

Metal Complexation of Calix[4]azacrown Derivatives – Evidence for Communication Between Upper and Lower Functionalised Rims

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Dedicated to the memory of Des Cunningham^[†]

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The coordination chemistry of calix[4]azacrowns obtained from the reaction of a diester calix[4]arene with diethylenetriamine provided unusual copper(II) and manganese(II) complexes in which calix[4]azacrown acts as a bidentate N,O-donor ligand, in some cases, but as a unidentate N-donor ligand, in other cases. The first example of a binuclear ruthenium(II)/manganese(II) complex, involving the ca-

lix[4]arene framework as the bridging ligand, is also reported. The calix[4]arene framework consists of a bipyridyl unit connected at the upper rim of the calix[4]arene, through an amide linkage, and an azacrown unit at the lower rim, also connected through amide groups.

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Introduction

Calix[4]arenes are versatile host molecules for supramolecular chemistry, which have been incorporated into

numerous elaborate structures.^[1] Double calix[4]arenes,^[2] for example, have been constructed covalently through

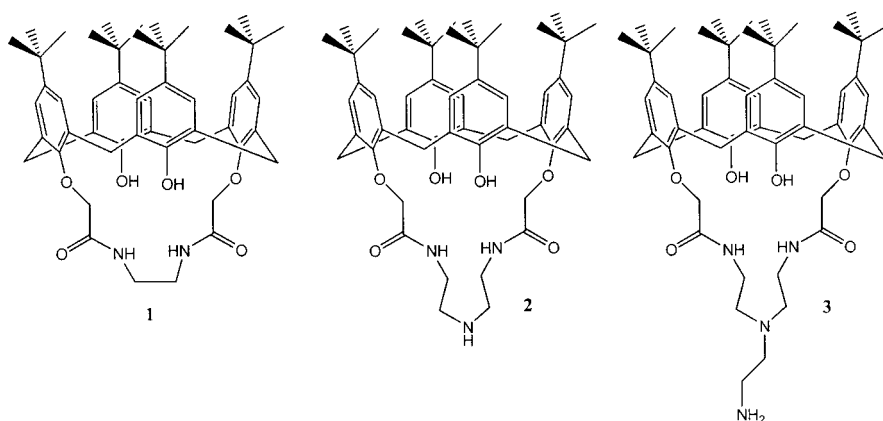


Figure 1. Calix[4]azacrowns.

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upper rim/upper rim linkage,^[3] lower rim/lower rim linkage^[4] or upper rim/lower rim linkage,^[5] and also noncovalently through hydrogen bonding.^[6] Incorporation of a crown ether into a rigid calix[4]arene creates a new type of supramolecular host, with interesting prospects for binding metal ions.^[7] The family of calix[4]azacrowns combine calix[4]arenes with azaethylene chains attached to the phenolic oxygen atoms by acetamido groups, which serve both as covalent linking functions and as potential chelating

groups. The first calix[4]azacrowns of type **1** (Figure 1) were prepared by reaction of either a calix[4]arene dimethyl ester or calix[4]arene diacyl chloride derivative with the appropriate diamine and were shown by FAB-mass spectrometry to complex divalent (Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}) and trivalent (Sc^{3+} , Y^{3+} , In^{3+} , Gd^{3+} , Bi^{3+}) metal cations.^[8]

We have previously reported upper- and lower-rim functionalised calix[4]arenes, capable of binding transition-metal and alkali-metal salts, as well as ligands capable of attachment to calix[4]arenes.^[9] One such calix[4]arene contained picolyl groups.^[9c] In extending this theme, we targeted the design of calix[4]azacrowns and, in particular, the calix[4]arenes **2** and **3** which are capped by a diamide bridge at the 1,3-position on the lower rim.

