been exploited to construct[17] complex structures and superstructures, such as rotaxanes and pseudorotaxanes.

Figure 8. Ball-and-stick representation of the X-ray crystal structure of the 1:1 second-sphere adduct formed between α-CD and $[Pt(1,1\text{-cyclobutanecarboxylate})(NH_3)_2]^{2+}$



Displacement of the chloride ligands of *cis*-$\{CoCl_2[(CH_2NH_2)_2]_2\}Cl$ with ammine ligands can be achieved by reacting the cobalt complex with primary alkylamines. In addition, it is well known that alkyl chains form inclusion complexes with cyclodextrins. Thus, reaction of *cis*-$\{CoCl_2[(CH_2NH_2)_2]_2\}Cl$ with diaminoalkanes in the presence of either α- or β-CD affords[18], respectively, the rotaxanes **1a–d** and **2a–d** which are shown in Figure 9. The cyclodextrin torus behaves as a second-sphere receptor, binding the alkyl portion of the diaminoalkane first-sphere ligands. However, the transition metal complexes at the ends of the thread-like component are bulky enough to trap mechanically the cyclodextrin receptor, preventing the dissociation of the second-sphere adduct, forming a rotaxane. Thus, the self-assembly of these rotaxanes in solution is a striking example of second-sphere coordination in operation. A similar approach has been employed[19] by other investigators in order to generate rotaxanes bearing cyclodextrin macrocycles stoppered by bulky transition metal complexes coordinated at both ends of the dumbbell-like component. In particular, the self-assembly of the rotaxanes **3a–f** (Figure 9) has been achieved[19c,d] by reacting the iron complex $[Fe(CN)_5(H_2O)]^{3+}$ with the bis(pyridiylpyridinium)-based thread-like component in the presence of α-CD.

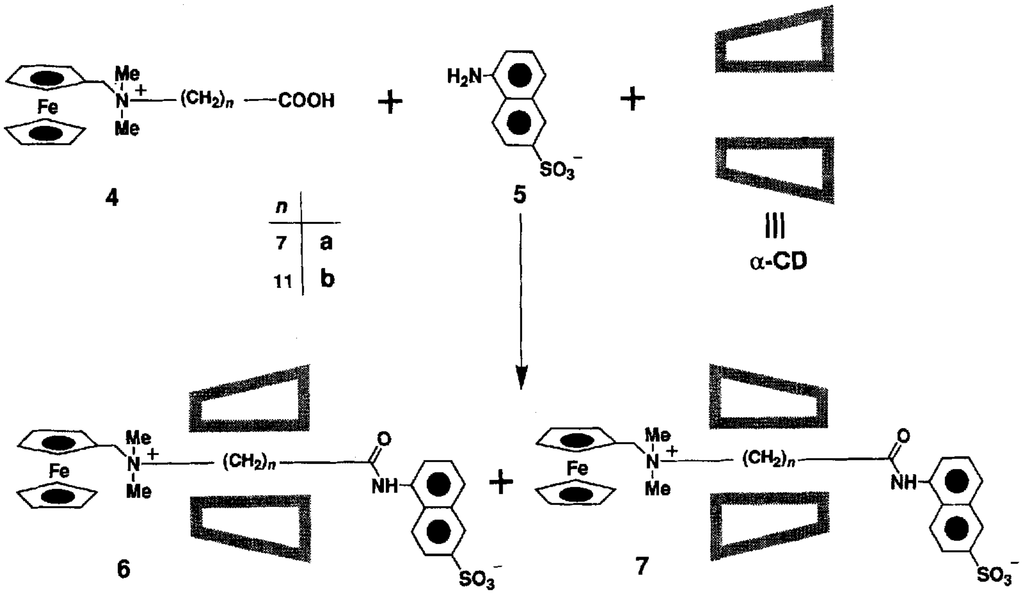
Figure 9. Second-sphere coordination within cyclodextrin-based rotaxanes



Another example of a rotaxane synthesis, as a result of second-sphere coordination, is illustrated in Figure 10. The ferrocene derivatives **4a** and **4b** are bound by α-CD in solution. Their subsequent reaction with **5** in the presence of α-CD gives[20] the isomers **6a** and **7a**, and **6b** and **7b**, respectively. Interestingly, as a result of the difference in size between the ferrocene-based and the naphthalene-based stoppers, as well as a consequence of the toroidal shape of the cyclodextrin component, the isomers **6a** and **6b** dissociate slowly while both **7a** and **7b** are stable.

