



# Building a molecular PrussianBlueAnalogue $\text{Fe}^{\text{II}}/\text{Co}^{\text{III}}$ cube around a $\text{Cs}^+$ ion; a preferred, tight, robust, water soluble, and kinetically inert encapsulator

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## ABSTRACT

The preparation of a caesium inclusion complex of the molecular cube  $[\{\text{Co}^{\text{III}}(\text{Me}_3\text{-tacn})\}_4\{\text{Fe}^{\text{II}}(\text{CN})_6\}_4]^{4-}$ , a mixed valent molecular Prussian Blue Analogue bearing bridging cyanido ligands, has been achieved by following a redox-triggered self-assembly process in aqueous solution. The assembly has been shown to be Cs-preferred as, even in the presence of  $\text{Na}^+$  in solution, no Na-encapsulated have been found in the assembled product when  $\text{Cs}^+$  is present in the reaction medium. Even so, the tightness of the system produces large amounts of a void cubic structure whenever not large excesses of  $\text{Cs}^+$  are present. The species is robust, extremely soluble in aqueous media, pH-stable in the 1–13 range, and redox inactive between  $-400$  and  $600$  mV. The molecular species has been characterised by UV-vis, ICP, multinuclear NMR spectroscopy, and electrochemistry. As expected from previous data reported, the complex in aqueous solution is totally inert to cation exchange, the leaching of the encapsulated  $\text{Cs}^+$  being hampered by the small size of the cube portal.

## 1. Introduction

Intensely coloured transition metal mixed valence complexes such as Prussian Blue have attracted the attention for centuries; the general use of Prussian Blue as a resistant and fairly innocuous inorganic colorant cannot be overstated. Molecular Prussian Blue Analogues (PBAs) have been used academically for the establishment of fundamental mixed valent classifications related to electronic coupling between the metal centres and the symmetry-allowed inner-sphere optical electron transfer occurring between them [1–8]. Recently, the use of this type of complexes in the development of photomagnetic switching materials has also been developed [9–13], and PBAs are also known to act as hosts for cationic guests, which has led to various applications [11,14–21]. A very interesting combination of both features occurring on molecular cubic structures containing alkali metals,

that are soluble and stable only in some organic solvents, has been recently published [22]. The use and applicability of PBAs in medicinal chemistry has also been recently reviewed [23].

The synthesis of PBAs in a controlled and reproducible manner is vital for any future application, but most of these species are isolated as crystalline insoluble polymeric compounds with well-defined structures, based on XRD data. The alternative preparative procedures involving pre-designed self-assembly aim to avoid such difficulties, a field in which we have been involved for the study of the self-assembly and reactivity of polynuclear tridimensional molecular structures for some time [24–28]. A concerted redox-triggered ligand substitution approach (Scheme 1) has led to the family of complexes with iron hexacyanido moieties indicated in Chart 1. In these, cyanido ligands bridge the metal centres while the remaining coordination sites are occupied by macrocyclic tri-, tetra- or pentaamine ( $\text{N}_3$ ,  $\text{N}_4$  or  $\text{N}_5$ ) ligands [29–35]. These

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Co/Fe molecular PBAs have remarkable thermal and pH stability, as well as reversible oxidation redox reactivity [34,36–39]. The assembly chemistry shown for these complexes has been successfully applied to other substitutionally inert metals such as Cr<sup>III</sup> or Rh<sup>III</sup> [30,40–42].

In this report we further focus on the inclusion properties of the molecular cubes indicated in Chart 1 (N<sub>3</sub> = 1,4,7-trimethyl-1,4,7-triazacyclononane, Me<sub>3</sub>-tacn) [35,43]. In our previous report we have indicated that the assembly of the cubic structures occurs **ON** the environment of the alkaline cation present in the reaction medium, and the exchange between different alkali cations is feasible. This process has been found to be energetically driven by the solvation/de-solvation of the different cations on exiting/entering (aquation/anation) the cubic cage. Even so, the XRD-determined and DFT-calculated structures indicated that, due to the portal size of the structure, caesium cations cannot be encapsulated by an exchange process from solution; recent examples have been reported where such a movement through the portal is possible only if a larger size of the encapsulating cubic structure occurs [44]. Studies that involve changes in the solvation and number of water molecules inside the cages have also been reported recently in view of the robustness of the encapsulation [45].