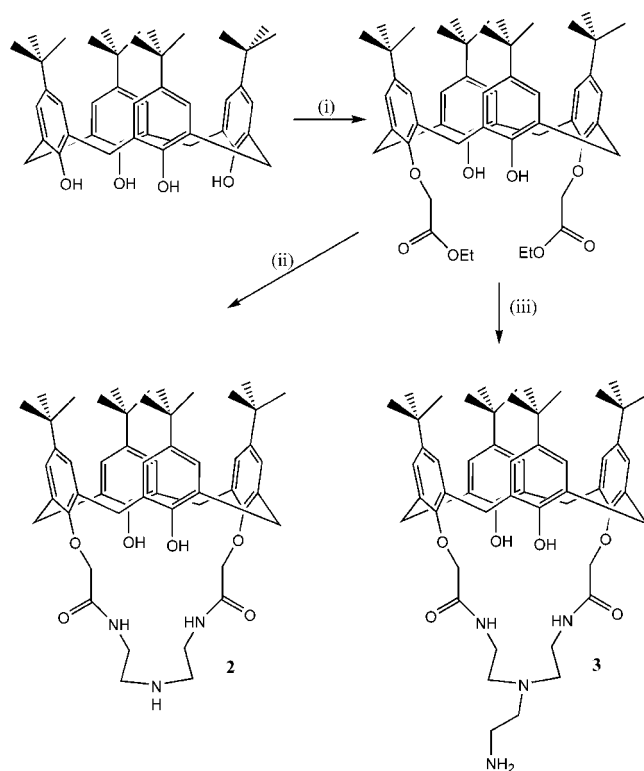
Transition-metal ions which are covalently linked to each other through a ligand system are of interest and importance for a variety of purposes.^[10–17] They can be used for studies into light-induced energy and electron transfer, as well as model systems for the development of supramolecular compounds which are capable of performing useful light induced processes such as photochemical devices. Indeed, the conversion of light energy into chemical energy is of current interest with particular focus on the development of efficient solar energy conversion schemes. To observe such transfer processes between the metal centres, they must be linked by a bridging ligand. These ligands have varied from chelating units linked by either flexible or rigid chains or by rod-like spacers.^[14,18–21] More recently, the cage compound 1,12-dicarba-*closo*-dodecaborane, known as *p*-carborane, has been used as the linker molecule.^[22] These linker or spacer molecules determine the spatial arrangement of the whole molecule while their chemical properties are important in influencing the spectroscopic and redox properties of the two metal centres as well as determining the rate of the electron/electron transfer process. We have focused our efforts on the construction of polynuclear complexes in which a photoactive and redox-active metal are linked by bridges based on a calix[4]arene derivative.^[9a] Extensive functionalisation has been carried out at both the upper and lower rims of the calix[4]arene. A calix[4]arene, with appropriate functionalisation at both the wide and narrow rims, is capable of maintaining a well-defined distance between two metal centres positioned at each rim. By the simple modification of the synthesis of the functionalised calix[4]arene, this distance can be easily altered. To the best of our knowledge, there has been no report of a calix[4]arene derivative as a spacer molecule in energy/electron transfer reactions.

Results and Discussion

Lower-Rim Complexes

The method used for preparation of lower-rim functionalised calix[4]azacrown (**2**) is shown in Scheme 1. Base-promoted reaction of *p*-*tert*-butylcalix[4]arene with ethyl bromoacetate in acetonitrile produced the diester 5,11,17,23-tetra-*tert*-butyl-25,27-bis(ethoxycarbonylmethoxy)calix[4]-

arene (diester calix[4]arene),^[9a,23] which was then stirred for 72 h with either diethylenetriamine or tris(2-aminoethyl)-amine in a methanol/toluene solvent mixture to give the cyclic amides **2** and **3** as white solids in good yield, similar to that described by Bitter et al.^[24] The IR spectra of **2** and **3** exhibit a strong C=O signal at 1678 and 1681 cm^{-1} respectively (compared to 1746 cm^{-1} in the starting diester calix[4]arene), indicative of the amide functional group, together with a sharp N–H signal at 3372 and 3399 cm^{-1} , which is not present in the spectrum of the starting diester derivative. The ^1H NMR spectrum suggests that the calix[4]arene molecules in **2** and **3** adopt a distorted cone conformation:^[25] a pair of AB-type doublets is observed for the diastereotopic methylene protons at $\delta = 4.16$ and 3.36 ppm in **2** and at $\delta = 4.17$ and 3.39 ppm in **3**, respectively, compared to $\delta = 4.43$ and 3.30 ppm for the corresponding signals in the starting diester calix[4]arene.



Scheme 1. Reagents and conditions: (i) K_2CO_3 , ethyl bromoacetate, MeCN, reflux, 18 h; (ii) diethylenetriamine, MeOH, toluene, 48 h; (iii) tris(2-aminoethyl)amine, MeOH, toluene, 48 h.

^1H NMR studies have previously indicated that macrocycles of this type show interesting binding properties;^[7c,7d,26] for example, while the tetra(*p*-*tert*-butyl)calix[4]azacrown **1** does not extract transition-metal ions, the corresponding 1,3-dimethoxy-*p*-*tert*-butylcalix[4]azacrown extracts Cu^{2+} ions selectively with respect to Co^{2+} and Ni^{2+} ions.^[7c,7d] Complexation behaviour of **2** towards alkaline-earth and transition-metal ions has been recently described^[26] and the X-ray crystal structure of the complex with Mg^{2+} revealed that the metal ion was not bound to any of the nitrogen atoms, but lay outside of the crown loop, forming a coordination polymer through metal-oxy-

gen bonds to carbonyl O atoms from different calix[4]arene entities. Oueslati et al.^[7d] found that metal extraction did not occur on attempted complexation of **2** with copper, nickel and cobalt picrates. Instead, crystals were formed in which a water molecule lies within the crown loop of **2** and picric acid accepts a hydrogen bond from this water molecule. In an effort to understand the binding, or lack thereof, of Cu^{2+} to calix[4]azacrowns, we undertook complexation reactions of **2** and **3** with various copper(II) salts, as well as investigating the complexation behaviour of MnCl_2 .