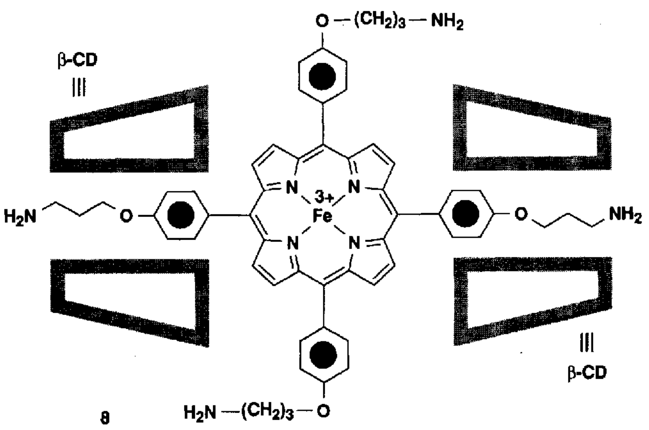
An amazing example of second-sphere coordination by cyclodextrins is the self assembly of **8** (Figure 11) in which the simultaneous encapsulation of a metalated porphyrin by two CD receptors is observed[21]. The iron center is located inside the cavity of the porphyrin, which behaves as a first-sphere receptor. However, the presence of long alkyl chains,

Figure 10. Self-assembly of isomeric rotaxanes as a result of second-sphere coordination



attached to the *meso*-positions of the porphyrin, provides suitable recognition sites for the simultaneous binding of two second-sphere receptors, namely two β-CDs.

Figure 11. A second-sphere adduct containing a metallated porphyrin bound by two cyclodextrins



## Cyclophanes as Second-Sphere Ligands

Ferrocene incorporates two π-electron rich cyclopentadienyl rings separated by an interplanar distance of 3.32 Å. These first-sphere ligands can sustain π-π stacking interactions with π-acceptors such as tetracyanoquinodimethane (TCNQ), tetracyanoethylene (TCNE), dichlorodicyanoquinone (DDQ), and bipyridinium-based units. As an example, the ferrocene derivative [$Fe(C_5Me_5)_2$] forms[22] with TCNE alternating donor/acceptor arrays in the solid state held together by π-π stacking interactions between the complementary π-units. These results suggested the possibility of employing ferrocene-based derivatives as templating agents in the synthesis of bipyridinium-based cyclophanes. Reaction (Figure 12) of the bis(hexafluorophosphate) salt **9** with the dibromide **10** in the presence of the template **11** affords[23] the organic molecular square, cyclobis(paraquat-4,4′-biphenylene) **12** in a yield of 32%, that is, some *sixteen times higher* than the meagre 2% yield obtained in the absence of any templating species under otherwise identical conditions. The second-sphere coordination of the bipyridinium units around the ferrocene template, which results from π-π stacking interactions between the complementary aromatic units in addition to hydrogen bonds between the polyether oxygen atoms and the acidic hydrogen atoms on the bipyridinium units, is responsible for the self-assembly of the adduct [**11**−**12**]. Dissociation of the second-sphere adduct is achieved by column chromatography, which yields the free tetracationic cyclophane **12** and the unaltered template **11** that can subsequently be recycled. The formation of the second-sphere adduct [**11**−**12**] in solution was confirmed by fast atom bombardment mass spectrometry and $^1$H-NMR spectroscopy. Finally, an association constant ($K_a$) of 1600 $\text{M}^{-1}$ for the 1:1 adduct was measured in MeCN at 25 °C.

The tetracationic cyclophane **13**, a structural analogue of **12**, forms[24] mosaic-like arrays in the solid state as a result of intermolecular π-π stacking interactions between the π-electron rich hydroquinone rings and the π-electron deficient bipyridinium units. In addition, the cavity of this cyclophane is large enough to accommodate a ferrocene molecule inside (Figure 13), affording second-sphere adducts that spontaneously self-organize in the solid state to generate the amazing three-dimensional nanoscale superstructure represented in Figure 14.