With these factors in mind, we have now explored the assembly of the cubic unit, indicated in Chart 1, around a caesium ion, aiming to the formation of a ‘jailed’ caesium cation in solution by a robust, soluble, pH- and redox-resistant, and highly coloured molecular mixed-valence cubic cage.

## 2. Results and discussion

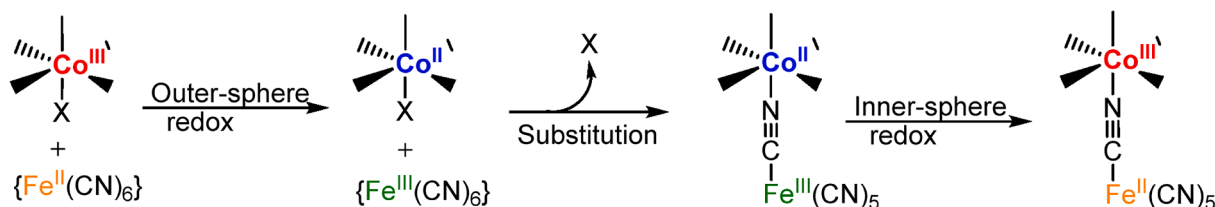
The caesium salt of the  $\{[Co^{III}(Me_3-tacn)]_4[Fe^{II}(CN)_6]_4\}^{4-}$  mixed valence molecular cube has been prepared using the well-developed mechanistically directed self-assembly process (see Scheme 1) described in previous literature reports for the structures indicated in Chart 1 [29,31–35,39,41,43,46,47]. The preparation of the complex has been conducted by the reaction of  $[Co^{III}(Me_3-tacn)Cl_3]$  with  $Na_4[Fe^{II}(CN)_6]$  in aqueous 2 M CsCl solution ( $[Cs^+] > 100 \times [Na^+]$ , see Experimental) at 50 °C overnight. The final self-assembly process from the  $\{Co^{III}-NC-Fe^{II}\}$  edge units is clearly evidenced by the absence of measurable amounts of any  $\{(Co^{III}-NC)_2-Fe^{II}\}$  or  $\{Co^{III}(-NC-Fe^{II})_2\}$  species in solution, even if large excesses of cobalt or iron building blocks are used [35,48].

The procedure for the obtention of the  $\{[Cs^+] \subset [Co^{III}(Me_3-tacn)]_4[Fe^{II}(CN)_6]_4\}^{4-}$  species parallels that used for the reported preparation of its lithium, sodium or potassium inclusion salts [35]. After Sephadex G-25 chromatographic workup (which produces an initial very dark band of an undefined polymeric material that accounts for ca. a 50 % of the starting cobalt material), a well-defined purple band is obtained that, once taken to dryness, exhibits a <sup>1</sup>H NMR spectrum with the neat signals of the C<sub>3v</sub>-symmetric  $\{Co^{III}(Me_3-tacn)\}$  moiety (Fig. 1a). The <sup>13</sup>C NMR spectrum of the same sample is also revealing (Fig. 1b), showing the presence of the aliphatic carbon signals *plus* the resonances in the cyanide region corresponding to the cubic structure. After repetitive desalting of the sample on a Sephadex G-25 column, the <sup>133</sup>Cs NMR spectrum of the compound was also measured at ca. zero ionic strength (Fig. 2a); a definitive signal of encapsulated caesium nuclei was observed at 59 ppm, apart from that of free Cs<sup>+</sup> at 7 ppm. The ICP

analyses of the sample produced a Fe:Co:Cs ratio of 0.95:1.0:1.0, which confirms the presence of  $Cs_4\{[Co^{III}(Me_3-tacn)]_4[Fe^{II}(CN)_6]_4\}$  salt in solution. In order to insure the expected inertness of the encapsulated cation (given the exchange data available) [43], the compound was loaded onto a Sephadex DEAE A-25 anion exchange column and thoroughly washed with water to eliminate all the free (non-encapsulated) cations in solution. Elution with 0.15 M NaCl produced a single purple band that, after being taken to dryness, shows a <sup>133</sup>Cs NMR signal that corresponds to the encapsulated caesium at a very high ionic strength (saturated aqueous NaCl) (Fig. 2b, top) at 41.5 ppm. Addition of a small amount of CsCl to the solution effectively shows the appearance of a new signal in the spectrum that corroborates the presence of free caesium cation in solution (Fig. 2b, bottom).