Copper(II) Complexes

Complexation reactions of **2** and **3** were carried out in MeOH at reflux temperature, using copper(II) acetate hydrate, copper(II) chloride dihydrate and copper(II) perchlorate hexahydrate, respectively, in each case in a 1:1 ratio. Intense blue solutions were obtained in all cases and most of the solvent had to be removed under reduced pressure before precipitation occurred. For the reaction involving **2** with copper(II) acetate, a blue/green complex **4** was obtained, which was shown by X-ray diffraction to be $\text{Cu}(\text{CH}_3\text{CO}_2)_2(\text{MeOH})_2$ (Figure 2). The Cu^{2+} ion is not complexed within the calix[4]azacrown, but instead is bound to two such units through interactions with the lone pairs on the NH of the crown ring and the C=O groups of the amide units. Thus, **2** acts as a bidentate N,O-donor ligand. The complex is centrosymmetric, and Cu^{2+} adopts a typical [4+2] distorted octahedral geometry. The Cu–N and Cu–O(acetate) bond lengths are 2.052(4) and 1.957(3) Å, respectively, while the axial Cu–O=C distances are 2.715(3) Å. The monomeric nature of the copper acetate unit, in contrast to the bridging structures, usually associated with simple copper(II) acetate salts,^[27] may be attributed to the steric bulk of the calix[4]azacrown ligand, which prevents further association. The coordinated amine group of **2** retains its proton, forming an N–H $\cdots$ O hydrogen bond to the unbound O atom of the acetate group. An O–H $\cdots$ O hydrogen bond is also formed from the phenolic OH group of **2** to the acetate group. In the solid state, MeOH molecules form O–H $\cdots$ O hydrogen bonds to the Cu-bound and unbound C=O groups of the amide bridge. The infrared spectrum of **4** shows two bands in the carbonyl region, as was expected from the X-ray crystal structure, at 1690 cm^{-1} , representative of an amide carbonyl bond, and also at 1578 cm^{-1} , representing the acetate carbonyl group. The reaction of **3** with copper(II) acetate also results in a green solid **5** which showed similar bands in the infrared spectrum, particularly in the carbonyl region at 1676 and 1555 cm^{-1} suggesting that the acetate was binding to the copper in an analogous manner. A broad band at 3360 cm^{-1} was also evident implying that the copper was bonding to **3** through the pendant amine. Elemental analysis on this compound also suggested a 1:2 metal/ligand complex as observed in **4**.

The complexation reactions of **2** and **3** with copper(II) perchlorate hexahydrate gave the green complexes **6** and **7**.

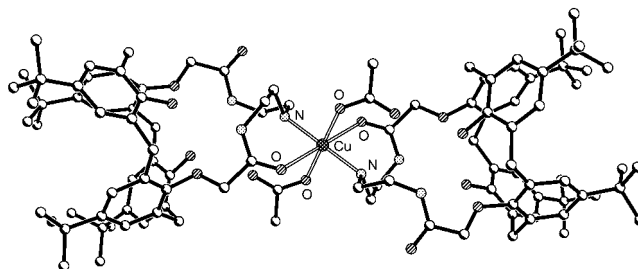


Figure 2. Molecular structure of **4** (H atoms omitted).

Comparison of the IR spectrum of **6** and **7** with that of **4** reveals slight differences in the spectra. The differences suggest that the mode of complexation of the calixazacrown derivative is not determined solely by the metal ion (although this clearly will have some bearing), but is also influenced by the anion and its coordinating ability. The more strongly complexing acetate anion remains bound to Cu^{2+} in **4**, while the weakly complexing perchlorate anions may be less likely to do so in **6** and **7**. Elemental analyses of both **6** and **7** suggest the presence of one perchlorate anions per Cu^{2+} ion as well as the presence of only one calix[4]-azacrown unit, requiring that the ligands of **2** and **3** be neutral, possibly using the lone pairs on the nitrogen atoms in the ring to bind Cu^{2+} internally in the calixazacrown loop. Furthermore, the metal complexes crystallise along with a molecule of methanol in both cases. To date, we have not been able to obtain suitable crystals of **6** or **7** to establish this conclusively.

For the complexation reaction of **2** with copper(II) chloride, a mixture of green **8** and blue **9** solids was obtained when the reaction was allowed to proceed for 120 min. On decreasing the reaction time to 20 min, the major product was **8**. The green material **8** has an IR spectrum similar to that of **4** (with the exception of the carbonyl stretching frequency due to the acetate group). This suggests that **8** comprises of copper(II) chloride bound between two calixazacrown ligands in a similar manner to the copper(II) acetate complex **4**. Since **8** is the major product obtained from the reaction after only a the short time period, complexation of copper(II) chloride by **2** appears to be the initial outcome. When the reaction proceeds for a longer time, the blue solid **9** is formed. Single crystals of **9** were obtained from the mother liquor after 90 min reaction, and single-crystal X-ray analysis^[28] confirmed that cleavage of the amide bonds had occurred, resulting in the simple copper-diethylenetriamine complex shown in Figure 3. This complex can also be obtained by direct reaction of diethylenetriamine with copper(II) chloride dihydrate in a 1:1 ratio.^[29] Cleavage of amide bonds by copper(II) chloride has been described previously.^[30] On repeating the reaction, we were also able to obtain the calix[4]arene di-acid derivative^[31] that is formed in the cleavage reaction. We have only observed the formation of **9** when the reaction mixture is heated for long periods of time. This suggests that the green complex **8** is relatively stable, and that it requires a considerable amount of energy before the cleavage reaction pro-

ceeds. One probable mechanism for this process involves Cu^{2+} moving from being externally coordinated (in the manner of **4**) to being internally coordinated, with this movement allowing the amide bonds to cleave.