## Polycyclic Receptors as Second-Sphere Ligands

In order to form stable second-sphere adducts of transition metal *cis*-diammine complexes, the bicyclic receptors **14**−**17** (Figure 15) were designed and synthesized[25]. These

Figure 12. Template-directed synthesis of an organic molecular square as a result of second-sphere coordination

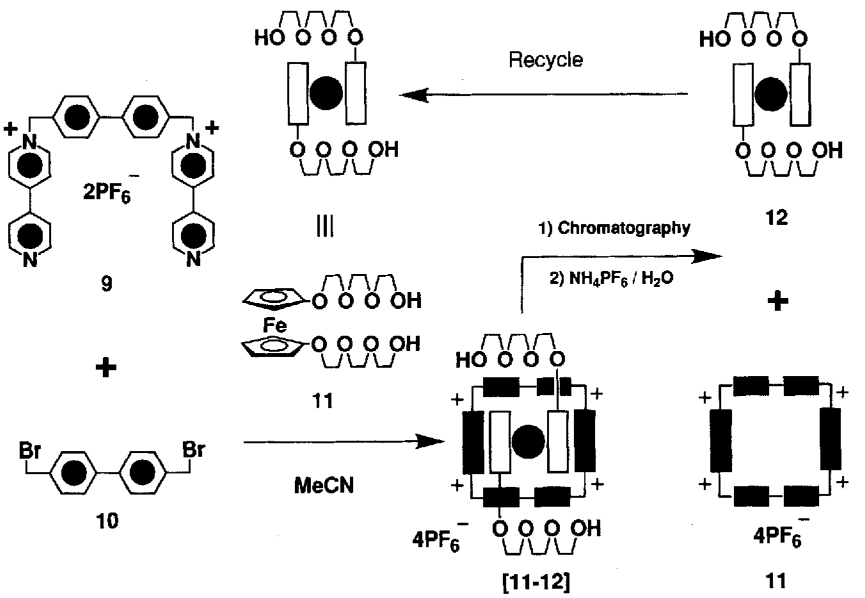


Figure 13. Ball-and-stick representation of the X-ray crystal structure of a 1:1 second-sphere adduct between ferrocene and an organic molecular square

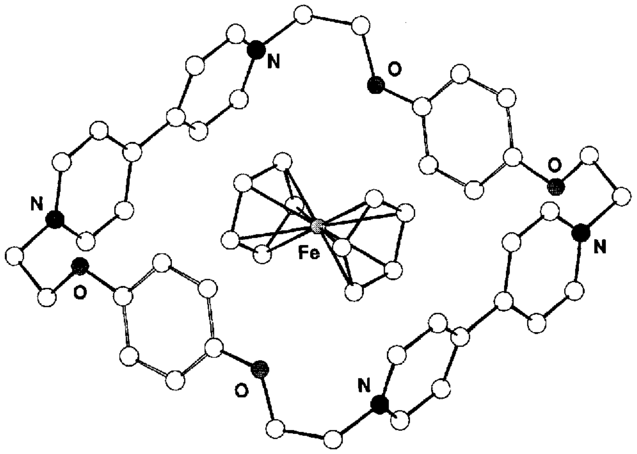
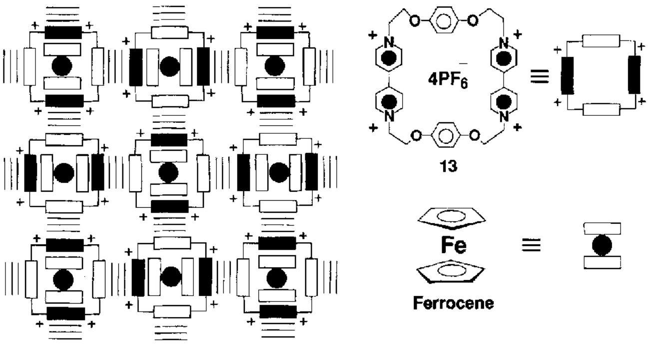


Figure 14. Self-organization in the solid state of a nanoscale three-dimensional superstructure