It is thus clear that the  $\{[Cs^+] \subset [Co^{III}(Me_3-tacn)]_4[Fe^{II}(CN)_6]_4\}^{4-}$  species is very robust and that on Sephadex DEAE A-25 absorption no exchange of the caesium ion is observed, even by the flooding sodium cations, as has been observed to occur for other alkali cations [43]. The UV–vis spectrum of the complex is collected in Fig. 3a, together with those of the already described *void* and potassium-containing cubic structures; the spectrum shows the intense MMCT (Fe<sup>II</sup> → Co<sup>III</sup>) band at ca. 525 nm, *plus* those associated to the d-d transitions of the  $\{Co^{III}(N)_6\}$  (shoulder at ca. 425) and  $\{Fe^{II}(CN)_6\}$  (320 nm) units [43]. The cyclic voltammogram of the species has also been recorded in water (Fig. 3b). The Figure shows the presence of the expected four Fe<sup>III</sup>/Fe<sup>II</sup> fully reversible signals, observed for species with spherical cationic units inside the molecular PBA cubic cage, at potentials that are the same within experimental error than those obtained for encapsulated potassium or rubidium and *void* cubic structures.

It should be stated that there the results indicate a clear preferred assembly of the cubic structure around the Cs<sup>+</sup> ions, as its encapsulation occurs despite the presence in the medium of sodium cations from the Na<sub>4</sub>[Fe(CN)<sub>6</sub>] starting material. In fact, the amount of sodium cations derived from this salt has been found enough to produce the exclusive formation of the sodium encapsulated  $\{[Na-OH_2]^+ \subset [Co^{III}(Me_3-tacn)]_4[Fe^{II}(CN)_6]_4\}^{4-}$  species already described [35,43]. Consequently, the same preparative procedure described above was conducted in a 0.25 M CsCl ( $[Cs^+] \approx 5 \times [Na^+]$ ) aqueous medium. All the preparative observations and chromatographic behaviour were found equivalent to those described for the procedure carried out at 2 M CsCl, except that the amount of undefined polymer exceeded the 60–70 % of the cobalt starting material. The 3.87 ppm signal, indicative of the presence of encapsulated  $\{Na-OH_2\}^+$  units [35,43], was also not observed in the <sup>1</sup>H NMR spectrum of the sample, thus indicating that no assembly has been conducted on the sodium cations present in solution. Surprisingly, though, concentration of the solution to a small volume produced the precipitation of a dark purple solid that was not evident in the previous preparation procedures in 2 M CsCl solution of the  $\{[Cs^+] \subset [Co^{III}(Me_3-tacn)]_4[Fe^{II}(CN)_6]_4\}^{4-}$  species. The same sort of behaviour has been typically observed in the assembly around Li<sup>+</sup> cations, where a *void* structure had been detected [43]; showing a 4- charge instead of the 3- resultant from alkali cation encapsulation. Effectively, on Sephadex DEAE A-25 adsorption, a precipitation of the sample occurs on elution with a 0.15 M NaCl solution. Repetitive washing of the column produces a purple solution that, when taken to dryness, and <sup>133</sup>Cs NMR monitored, shows no indication of encapsulated caesium cations.



Scheme 1. .

Furthermore,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra show the expected signals of the  $\text{C}_{3v}$  cubic structure, but no signal of any encapsulated  $\{\text{Na-OH}_2\}^+$  ( $^1\text{H}$  NMR signal at 3.87 ppm, see above) was observed. The rather distinct solubility behaviour, typical for the sodium and lithium salts of the *void* structure, has been already described [43].

In view of this data, DFT calculations were conducted to ascertain the feasibility of *void* and caesium-containing cubic structures. Both structures could be successfully computed, inclusion of a caesium cation within the *void* cubic species produces only subtle changes in its computed structural features (Fig. 4, supporting Information). For instance, upon  $\text{Cs}^+$  encapsulation the average  $\{(\text{Co}^{\text{III}})_2(\text{-NC-Fe}^{\text{II}})_2\}$  portal width increases from 4.91 to 4.94 Å, the average Co-Co distance increases from 6.99 to 7.10 Å, and the average Fe-Fe distance slightly decreases from 6.90 to 6.86 Å. These data indicates that the self-assembled cage in the presence of  $\text{Cs}^+$  is not seriously disturbed with respect to that of the *void* structure. Nevertheless, energetically, the encapsulation of the caesium cation into the heterometallic cube is favoured, by a difference in energy of  $-25.5 \text{ kcal mol}^{-1}$ . The equivalent energy gain for the smaller alkaline cationic units having a XRD structure determined, i.e.  $\{\text{Li-OH}_2\}^+$  and  $\{\text{Na-OH}_2\}^+$ , has been computed as 12.7 and 16.9  $\text{kcal mol}^{-1}$ , respectively, suggesting a preferred encapsulation on the surface of the  $\text{Cs}^+$  ion even in the presence of  $\text{Na}^+$  cations, as experimentally found. Furthermore, once formed the portal of the cube does not allow the caesium cation to move in and out of the structure due to its larger size (181 pm) when compared to lithium (90 pm) and sodium (116 pm), cations that have been found to bleach out of the cage, probably because their higher solvation energies [43].