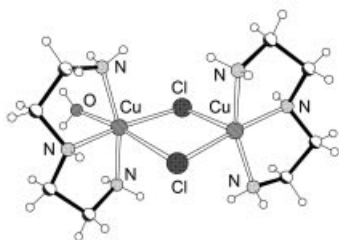


Figure 3. Molecular structure of the cleavage product **9**.

The complexation reaction of **3** with copper(II) chloride results only in a single green complex **10**. The infrared spectrum of this compound was very similar to that obtained for **8** which suggested that the copper was bonded to the free amine of the calix[4]azacrown. Microanalysis suggested the presence of only one chloride anion which would mean that the calix[4]azacrown was acting as a unidentate ligand through loss of a proton from the pendant amine group. The remaining coordination sites about the copper atom were occupied by water molecules. There was no evidence in this case of any cleavage reactions occurring or of two calix[4]azacrown units bonding to the copper atom.

Manganese(II) Complexes

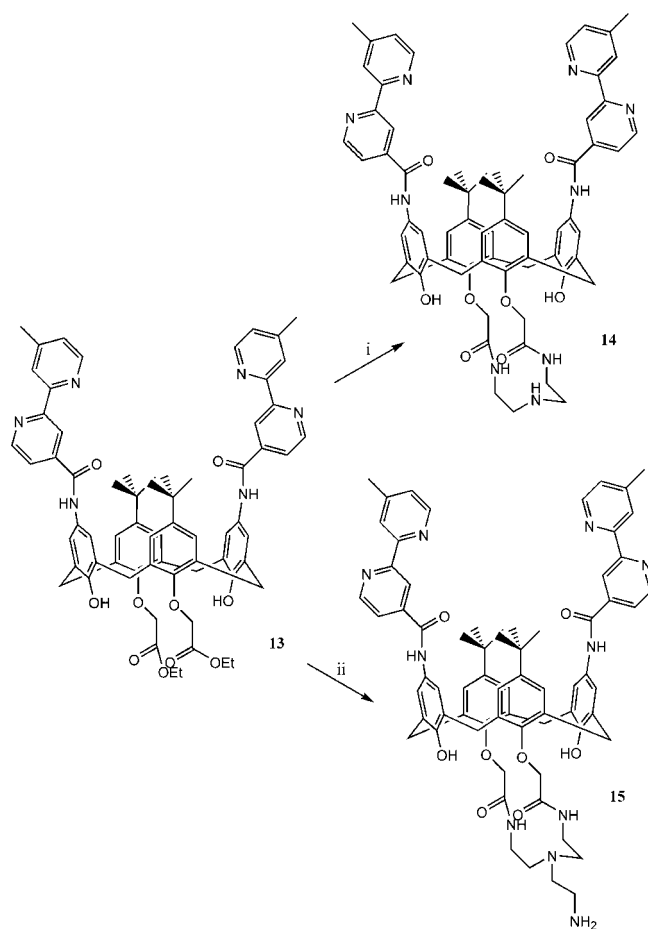
As in the case of the copper complexations described above, the complexation reactions of **2** and **3** with manganese(II) chloride tetrahydrate were carried out in MeOH at reflux temperature, respectively, in each case in a 1:1 ratio. Brown solutions were obtained in both cases and most of the solvent had to be removed under reduced pressure before precipitation occurred. Compound **11** crystallises with a molecule of methanol present as solvent of crystallisation. Elemental analyses for **11** and **12** suggest the presence of only one chloride anion which would mean that the calix[4]azacrown **3**, in each case, was acting as a unidentate ligand through loss of a proton from the pendant amine group. The remaining coordination sites about the metal atom were occupied by water molecules.

The EPR spectra of the Mn^{II} complexes without any functionalisation on the upper rim (**11**–**12**) were obtained as glasses in dimethylformamide (DMF) at 120 K. Both spectra were almost identical, showing jagged six-line spectra; the six-line spectrum in each case arising from the fact that Mn^{II} has $I = 5/2$. These spectra indicate that the coordination of Mn^{II} is very similar in each case. We believe that the manganese atom is bonded to the amine nitrogen of the azacrown ring, either NH or NH_2 depending on the calix[4]arene derivative **2** or **3**, similar to the bonding of the copper metal in the X-ray crystal structure of **4**. The remaining coordination sites around the manganese metal

are occupied by water molecules. Elemental analyses and the infrared spectra of these complexes support this hypothesis.

Ruthenium(II)/Manganese(II) Complexes

We have previously investigated the complexation of copper(I) to a pyridyl derivative of a calix[4]arene and were able to oxidise the metal centre while retaining complexation.^[9c] Retention of this bonding is important, because if energy or electron transfer occurs from one rim to the other, then a change in the oxidation state of the metal at the lower rim must happen. Thus, it is essential that the metal–ligand bonding is retained at the lower rim. To achieve a scaffold capable of holding two different metals at different coordination sites, we have functionalised both the upper and lower rim of a calix[4]arene (Scheme 2); the synthesis of **13** has been reported previously.^[9a]



Scheme 2. Reagents and conditions: (i) diethylenetriamine, MeOH, toluene, 48 h; (ii) tris(2-aminoethyl)amine, MeOH, toluene, 48 h.