macrobicyclic polyethers possess two well-defined cavities lined with oxygen atoms which are able to sustain hydrogen bonding interactions with the ammine ligands of a transition metal *cis*-diammine complex. Furthermore, the presence of a "central" polyether chain linking the two benzene rings forces the molecule to adopt a bowl-like conformation. As a result, a pronounced cleft, inside of which a guest transition metal complex can be accommodated, is defined by the receptor. Nonetheless, these macrobicyclic polyethers can undergo conformational changes in solution. In particular, the inversion of the "central" polyether chain, through the cavity defined by the other two polyether chains, can be followed by variable temperature $^1$H-NMR spectroscopy. Upon adduct formation, the energy barrier to inversion increases dramatically since dissociation of the adduct must occur in order to allow the dynamic process to take place. It follows that these energies of activation provide a measure of the stabilities of the second-sphere adducts. Addition of the cyclooctadiene (cod) rhodium complex $[Rh(cod)(NH_3)]^+$ to $CD_2Cl_2$ solutions of **14** and **15** increases the energies of activation for their inversion by 2.9 and 3.2 kcal mol$^{-1}$, respectively, suggesting that second-sphere adducts do form in solution. In order to increase the degree of preorganization associated with such receptors, substituents bulky enough to inhibit the conformational change have been introduced into the "central" polyether chain of the macrobicycles, for example, as in **16** and **17**. X-Ray crystallographic analyses revealed the formation, in the solid state, of 1:1 second-sphere adducts held together by hydrogen bonding interactions between the ammine first-sphere ligands and the polyether oxygen atoms. Similarly, the complex $[Pt(NH_3)_4]^{2+}$ is bound[26] by the macrobicyclic receptor **15**, as illustrated by the X-ray crystal structure of the corresponding 1:1 second-sphere adduct shown in Figure 16.

The macropolycyclic compound **18**[27] (Figure 17) – namely, a hemicarcerand – is composed of two bowl-shaped

Figure 15. Second-sphere adducts incorporting polycyclic second-sphere ligands

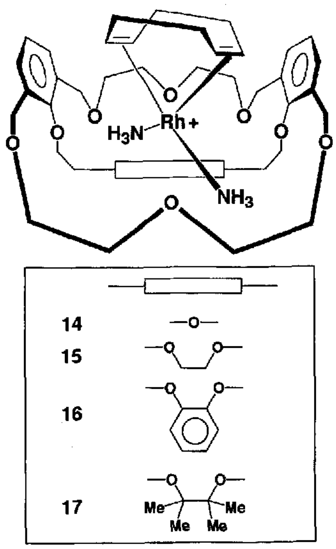


Figure 16. Ball-and-stick representation of the X-ray crystal structure of a 1:1 second-sphere adduct a macrobicyclic receptor and $[Pt(NH_3)_4]^{2+}$

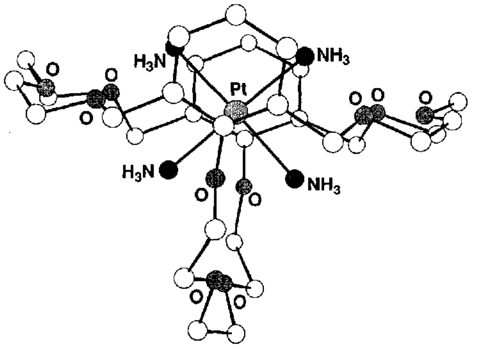
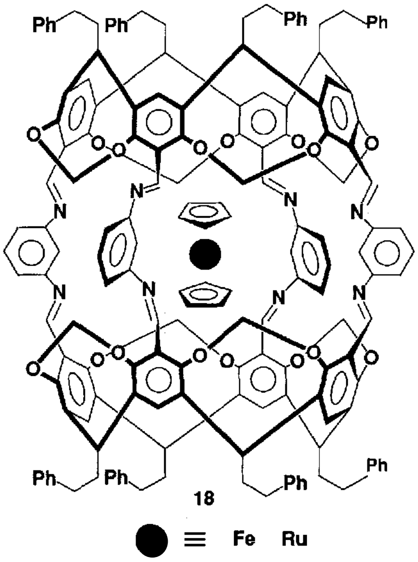


Figure 17. Second-sphere coordination as a result of constrictive binding



components, linked together by four covalent bridges. The inclusion of small molecules inside the spherical cavity of **18** can occur after their passage through one of the four portals of the hemicarcerand. In particular, transition metal complexes such as ferrocene or ruthenocene can be encapsulated inside this hemicarcerand after heating (80–120 °C) a solution of **18** and the metallocene in a high boiling solvent. The resulting hemicarceplexes are unusual examples of second-sphere coordination as a consequence of constrictive binding.