Given the large size of the cubic cavity of the structure in Fig. 4a, the computed stability of this empty *void* structure has been compared with those containing water molecules within the cavity. Fig. 5 shows the cubic structures encapsulating one, two and three water molecules. While the structure with a single water molecule in the cavity is favoured by 8.8  $\text{kcal mol}^{-1}$ , the incorporation of more than one water molecule produces a dramatic deformation of the structure due to the strong hydrogen bonding between the guest water molecules, which is maintained within the cavity. When two water molecules are set within the cage, the cube shrinks due to the interaction of the outer hydrogen atoms with the bridging cyanide groups, and the energy increases by 13.8  $\text{kcal mol}^{-1}$  from the empty structure. If three water molecules are incorporated (in the shape of a hexagonal trimer ring), the cubic structure is forced to expand in order to accommodate the guests and the energy increases by 36.0  $\text{kcal mol}^{-1}$ . Therefore, despite the size of the

cavity, the calculations seem to indicate that the *void* structure is not empty and only accommodates a single water molecule.

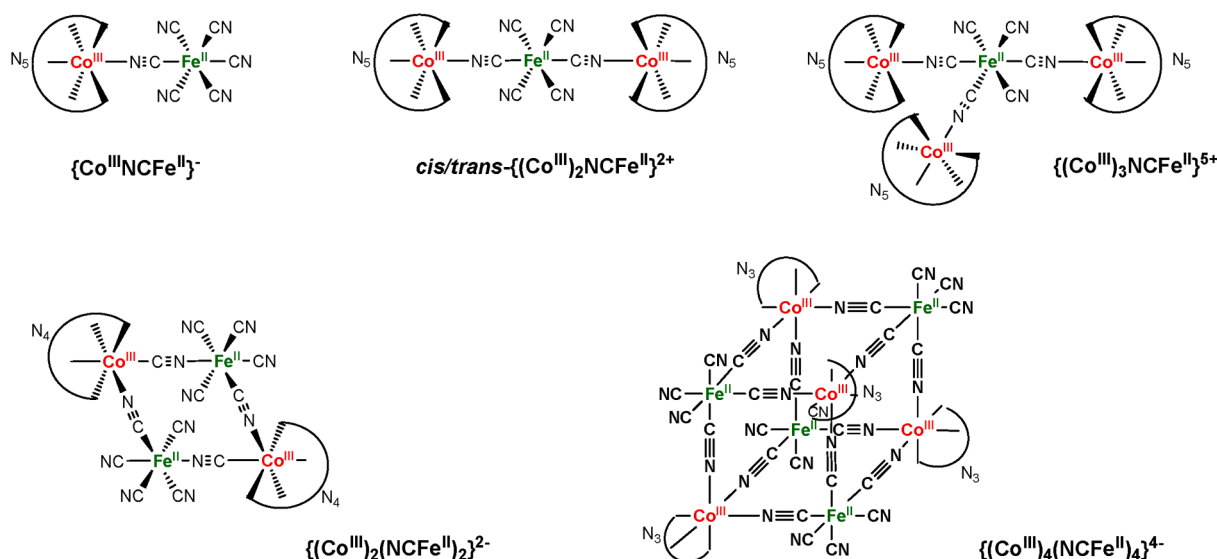
### 3. Conclusions

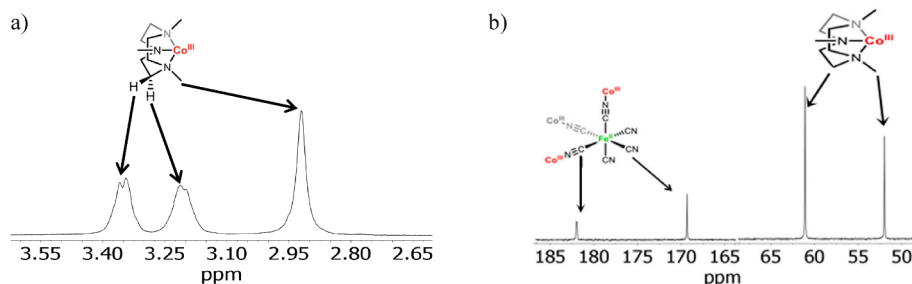
As already reported, the redox-triggered assembly reaction of molecular cubic mixed-valence cyanide bridged  $\text{Co}^{\text{III}}/\text{Fe}^{\text{II}}$  anionic compounds  $\{[\text{Co}^{\text{III}}(\text{Me}_3\text{-tacn})_4\{\text{Fe}^{\text{II}}(\text{CN})_6\}_4\}^{4-}$  (molecular PBAs) can be easily achieved. Although the overall process had been proved to encapsulate and exchange alkaline counter cations present in the reaction medium, the size of caesium does not allow for its entry or exit from the cubic cage; DFT calculations confirm this fact. The alternative assembly of the cage