The bis(bipy) diester calix[4]arene **13** was treated with 0.5 equiv. of either diethylenetriamine or tris(2-aminoethyl)amine in methanol/toluene^[24] to give the calix[4]azacrown derivatives **14** and **15**. The Ru^{II} complexes **16** and **17** were prepared by reacting **14** or **15** with 1.1 equiv. of $\text{Ru}(\text{bipy})\text{Cl}_4$ ^[32] in refluxing absolute ethanol and, on cooling, a

brown solid precipitated in each case and recrystallised from chloroform. These solids were kept in the dark during the filtering and drying stages and were stored at room temperature in the dark. All efforts to obtain ^1H NMR spectra of both **16** and **17** failed in all solvents, due to lack of solubility in the deuterated solvents. Elemental analyses for both products showed the presence of three molecules of chloroform. The $\text{Ru}^{\text{II}}/\text{Mn}^{\text{II}}$ complexes **18** and **19** were prepared by the reaction of the appropriate Ru^{II} complexes **16** or **17** with manganese(II) chloride tetrahydrate in refluxing methanol. Elemental analyses for **18** and **19** suggest the presence of only one chloride anion which would mean that the calix[4]azacrowns **16** and **17**, in each case, were acting as a unidentate ligand through loss of a proton from the pendant amine group. The remaining coordination sites about the metal atom were occupied by water molecules. Furthermore, in both cases, two molecules of chloroform were also present as solvent of crystallisation, the chloroform being present from the washing of the solid to remove any unreacted calix[4]azacrown scaffold. Interestingly, the two metal centres are not directly connected through the same aromatic ring of the calix[4]arene. This is simply due to the synthetic path chosen. The first step in the functionalisation process is the etherification reaction at the lower rim, which has a dual role; firstly, it protects two of the phenol groups on the narrow rim while conferring cone conformation on the molecule, and secondly, it directs the functionalisation of the wide rim opposite the remaining free hydroxy groups of the narrow rim. It is this second function which does not allow a direct connection between both metal centres.

The EPR spectra of the complexes **18** and **19** were obtained as glasses in DMF at 120 K. Both spectra were almost identical. Some very small peaks for Ru^{III} were observed, which was not unexpected as it was impossible to keep the sample under light-free conditions at all times during the preparation of the sample for the experiment. The very similar, jagged six-line spectra for **18** and **19** indicate that the coordination of Mn^{II} is very similar in both complexes. We believe that, in both cases, the Mn atom is bonded to one nitrogen atom from the azacrown unit and that the remaining five coordination sites of the manganese are occupied by water molecules. These results are similar to those observed by Berg et al., where they had synthesised $[\text{Ru}(\text{bipy})_3]^{2+}$ complexes covalently attached to bis(picolylamine) or tris(picolylamine) functional groups to which Mn^{II} could be attached.^[33]

The $\text{Ru}^{\text{II}}/\text{Mn}^{\text{II}}$ complexes **18** and **19** were partially oxidised to obtain the mixed valence $\text{Ru}^{\text{III}}/\text{Mn}^{\text{II}}$ complexes. The reactions were preformed using ammonium cerium(IV) nitrate as the oxidant in a 3:1 mixture of DMF and methanol, similar to that described by Ghirotti et al.^[22] Dimethylformamide was one of the two solvents in which these compounds would dissolve, the other was methyl sulfoxide. The oxidation was monitored using EPR spectroscopy. On cooling the partially oxidised sample, no decrease in the signal intensity of the six-line region of the spectra, associated with the Mn^{II} signals, was observed. There was, how-

ever, a substantial increase in the signals for a Ru^{III} species, which indicated that the oxidation had occurred only at the Ru^{II} sites. The samples were then warmed to 273 K and re-cooled to 120 K. This was to allow any energy or electron transfer to occur. On recording the spectra again, the spectra looked identical to the initial partially oxidised spectra. However, closer examination revealed that the intensity of both the Mn^{II} and Ru^{III} species had decreased by ca. 30%, indicating that either energy or electron transfer was occurring from the Mn^{II} centre to the Ru^{III} centre, with consequent oxidation of the Mn^{II} to Mn^{III} , an EPR-silent species. Importantly, this suggests that the two metals are in communication with each other, despite the fact that there is no direct pathway between them, since they are not attached to the same benzene ring. More unprecedented was that the result could be observed using the relative slow EPR spectroscopy technique, instead of having to use transient spectroscopy with nanosecond laser flash photolysis. This would indicate that the charge recombination reaction in this case is very slow, implying that the charge-separation between the metal species is close to an optimum distance.

Conclusions

We have shown that binding of copper(II) and manganese(II) to calixazacrowns can be achieved, and that the particular mode of coordination appears to be influenced by the coordination ability of the associated anion. We have also synthesised mixed metal complexes with ruthenium(II) at the upper rim of our calix[4]arene scaffold and manganese(II) at the lower rim. Furthermore, initial EPR studies of these complexes indicate that the metals are able to communicate with each other, although they are not bound to the same aromatic ring of the calix[4]arene structure. We are currently examining the amide cleavage reaction in more detail and also looking at the coordination chemistry of other transition metals with **2** and **3**, as well as carrying out transient spectroscopy on the mixed metal species in an effort to understand the communication processes being undertaken.