## Simultaneous First- and Second-Sphere Coordination

The simultaneous first- and second-sphere coordination of transition metals has been achieved[28] by employing macrocyclic receptors incorporating functional groups that can act as first- and second-sphere ligands. Nonetheless, the first examples of simultaneous first- and second-sphere coordination were discovered fortuitously. On mixing in $CH_2Cl_2$ the complex $[Rh(cod)(NH_3)_2][PF_6]$ and diaza-18-crown-6, rapid solubilization of the transition metal complex occurred[28c]. However, somewhat unexpectedly, the X-ray crystal structure (Figure 18) of the corresponding adduct revealed the displacement of one of the $NH_3$ first-sphere ligands for one of the NH groups of the crown ether. In addition, the second $NH_3$ first-sphere ligand is hydrogen bonded to the polyether oxygen atoms of the crown ether, which acts simultaneously as a first- and second-sphere ligand with respect to the two rhodium centers. Recently, transition metal complexes in which first-sphere σ-donation is accompanied by second-sphere hydrogen bonding and/or π-π stacking interactions have been prepared[29] by metallation of appropriate thiacyclophanes. Careful design of such macrocyclic receptors has allowed the recognition of simple substrates, such as water, ammonia, amines, hydrazine, and nucleobases. Complex **19** (Figure 19) is composed of a palladium center connected to the two sulfur atoms and one of the aryl carbon atoms of the macrocyclic receptor. In addition, a water molecule is coordinated by the metal center via the oxygen atom and by the polyether chain of the macrocyclic receptor via hydrogen bonding interactions involving the two hydrogen atoms. Similarly, in **20** *n*-butylamine is bound by the metalloreceptor, again, as a result of simultaneous first- and second-sphere coordination. Interestingly, in competition experiments between *n*-butylamine and *n*-butylmethylamine for this receptor, exclusive binding of the primary amine was observed, despite the lower Lewis basicity of primary with respect to secondary amines. This result is a consequence of the ability of the primary amine to sustain two rather than one hydrogen bonding interactions with the polyether chain of the metalloreceptor. Thus, second-sphere coordination is responsible for the selectivity observed upon complexation. The complexation of nucleobases can be also achieved by employing simultaneously first- and second-sphere coordination. The

X-ray crystallograpic analysis of the complex **21** shows that the nucleobase guanine is coordinated to the metal center via one of its nitrogen atoms and, simultaneously, π-π stacking interactions between the aryl rings of the metalloreceptor and the nucleobase, as well as a bifurcated hydrogen bonding interaction involving the hydrogen atoms of the ammine group and the polyether oxygen atoms, are observed.

Figure 18. X-ray crystal structure showing the simultaneous first- and second-sphere coordination of rodhium(I) complexes

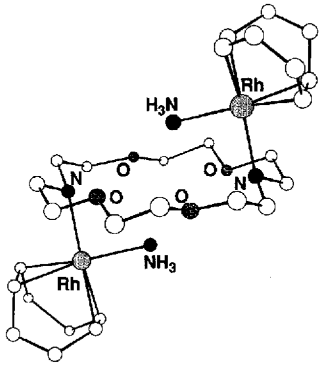
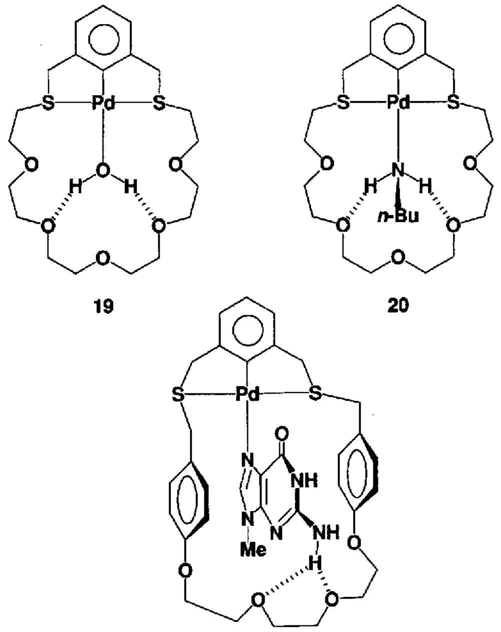


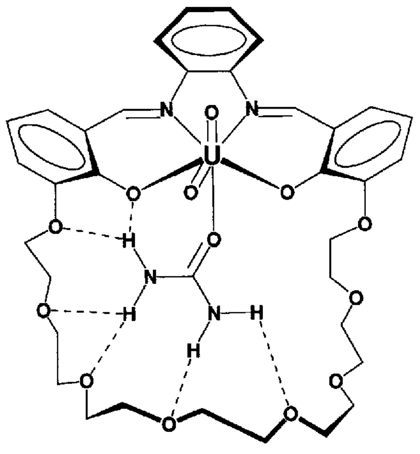
Figure 19. Examples of simultaneous first- and second-sphere coordination



**19** **20** **21**

An amazing example of simultaneous first- and second-sphere coordination is the adduct **22** shown in Figure 20[28g,f]. The X-ray crystallographic analysis revealed the coordination of the two immino nitrogen atoms and the two phenoxy oxygen atoms of the macrocyclic receptor and of the carbonyl oxygen atom of the urea ligand in the first-sphere of dication $UO_3^{2+}$. In addition, hydrogen bonding interactions between the amine groups of the urea ligand and six oxygen atoms of the macrocyclic receptor are achieved.

