Caesium ion sequestration by a fluoro-metallocrown [16]-MC-8†

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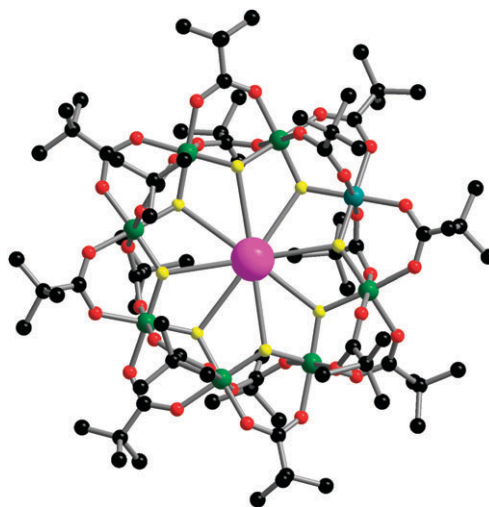
A fluoro-metallocrown selectively binds caesium, extracting it from aqueous solutions into an organic layer; the binding of Cs is monitored by ^{1}H-NMR of the paramagnetic complexes.

The first metallocrown was reported by Lah and Pecoraro in 1989.[1] The mixed valent complex has the formula [Mn(II){Mn(III)(salicylhydroximate)}$_4$(acetate)$_2$(DMF)$_6$] and is classified as a 12-metallocrown-4, ([12]-MC-4), containing the repeating motif –O–Mn(III)–N– four times, binding to a central Mn(II). The range of metallocrowns is expansive,[2] with promising leads in ion recognition,[3] catalysis,[4] as single-molecule magnets,[5] as MRI contrast agents[6] and as anti-bacterial agents.[7] Fluoro-metallocrowns have been reported to bind small cations by Jones et al.,[8,9] though they were unable to ascertain the extent to which the guests were bound in solution. The homometallic ring [CrF(tBuCO$_2$)$_2$]$_8$ has also been discussed as a possible fluoro-crown.[10]

Heterometallic [Cr$_7$MF$_8$(tBuCO$_2$)$_{16}$]$^-$ (M = Ni, Co) wheels have been shown to host a wide variety of primary and secondary alkyl ammonium guests in the solid state.[11] ^{1}H-NMR studies show that guest ammonium ions also remain inside the ring cavity in solution.[12] Their cation binding capacity is no doubt due to the charge imbalance created by replacing the trivalent chromium(III) with a divalent metal. The removal of primary and cyclic alkyl ammonium species with concomitant replacement by hydroxonium or sodium ion upon column chromatography has also been demonstrated.[12]

Treatment of [(H$_3$N^{n}Pr)Cr$_7$CoF$_8$(tBuCO$_2$)$_{16}$], **1**,[12] with excess caesium pivalate followed by recrystallisation from diethyl ether/acetonitrile gives [Cs⊂Cr$_7$CoF$_8$(tBuCO$_2$)$_{16}$]·0.5MeCN, **2**. Compound **2** can also be made directly from reaction of hydrated chromium fluoride with pivalic acid in the presence of cobalt pivalate and caesium pivalate.‡ X-Ray crystallographic studies show the caesium ion centrally bound to all eight fluorides and co-planar with the heterometals of the wheel (Fig. 1). The data also clearly show that, in the solid state, four axial pivalate groups on one side of the wheel lean towards the central ion, four on the other side lean away slightly. On this exposed side the caesium is bound to solvate acetonitrile, however, this conformation is not evident in solution.

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Fig. 1 The structure of **2** (omitting MeCN) in the crystal. Colours: Cs, pink; Cr, green; Co, teal; O, red; F, yellow; C, black; H, omitted.