Experimental Section

^1H and ^{13}C NMR (δ in ppm; J in Hz) spectra were recorded with either a JEOL JNM-LA300 FT-NMR spectrometer or a Bruker Avance 300 MHz spectrometer using saturated CDCl_3 solutions with Me_4Si reference, unless indicated otherwise, with resolutions of 0.18 Hz and 0.01 ppm, respectively. Infrared spectra (cm^{-1}) were recorded as KBr discs or liquid films between KBr plates with a Nicolet Impact 410 FT-IR. All UV/Vis spectra were recorded on a Shimadzu UV-160A spectrometer. Melting point analysis was carried out using a Stewart Scientific SMP 1 melting point apparatus and are uncorrected. The EPR spectra were recorded either at room temperature or in frozen glass at 120 K using a Bruker EMX spectrometer operating at the X-band. Microanalysis was carried out at the Microanalytical Laboratory of either University College, Dublin or the National University of Ireland Cork. Standard Schlenk techniques were used throughout. Starting materials were

commercially obtained and used without further purification. The synthesis of compounds 4-*tert*-butylcalix[4]arene,^[34] 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxycarbonylmethyloxycalix[4]arene,^[9a,23] calix[4]azacrown **2**,^[35] and 5,17-di-*tert*-butyl-11,23-bis[(4'-methyl-2,2'-bipyridin-4-yl)carbonylamino]-25,27-bis(ethoxycarbonylmethoxy)calix[4]arene (**13**)^[9a] and Ru^{II}(bipy)Cl₄^[32] have been described in the literature previously.

Synthesis of Calix[4]azacrown 3: A solution of diester calix[4]arene (2.0 g, 2.5 mmol) and tris(2-aminoethyl)amine (2.26 mL, 15.1 mmol) in a mixture of methanol (25 mL) and toluene (25 mL) was stirred at room temperature for 3 d. After this time, the solution was concentrated under reduced pressure. The solid residue was suspended in methanol and filtered to give a white solid.

Calix[4]azacrown 3: Yield 1.23 g (56.4%). C₅₄H₇₄N₄O₆ (875.19): calcd. C 74.10, H 8.52, N 6.40; found C 74.25, H 8.40, N 6.43; m.p. 262–264 °C. IR (KBr): $\tilde{\nu}_{\max}$ = 3390 (NH), 1680 (amide C=O) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 8.29 (br. t, 2 H, CONHCH₂), 7.12 (s, 4 H, Ar-H), 6.70 (s, 4 H, Ar-H), 6.33 (s, 2 H, OH), 4.48 (s, 4 H, OCH₂CO), 4.18 (d, ¹J = 13.0 Hz, 4 H, Ar-CH_aH_b-Ar), 3.52 (m, 6 H, CH₂), 3.39 (d, ¹J = 13.0 Hz, 4 H, Ar-CH_aH_b-Ar), 2.95 (m, 6 H, CH₂), 1.33 (s, 18 H, *t*Bu), 0.88 (s, 18 H, *t*Bu) ppm.

General Synthesis of Copper(II) Complexes 4–10: To a solution of the calix[4]azacrown (0.5 mmol) in chloroform (5 mL) was added the appropriate copper(II) salt (0.5 mmol) in methanol (5 mL) and the resulting blue solution was heated to reflux for 2 h. On cooling, the solution was allowed to stand and, after several days, either a powder or crystals appeared, which was collected by filtration and dried.

4: Blue solid, yield 0.39 g (84%). C₁₁₂H₁₆₀CuN₆O₂₀ (1974.04): calcd. C 68.14, H 8.17, N 4.26; found C 67.78, H 8.00, N 4.43; m.p. 179–180 °C. IR (KBr): $\tilde{\nu}_{\max}$ = 3360 (NH), 1690 (amide C=O) cm⁻¹, 1578 (COO_{asym}) cm⁻¹, 1448 (COO_{sym}) cm⁻¹.

5: Green/blue solid, yield 0.42 g (88%). C₁₁₂H₁₅₄CuN₆O₁₆ (1932.01): calcd. C 69.62, H 8.03, N 5.80, found C 69.78, H 8.00, N 5.43; m.p. 179–180 °C. IR (KBr): $\tilde{\nu}_{\max}$ = 3360 (NH), 1690 (amide C=O) cm⁻¹, 1578 (COO_{asym}) cm⁻¹, 1448 (COO_{sym}) cm⁻¹.

6: Green solid, yield 0.42 g (86%). C₅₃H₇₂ClCuN₃O₁₁ (1026.15): calcd. C 62.03, H, 7.07, N 4.09; found C 61.93, H 6.98, N 4.32; m.p. 200 °C (dec.). IR (KBr): $\tilde{\nu}_{\max}$ = 3359 (NH), 1677 (amide C=O), 1109 (ClO₄) cm⁻¹, 625 (ClO₄) cm⁻¹.