around the  $\text{Cs}^+$  cation has been found to be highly effective and preferred producing a  $\{\text{Cs} \subset [(\text{Co}^{\text{III}}(\text{Me}_3\text{-tacn})_4\{\text{Fe}^{\text{II}}(\text{CN})_6\}_4)]^{4-}$  cubic species which is extremely inert to caesium leach to solution, and it is also resistant to wide pH and redox ranges. Interestingly, when the equivalents of  $\text{Cs}^+$  present in the assembly reaction are less than 10-fold, the caesium encapsulation process, although still preferred, is less efficient, and even a *void* structure is obtained. DFT calculations confirm that this structure is feasible with a single water inside, which is held up by strong hydrogen bonds with the bridging cyanide groups. The assembly of the *void* or caesium-containing structures occurs despite the presence of only a 5-fold excess of caesium cations in the reaction medium with respect to sodium cations, which indicates that the outer-sphere interaction on assembly of the building block is preferred with the larger poorly solvated cation.

### 4. Experimental

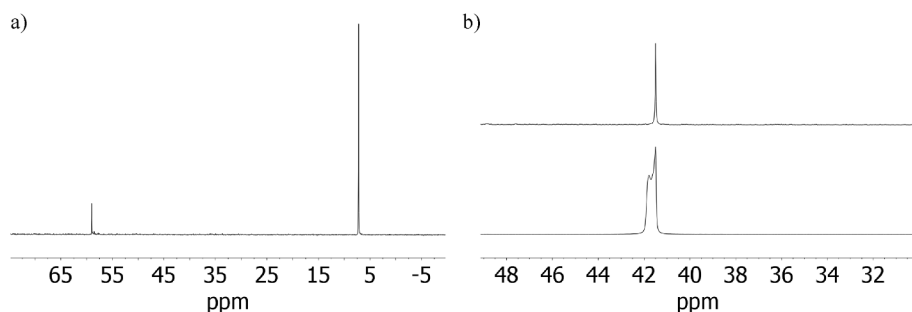
#### 4.1. Physical methods

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker-400Q spectrometer at 25 °C at the Unitat de RMN d'Alt Camp de la Universitat de Barcelona,  $^{133}\text{Cs}$  NMR spectra were recorded on a Bruker-500 instrument. ICP-OES and ICP-MAS was carried out at the Centres Científics i Tecnològics (Universitat de Barcelona) on a Perkin Elmer Optima instrument. UV-vis spectra were recorded on HP5483 or Cary50 instruments. IR spectra were recorded on a Thermo Scientific Nicolet iS5 FT-IR instrument using an ATR system. Electrochemistry experiments were carried out at 25 °C and at 100  $\text{mV s}^{-1}$ , with a BioLogic SP-150 instrument. A glassy carbon working electrode, a Ag/AgCl (saturated KCl) reference electrode and platinum wire counter electrode were used