Most paramagnetic samples suffer from greatly broadened resonances as a consequence of the rapid nuclear relaxation of the metal nuclei. Octahedral high-spin Co(II) is unusual in exhibiting very slow nuclear relaxation[13] and consequently the net effect of the {Cr$_7$Co} system is such that spectral features are sharp enough to impart real chemical insight.[12]

^{1}H-NMR spectroscopy for this new caesium-centred wheel reveals eight proton environments for the sixteen pivalates (Fig. 2b), as a result of the C_2 symmetry axis which extends from the cobalt ion via the centre of the caesium and through to the distal chromium. This evidence suggests either a conformation where all eight axial pivalates are perpendicular
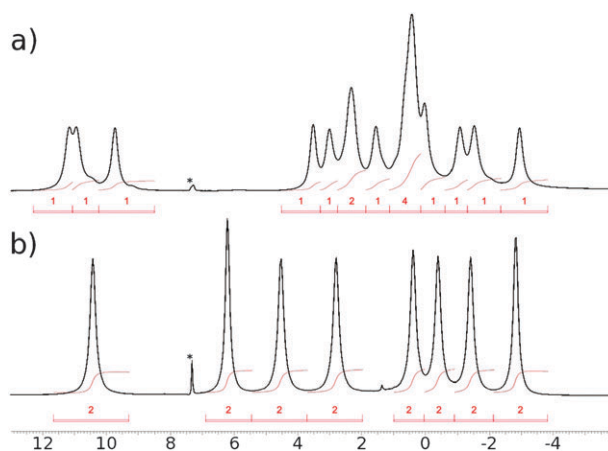
Fig. 2 ^{1}H-NMR of (a) **1** and (b) **2** at 300 MHz in CDCl$_3$. * Indicates protio-solvent impurity.
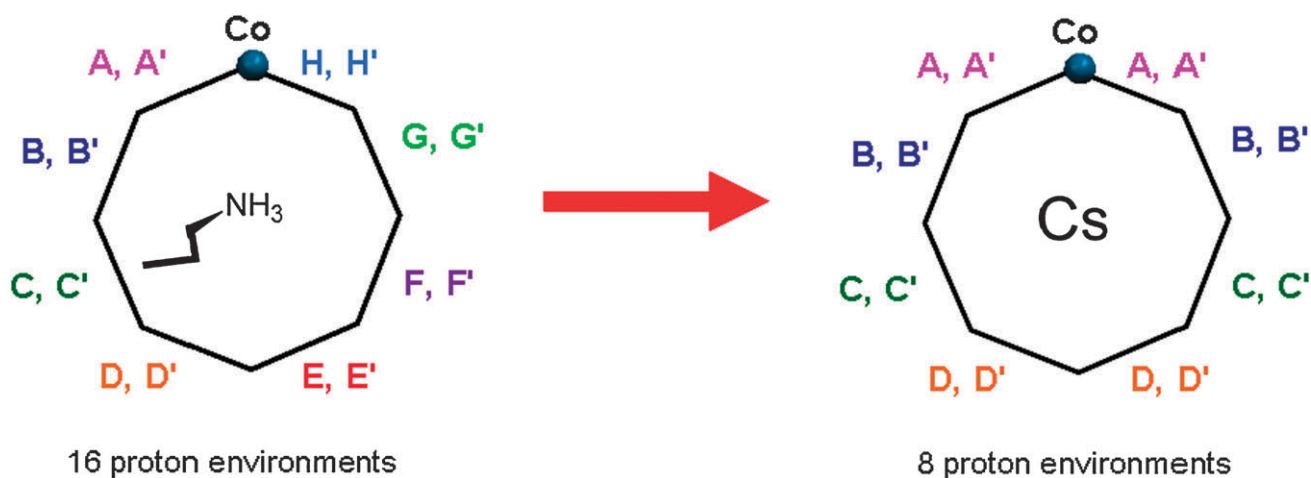
Fig. 3 Schematic showing guest exchange and accompanying increase in symmetry.

to the plane of the wheel or each set of pivalates flips between leaning towards and away from the caesium ion (as in the crystal structure) at a rate that is faster than the NMR timescale (at 300 MHz and RT).