7: Green solid, yield 0.41 g (78%). C₅₅H₇₇ClCuN₄O₁₁ (1069.22): calcd. C 61.78, H 7.22, N 5.24, found C 62.19, H 6.83, N 5.32; m.p. 212 °C (dec.). IR (KBr): $\tilde{\nu}_{\max}$ = 3355 (NH) cm⁻¹, 1668 (amide C=O) cm⁻¹, 1110 (ClO₄) cm⁻¹, 625 (ClO₄) cm⁻¹.

8: Green solid, yield 0.38 g (85%). C₁₀₄H₁₃₈Cl₂CuN₆O₁₂ (1798.69): calcd. C 69.45, H 7.73, N 4.67; found C 69.68, H 7.36, N 5.01; m.p. 150 °C (dec.). IR (KBr): $\tilde{\nu}_{\max}$ = 3340 (NH), 1678 (amide C=O) cm⁻¹.

9: Blue solid, yield 0.18 g (88%). C₈H₂₆Cl₂Cu₂N₆O (420.33): calcd. C 22.86, H 6.23, N 19.99; found C 22.87, H 5.84, N 19.90; m.p. 160 °C (dec.). IR (KBr): $\tilde{\nu}_{\max}$ = 3240 (NH) cm⁻¹.

10: Green solid, yield 0.24 g (80%). C₅₄H₈₄ClCuN₄O₁₁ (1064.26): calcd. C 60.94, H 7.96, N 5.26; found C 60.42, H 7.47, N 5.64; m.p. 160 °C (dec.). IR (KBr): $\tilde{\nu}_{\max}$ = 3340 (NH, OH), 1681 (C=O amide) cm⁻¹.

General Synthesis of Manganese(II) Complexes 11–12: To a solution of the calix[4]azacrown (0.5 mmol) in chloroform (5 mL) was added manganese(II) chloride (0.5 mmol) in methanol (10 mL) and the

resulting brown solution was stirred for 2 h. The solution was allowed to stand and, after several days, a brown powder precipitated, which was collected by filtration and dried.

11: Brown solid, yield 0.39 g (75%). C₅₃H₈₂ClMnN₃O₁₂ (1043.62): calcd. C 61.00, H 7.92, N 4.03; found C 61.19, H 8.15, N 4.48; m.p. 220 °C (dec.). IR (KBr): $\tilde{\nu}_{\max}$ = 3343 (NH) cm⁻¹, 1680 (amide C=O) cm⁻¹.

12: Brown solid, yield 0.40 g (76%). C₅₄H₈₃ClMnN₄O₁₁ (1054.65): calcd. C 61.50, H 7.93, N 5.31; found C 61.99, H 7.55, N 5.74; m.p. 220 °C (dec.). IR (KBr): $\tilde{\nu}_{\max}$ = 3357 (NH) cm⁻¹, 1667 (amide C=O) cm⁻¹.

Synthesis of Extended Calix[4]azacrown 14: A solution of the bis(bipy) calix[4]arene **13** (0.4 mmol) and diethylenetriamine (1.6 mmol) in a mixture of methanol (20 mL) and toluene (20 mL) was stirred at room temperature for 5 d. After this time, the solution was concentrated under reduced pressure. The solid residue was dissolved in methanol, recrystallised and filtered to give a white solid.

Calix[4]azacrown 14: Yield 0.26 g (67%). C₆₈H₇₁N₉O₈ (1142.35): calcd. C 71.50, H 6.26, N 11.04; found C 71.39, H 6.04, N 11.09; m.p. 250 °C (dec.). IR (KBr): $\tilde{\nu}_{\max}$ = 3400 (NH, OH), 1671 (amide C=O) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 8.89 (d, ¹J = 7.2 Hz, 2 H, 6-H), 8.78 (s, 2 H, 3-H), 8.59 (d, ¹J = 7.2 Hz, 2 H, 6'-H), 8.35 (s, 2 H, 3'-H), 8.20 (s, 2 H, OH), 8.05 (br. t, 2 H, CONHCH₂), 7.94 (d, ¹J = 7.2 Hz, 2 H, 5-H), 7.52 (s, 4 H, Ar-H), 7.23 (d, ¹J = 7.2 Hz, 2 H, 5'-H), 6.79 (s, 4 H, Ar-H), 6.28 (s, 1 H, NH), 4.47 (s, 4 H, OCH₂CO), 4.21 (d, ¹J = 14.0 Hz, 4 H, Ar-CH_aH_b-Ar), 3.55 (m, 4 H, CH₂), 3.47 (d, ¹J = 14.0 Hz, 4 H, Ar-CH_aH_b-Ar), 2.94 (m, 4 H, CH₂), 2.49 (s, 6 H, CH₃), 0.96 (s, 18 H, *t*Bu) ppm.

Synthesis of Extended Calix[4]azacrown 15: A solution of **13** (0.5 mmol) and diethylenetriamine (2.0 mmol) in a mixture of methanol (15 mL) and toluene (15 mL) was stirred at room temperature for 5 d. After this time, the solution was concentrated under reduced pressure. The solid residue was dissolved in methanol, recrystallised and filtered to give a white solid.