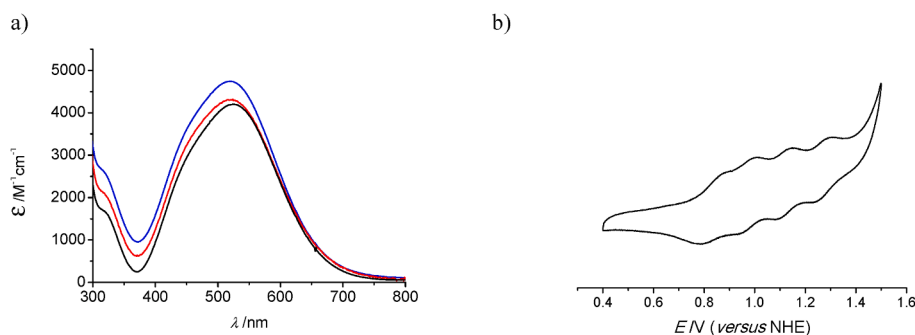




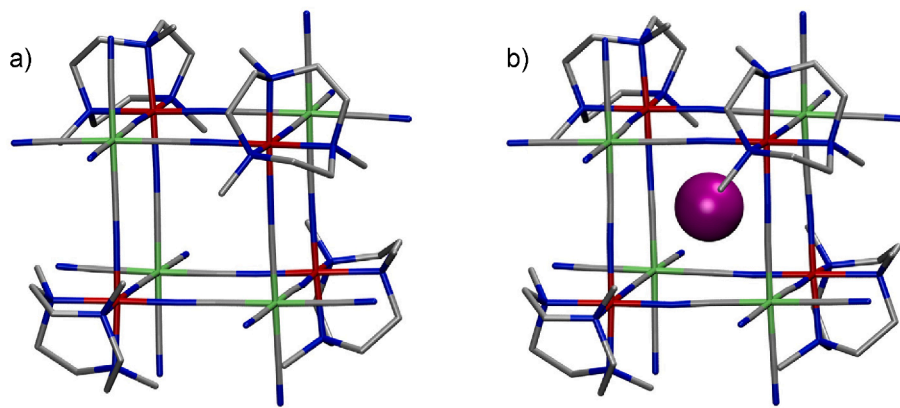
**Fig. 1.** a)  $^1\text{H}$  NMR spectrum of the Sephadex G-25 purple eluate obtained from the crude preparation mixture of the caesium salt of the  $[\{\text{Co}^{\text{III}}(\text{Me}_3\text{-tacn})\}_4\text{-Fe}^{\text{II}}(\text{CN})_6\}_4]^{4-}$  cubic cage; b)  $^{13}\text{C}$  NMR spectrum of the same sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 2.** a)  $^{133}\text{Cs}$  NMR spectra of the desalted crude preparation mixture of the  $\{\{\text{Cs}^+\} \subset [\{\text{Co}^{\text{III}}(\text{Me}_3\text{-tacn})\}_4\text{-Fe}^{\text{II}}(\text{CN})_6\}_4]^{4-}$  species. b)  $^{133}\text{Cs}$  NMR spectra of the same compound at ca. 3 M NaCl after solution exchange to  $\text{Na}^+$  on a Sephadex DEAE A-25 chromatographic column (top) and on addition of a small amount of solid CsCl (bottom).



**Fig. 3.** a) Electronic spectra of the  $\{\{\text{Cs}^+\} \subset [\{\text{Co}^{\text{III}}(\text{Me}_3\text{-tacn})\}_4\text{-Fe}^{\text{II}}(\text{CN})_6\}_4]^{4-}$  species in water (black) and its void (red) and potassium (blue) analogues [43]. b) Cyclic voltammogram of the  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  region of the caesium-containing cubic cage; 25 °C, 100  $\text{mV s}^{-1}$ , glassy carbon working electrode, Ag/AgCl (saturated KCl) reference electrode, platinum wire counter electrode, 0.1 M of CsCl as supporting electrolyte. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 4.** Computed structures for the (a) void and (b) Cs-encapsulated cubic species (Colour code: C = grey, N = blue, Fe = green, Co = scarlet, Cs = purple, all H atoms have been omitted for clarity). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