An additional peak at -10 ppm can be attributed to fluxionally coordinating adventitious water, as has been reported previously.[12]

Treatment of $[(H_3N^nPr)Cr_7CoF_8(tBuCO_2)_{16}]$ with rubidium pivalate leads to similar results in both X-ray crystal structure, solution state NMR and electrospray mass spectrometry (ES-MS). The major difference of note is that compound **2** crystallises in the monoclinic space group, $C2/c$; whereas $[Rb \subset Cr_7CoF_8(tBuCO_2)_{16}]$ **3** crystallises in the tetragonal space group $P4$. The latter space group is found for smaller dialkylammonium cation (*e.g.* $Me_2NH_2^+$) centred rings.[11]

Time-resolved ^1H-NMR can be used to follow the extent of exchange between the guest species. The primary ammonium template in **1** lowers the symmetry of the ring from that found in **2** (Fig. 3). In principle within $[(H_3N^nPr)Cr_7CoF_8(tBuCO_2)_{16}]$, **1**, there are sixteen proton environments on the pivalate groups; in the measured NMR spectrum some of the resonances coincidentally overlap to give just twelve peaks (Fig. 2a). Further peaks are observed downfield corresponding to the alkyl ammonium. The $-NH_3$ gives a very broad peak and experiences the greatest chemical shift (*circa* -100 ppm). Caesium pivalate was added to **1** (dissolved in deuterated solvent) and spectra recorded every 2.5 min. The symmetry change on replacing the alkyl ammonium guest with caesium changes the number of proton environments from sixteen to eight and at $T > 5$ minutes only peaks of **2** are present. An additional peak is present in the reaction solution due to free pivalate from the caesium source. Peaks due to paramagnetically shifted protons from the ammonium alkyl guest also disappear within 10 min from the start of the reaction (Fig. 4). The result indicates a definite preference for the caesium cation and there is no indication of an intermediate species.

X-Ray crystal structures for $[Cs \subset Cr_7MF_8(tBuCO_2)_{16}]$ (M = Ni, Cu, Fe, Mn, Zn) have also been obtained and are isostructural with that of the cobalt analogue. We can also make analogous metallocrowns with carboxylates other than pivalate (*tert*-butylacetate, methacrylate, *o*-toluate,
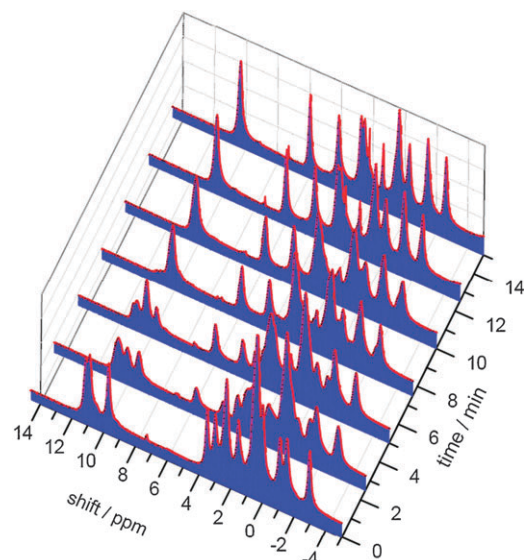

Fig. 4 Pivalate region of the NMR spectra tracing the extent of guest exchange in solution.

diethylacetate and 2,2-dimethylbutyrate). These metallocrowns all show preference for binding to caesium.

Preliminary experiments also suggest that **1** will extract $Cs^+_{(aq)}$ from water into dichloromethane. In a typical experiment, **1** (2.13 mmol) was dissolved in CH_2Cl_2 (25 mL), and CsX (0.44 mmol) (X = Cl^-, NO_3^-) dissolved in H_2O (10 mL) was added as a separate layer. The extraction was monitored by electrospray mass spectrometry (ES-MS); solutions of **2** have the most abundant peak for $[2 + Na]^+$ (Fig. 5). Mass spectral analysis of the organic layer, after extraction was carried out for 18 hours, showed the major peak was again $[2 + Na]^+$ and no peaks that could be assigned to **1**. The precise caesium salt seems unimportant for the phase transfer. Caesium is also extracted preferentially from the water layer in the presence of sodium, potassium and rubidium ions.