Calix[4]azacrown 15: Yield 0.21 g (44%); m.p. 200 °C (dec.). C₇₀H₇₆N₁₀O₈ (1185.42): calcd. C 70.92, H 6.46, N 11.82; found C 71.39, H 6.04, N 11.59. IR (KBr): $\tilde{\nu}_{\max}$ = 3360 (NH, OH), 1666 (amide C=O) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 8.85 (d, ¹J = 7.2 Hz, 2 H, 6-H), 8.80 (s, 2 H, 3-H), 8.55 (d, ¹J = 7.2 Hz, 2 H, 6'-H), 8.31 (s, 2 H, 3'-H), 8.13 (br. t, 2 H, CONHCH₂), 7.92 (d, ¹J = 7.2 Hz, 2 H, 5-H), 7.53 (s, 4 H, Ar-H), 7.30 (s, 2 H, OH), 7.18 (d, ¹J = 7.2 Hz, 2 H, 5'-H), 6.84 (s, 4 H, Ar-H), 4.52 (s, 4 H, OCH₂CO), 4.18 (d, ¹J = 14.0 Hz, 4 H, Ar-CH_aH_b-Ar), 3.53 (m, 6 H, CH₂), 3.46 (d, ¹J = 14.0 Hz, 4 H, Ar-CH_aH_b-Ar), 2.76 (m, 6 H, CH₂), 2.50 (s, 6 H, CH₃), 0.97 (s, 18 H, *t*Bu) ppm.

General Synthesis of Ruthenium(II) Complexes 16 and 17: To a solution of the calix[4]azacrown **14** or **15** (0.185 mmol) in absolute ethanol (20 mL) was added Ru^{II}(bipy)Cl₄ (0.37 mmol) in absolute ethanol (20 mL) and the resulting brown solution was heated to reflux for 3 h. On cooling, a brown precipitate resulted in each case. The precipitate was collected by filtration, dried and stored in the dark.

16: Red/brown solid, yield 0.32 g (83%). C₉₁H₉₀Cl₁₃N₁₃O₈Ru₂ (2156.8): calcd. C 50.68, H 4.21, N 8.44; found C 50.48, H 4.00, N 8.73; m.p. > 300 °C. IR (KBr): $\tilde{\nu}_{\max}$ = 3385 (NH, OH), 1663 (amide C=O) cm⁻¹.

17: Red/brown solid, yield 0.30 g (76%). C₉₃H₉₅Cl₁₃N₁₄O₈Ru₂ (2180.8): calcd. C 50.78, H 4.32, N 8.91; found C 50.48, H 4.01, N 8.43; m.p. > 300 °C. IR (KBr): $\tilde{\nu}_{\max}$ = 3385 (NH, OH), 1661 (amide C=O) cm⁻¹.

General Synthesis of Ruthenium(II)/Manganese(II) Complexes 18 and 19: To a solution of the ruthenium(II) calix[4]azacrown **16** or **17** (0.11 mmol) in methanol (10 mL) was added manganese(II) chloride tetrahydrate (0.11 mmol) in methanol (10 mL) and the resulting brown solution was stirred at room temperature for 2 h. During the course of the reaction, a dark brown solid precipitated in each case. The precipitate was collected by filtration, washed with CHCl_3 , dried and stored in the dark.

18: Brown solid, yield (62%). $\text{C}_{90}\text{H}_{98}\text{Cl}_{11}\text{MnN}_{13}\text{O}_{13}\text{Ru}_2$; calcd. C 48.76, H 4.46, N 8.21; found C 48.21, H 4.39, N 8.72; m.p. > 300 °C; IR (KBr): $\tilde{\nu}_{\text{max}}$ = 3374 (NH, OH), 1662 (amide C=O) cm^{-1} .

19: Brown solid, yield 0.14 g (57%). $\text{C}_{92}\text{H}_{103}\text{Cl}_{11}\text{MnN}_{14}\text{O}_{13}\text{Ru}_2$ (2216.9); calcd. C 48.89, H 4.59, N 8.68; found C 49.19, H 4.63, N 9.17; m.p. > 300 °C. IR (KBr): $\tilde{\nu}_{\text{max}}$ = 3378 (NH, OH), 1660 (amide C=O) cm^{-1} .

X-ray Crystallography: Crystal data for **4**: $\text{C}_{112}\text{H}_{160}\text{CuN}_6\text{O}_{20}$, M = 1974.00, monoclinic, a = 12.2259(8) Å, b = 24.0471(17) Å, c = 19.5251(13) Å, β = 101.262(3)°, U = 5629.8(7) Å³, T = 180(2) K, space group $P2_1/n$, Z = 2, $\mu(\text{Mo}-K_\alpha)$ = 0.261 mm^{-1} . 66796 reflections measured, 9751 unique (R_{int} = 0.0913) which were used in all calculations. The final R_1 = 0.0824, wR_2 (all data) = 0.2874, goodness-of-fit on F^2 = 1.09. Data were collected at 180(2) K with a Bruker Nonius X8 APEX II diffractometer,^[36] and a multi-scan correction was applied.^[37] The structures were refined against F^2 using all data.^[38] Hydrogen atoms were placed at calculated positions and refined using a riding model.

CCDC-616020 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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