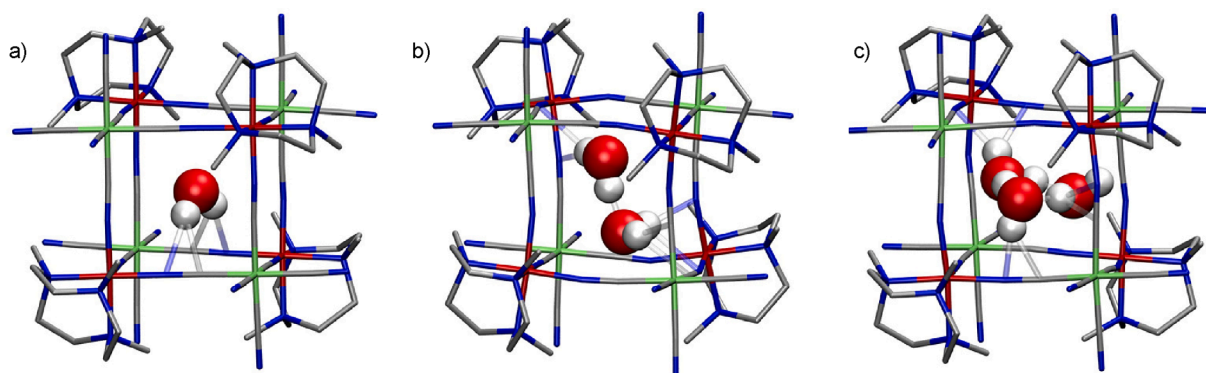


Fig. 5. Computed cubic structures containing (a) one, (b) two and (c) three water molecules (Colour code: H = white, C = grey, N = blue, O = red, Fe = green, Co = scarlet, H atoms of the cubic cage have been omitted for clarity). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

on  $5 \times 10^{-4}$  M solutions of the sample and using 0.1 M of CsCl as supporting electrolyte. All potentials are given *versus* NHE, once corrected for the reference electrode used.

#### 4.2. Materials

Compound  $[\text{Co}(\text{Me}_3\text{-tacn})\text{Cl}_3]$  was prepared according to literature methods [48].  $\text{Na}_4[\text{Fe}^{\text{II}}(\text{CN})_6]$  was recrystallized twice from the commercially available material before use. All the other commercially available chemicals were of analytical grade and were used as received.

#### 4.3. Compounds

The preparation and isolation of the caesium salts of the  $[\{\text{Co}^{\text{III}}(\text{Me}_3\text{-tacn})\}_4\{\text{Fe}^{\text{II}}(\text{CN})_6\}_4]^{4+}$  cube have been carried out by the same procedure, that has been already described [35], but using a 2 M CsCl or 0.25 M aqueous solutions as the reaction media with  $[\text{Na}_4[\text{Fe}^{\text{II}}(\text{CN})_6]] = 3 \times [\text{Co}^{\text{III}}(\text{Me}_3\text{-tacn})\text{Cl}_3] = 15$  mM. The resulting mixture becomes very dark and, after left stirring overnight at 40–50 °C, is filtered to eliminate any precipitated solids and loaded onto a Sephadex G-25 size exclusion chromatographic column ( $2 \times 25$  cm) in several aliquots. The retained dark band is eluted with water; an initial grey-blue dark polymer is discarded, while the central part of the remaining purple band (account for ca. 50 % of the initial cobalt complex) is collected; a final trailing off-yellow band (excess of hexacyanidoferrate(II)) is also discarded. The procedure was repeated four times. After concentration to a small volume at 45–50 °C, the remaining solution was left to evaporate to dryness in the air and the final solid sample was analysed.

*For the procedure carried out in 2 M CsCl:*

ICP-OES: Ratio Fe:Co  $1.05 \pm 0.03$ ; Fe:Cs  $1.01 \pm 0.01$ .

$^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ , 298 K): ( $\delta/\text{ppm}$ ) 2.92 (s br, 36H,  $\text{CH}_3$ ), 3.20–3.21 (m, 24H,  $\text{CH}_2$  *anti*), 3.34–3.36 (m, 24H,  $\text{CH}_2$  *syn*).

$^{13}\text{C}$  NMR (100.6 MHz,  $\text{D}_2\text{O}$ , 298 K) ( $\delta/\text{ppm}$ ): 52.0 (s,  $\text{CH}_3$ ), 61.1 (s,  $\text{CH}_2$ ), 169.3 (s, terminal  $\text{C}\equiv\text{N}$ ), 182.0 (br s, bridging  $\text{C}\equiv\text{N}$ ).

$^{133}\text{Cs}$  NMR (65.59 MHz,  $\text{D}_2\text{O}$ , 298 K) ( $\delta/\text{ppm}$ ): 7 ( $\text{Cs}_{\text{aq}}^+$ ), 59 ( $\text{Cs}_{\text{encapsulated}}^+$ ).

UV-vis ( $\text{H}_2\text{O}$ ) ( $\text{nm}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ )): 317 (1700), 455 (sh, 3150), 524 (4250).

IR (ATR) ( $\text{cm}^{-1}$ ): 2155 m, 2124 s, 2053 vs  $\nu(\text{C}\equiv\text{N})$ .