Sequestration of long lived radioactive caesium isotopes from high-level radioactive waste following reprocessing of nuclear fuels has long remained an issue for separation scientists. As well as precipitation[14] and ion exchange,[15]
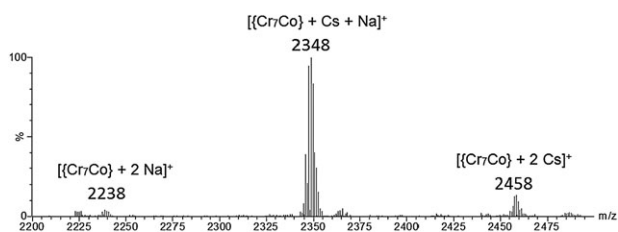
Fig. 5 The ES-MS of **2** run in MeOH.

host-assisted solvent extraction offers viable means of removal. Suitable proposed hosts including complex calixarenes,[16] hydroborate clusters[17] and metallaboranes[18] all have the common drawback of non-trivial fabrication. To this end we suggest that our fluoro-metallocrown represents a novel complexant for such a purpose with the considerable benefit of facile one pot synthesis from commercially available starting materials. As such, future work will quantify our strength of caesium binding, especially from aqueous media.

Notes and references

‡ Synthesis of **2**: **1** (564 mg, 250 mmol) and Cs(*t*BuCO$_2$) (117 mg, 500 mmol) was dissolved in a solution of Et$_2$O (40 ml), DMSO (350 mg) and *t*BuCO$_2$H (350 mg). Following stirring for 2 h the solution was filtered and diluted with MeCN (40 ml). Slow evaporation of the Et$_2$O filtrate yields large green crystals (suitable for X-ray crystallography). These were washed in MeCN and air dried to yield **2** (558 mg, 240 mmol, 96.0%). Microanalysis for **2** (C$_{80}$H$_{144}$CoCr$_7$CsF$_8$O$_{32}$) calcd: C, 41.31; H, 6.24; N, 0.0; Cr, 15.65; Co, 2.53%. Found: C, 41.03; H, 6.27; N, 0.0; Cr, 15.24; Co 2.52%. ES-MS +ve (*m/z*): 2348 [M + Na]$^+$. Synthesis of **3** as for **2**, replacing Cs(*t*BuCO$_2$) with Rb(*t*BuCO$_2$) gave green crystals of **3** (525 mg, 230 mmol, 92.0%). Microanalysis for **3** (C$_{80}$H$_{144}$Co$_1$Cr$_7$F$_8$O$_{32}$Rb) calcd: C, 42.17; H, 6.37; N, 0.0; Cr, 15.98; Co, 2.59%. Found: C, 41.37; H, 6.43; N, 0.0; Cr, 15.63; Co 2.43%. ES-MS +ve (*m/z*): 2301 [M + Na]$^+$. Crystal data for **2**: C$_{81}$H$_{145.5}$CoCr$_7$CsF$_8$N$_{0.5}$O$_{32}$, M = 2346.32, monoclinic, space group *C*2/*c*, *a* = 45.069(2), *b* = 16.3923(3), *c* = 34.8600(19) Å, β = 114.009(5)°, V = 23526.1(18) Å^3, T = 100(2) K, Z = 8, 45431

reflections measured, 23 954 independent reflections (R_{int} = 0.0480). The final *R*-values were: R_1 = 0.0812, wR_2 = 0.2288 (*I* > 2σ(*I*)); R_1 = 0.1401, wR_2 = 0.2559 (all data). Crystal data for **3**: C$_8$H$_{144}$CoCr$_7$F$_8$O$_{32}$Rb, M = 2278.35, tetragonal, space group *P*4, *a* = *b* = 19.8632(3), *c* = 16.1639(7) Å, V = 6377.4(3) Å^3, T = 100(2) K, Z = 2, 36 433 reflections measured, 11 626 independent reflections (R_{int} = 0.0881). The final *R*-values were: R_1 = 0.1058, wR_2 = 0.2757 (*I* > 2σ(*I*)); R_1 = 0.1315, wR_2 = 0.2914 (all data).

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