Figure 20. Binding of urea as a result of simultaneous first- and second-sphere coordination



**22**

## Effect of Second-Sphere Coordination

The second-sphere coordination of transition metals has a significant effect upon the electrochemical, magnetic, and photochemical properties of the metal and the resulting adducts often behave differently from the parent first-sphere complexes. The photochemical properties of the second-sphere adduct, shown in Figure 6, were investigated[30] in $CH_2Cl_2$ as well as in MeCN solutions. A strong charge transfer band is detected in the absorption spectrum as a result of the π-π stacking interaction between the cathecol rings and the 2,2′-bipyridinium unit. In addition, the luminescence properties of the adducts are dramatically different from those of the free components. The source of the luminescence is a low energy "supramolecular level".

The ferromagnetic behavior of second-sphere charge transfer adducts of ferrocene derivatives and a series of π-acceptors (vide supra) has been the subject of a review[31]. In addtion to paramagnetic and metamagnetic phases, the second-sphere adduct $[Fe(C_5Me_5)_2][TCNQ]$ crystallizes[32] in a third crystallographically-distinct ferromagnetic phase. Subtle structural changes have a dramatic effect upon the magnetic properties and $[Fe(C_5Me_5)_2][TCNQ]$ is a rare example of an adduct giving rise to three distinct magnetic phenomena.

The crown ether 18-crown-6 is able (vide supra) to form second-sphere adducts with ammine transition metal complexes as a result of three-point hydrogen bonding interactions between the ammine hydrogen atoms and the polyether oxygen atoms. The ruthenium complexes $[Ru(NH_3)_5L][PF_6]_n$ (L = pyrazine and isonicotinamide for $n = 2$, and L = 4-dimethylaminopyridine and 4-aminopyridine for $n = 3$, respectively) are bound[33] by 18-crown-6 with 1:1 and 2:1 stoichiometries when $n$ is equal to two and three, respectively. Upon adduct formation, a red shift of the metal-to-ligand charge transfer band for the ruthenium(II) complex and a blue shift of the ligand-to-metal charge transfer band of the ruthenium(III) complex were revealed and their linear correlation with the reciprocal of the dielectric constant of the solvent was observed. Furthermore, the redox potential of the ruthenium(III)/ruthenium(II) couple was measured cyclic voltammetrically by varying the concentration of the second-sphere receptor 18-crown-6 in MeCN solution. The redox potentials are shifted to more negative values on increasing the amount of crown ether in solution, suggesting that tuning of the redox potential of a transition metal complex can be achieved by taking advantage of second-sphere coordination.

## Conclusions and Reflections

Transition metal complexes are composed of a metal center directly linked to first-sphere ligands. Noncovalent bonding interactions such as hydrogen bonding, π-π stacking, and hydrophobic interactions between the first-sphere ligands and appropriate receptors can bring about the formation second-sphere adducts – namely, complexes of complexes. Numerous macrocyclic receptors such as crown ethers, cyclodextrins, and cyclophanes have been designed and synthesized in order to recognize and bind specific transition metal complexes as a result of second-sphere coordination and, in some instances, as a consequence of simultaneous first- and second-sphere coordination. The self-assembly of complex molecular compounds, such as rotaxanes, and the template-directed synthesis of macrocyclic species – otherwise obtained in very low yields – has been achieved via second-sphere coordination, demonstrating its potential as a synthetic paradigm. Furthermore, the chemical, electrochemical, magnetic, photochemical, and structural properties of numerous transition metal complexes can be modified as a result of second-sphere coordination. Thus, designing appropriate second-sphere receptors provides the possibility of modulating the behavior of transition metal complexes. In conclusion, the potential of second-sphere coordination adds a completely new dimension to metallosupramolecular chemistry. It is likely that more and more interest and effort will be directed into this research area at the boundary between organic and inorganic chemistry in the near future.

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