Electrochemistry:  $\text{Fe}^{\text{III/II}}$  potentials (mV vs NHE): 821, 970, 1050, 1310.  $\text{Co}^{\text{III/II}}$  potentials (mV vs NHE): –400, irreversible.

The free (non-encapsulated) caesium ions of the  $\text{Cs}_3\{\text{Cs} \subset [\{\text{Co}^{\text{III}}(\text{Me}_3\text{-tacn})\}_4\{\text{Fe}^{\text{II}}(\text{CN})_6\}_4]\}$  characterized salt were exchanged to sodium by DEAE A-25 Sephadex chromatography. A solution of the prepared compound ( $I = 0.05$  M) is loaded onto the column, after through washing with water, a single band is eluted with 0.2 M NaCl. The eluate is then taken to dryness and the solid obtained analysed by

$^{133}\text{Cs}$  NMR (65.59 MHz,  $\text{D}_2\text{O}$ , NaCl saturated, 298 K) ( $\delta/\text{ppm}$ ): 41.5 ( $\text{Cs}_{\text{encapsulated}}^+$ ).

*For the procedure carried out in 0.25 M CsCl:*

ICP-OES: Ratio Fe:Co  $0.95 \pm 0.03$ ; Fe:Cs  $1.01 \pm 0.01$ .

$^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ , 298 K): ( $\delta/\text{ppm}$ ) 2.92 (s br, 36H,  $\text{CH}_3$ ), 3.20–3.21 (m, 24H,  $\text{CH}_2$  *anti*), 3.34–3.36 (m, 24H,  $\text{CH}_2$  *syn*).

$^{13}\text{C}$  NMR (100.6 MHz,  $\text{D}_2\text{O}$ , 298 K) ( $\delta/\text{ppm}$ ): 52.0 (s,  $\text{CH}_3$ ), 61.1 (s,  $\text{CH}_2$ ), 169.3 (s, terminal  $\text{C}\equiv\text{N}$ ), 182.0 (br s, bridging  $\text{C}\equiv\text{N}$ ).

$^{133}\text{Cs}$  NMR (65.59 MHz,  $\text{D}_2\text{O}$ , 298 K) ( $\delta/\text{ppm}$ ): 10 ( $\text{Cs}_{\text{aq}}^+$ ).

UV-vis ( $\text{H}_2\text{O}$ ) ( $\text{nm}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ )): 317 (1700), 455 (sh, 3150), 524 (4250).

IR (ATR) ( $\text{cm}^{-1}$ ): 2155 m, 2124 s, 2053 vs  $\nu(\text{C}\equiv\text{N})$ .

The free caesium ions of the above  $\text{Cs}_4[\{\text{Co}^{\text{III}}(\text{Me}_3\text{-tacn})\}_4\{\text{Fe}^{\text{II}}(\text{CN})_6\}_4]$  salt were exchanged to sodium by DEAE A-25 Sephadex chromatography. On through washing with water the retained compound changes to a precipitated sample that is not eluted by 0.5 M NaCl. Repetitive washing of the column with water finally produces the elution of most of the compound as a very diffuse purple band. Concentration of the solution produces a very dark purple precipitate and a rather clear solution of brine. Isolation of the dark solid by filtration produces a solid with the same  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra than before the exchange.

#### 4.4. Computational details

All the density functional theory (DFT) calculations have been carried out using with the Gaussian09 (rev. D.01) [49] software. The pure PBE functional has been employed [50,51] for all the calculations along with def2svp [52,53] basis set for all the atom types. Ultrafine integration grids have been used in all calculations to ensure a satisfactory convergence. In all cases the solvation energies are computed in water with the (IEF-PCM) continuum dielectric solvation model [54,55] using the SMD radii and non-electrostatic terms [56]. The dispersion energy correction terms have been included by using the D3 method of Grimme [57]. Vibrational analyses have been performed for all the computed structures to ensure the nature of the stationary points, which have zero imaginary frequencies.

The DFT optimized structures can be freely accessed through the ioChem-BD repository: <https://doi.org/10.19061/iochem-bd-1-212>.

#### CRediT authorship contribution statement

**Albert Gallen:** Investigation. **Jesús Jover:** Formal analysis. **Montserrat Ferrer:** Conceptualization, Writing – review & editing, Supervision. **Manuel Martínez:** Conceptualization, Methodology, Writing – review & editing, Supervision.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ica.2022.121282>.

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