Self-assembly and properties of a discrete water-soluble *P*russian*B*lue*A*nalog Fe^{II}/Co^{III} cube; confinement of a water molecule in aqueous solution

Miguel A. Gonzálvez, Albert Gallen, Montserrat Ferrer, [*] *Manuel Martínez* [*]

Secció de Química Inorgànica, Departament de Química Inorgànica i Orgànica, Universitat de Barcelona.

montse.ferrer@qi.ub.edu, manel.martinez@qi.ub.edu

Abstract

A novel type of water-soluble anionic cubic cages $K_4[\{Co^{III}(Me_3\text{-Tacn})\}_4\{Fe^{II}(CN)_6\}_4]$ and $Na_4[\{Co^{III}(Me_3\text{-Tacn})\}_4\{Fe^{II}(CN)_6\}_4]$ were prepared by means of a mechanistically designed self-assembly process between $[Co(Me_3\text{-Tacn})Cl_3]$ and $M_4[Fe^{II}(CN)_6]$ for M = Na or K, respectively; consisting on a rate limiting outer-sphere redox step followed by a fast substitution/inner-sphere redox reaction sequence. These compounds show a remarkable stability in aqueous solution at different pH ranges, displaying neat protonation processes and a reversible oxidation with peroxodisulfate to its neutral $\{Fe^{III}{}_4Co^{III}{}_4\}$ form. Furthermore, the cages behave as a robust and water-soluble molecular *PrussianBlueAnalog* capable of encapsulating $\{Na\text{-}OH_2\}^+$ pairs and K^+ cations in aqueous solution, where the cubic structure of the complex is preserved. The substitution of the $\{Na\text{-}OH_2\}^+$ pairs by K^+ is easily accomplished, and the electrochemical properties of the sodium and potassium salts of the new cages have been found dramatically dependent on the encapsulated units.

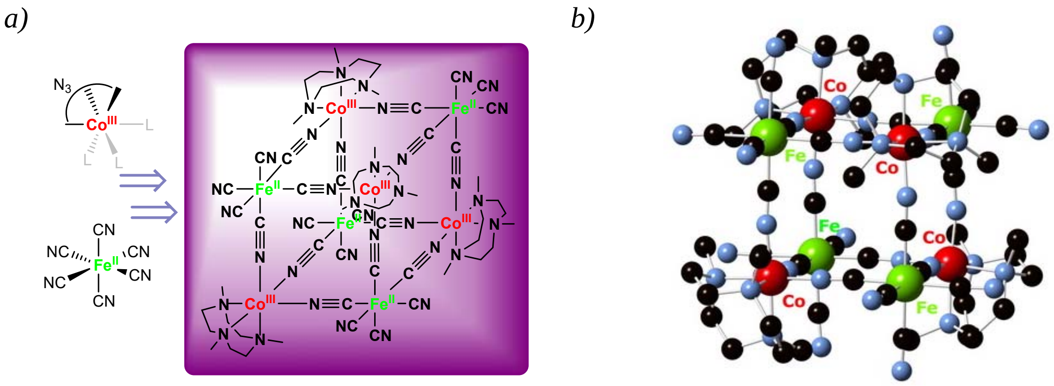
Mixed-valence complexes derived from hexacyanidometallate units (***P***russian ***B***lue ***A***nalogues, PBAs), are compounds with an $A_yM_A[M_B(CN)_6]_x{\cdot}nH_2O$ chemical composition. A being an alkaline cation and M_A and M_B a transition metal (Fe, Co, Ni, among others).[1,2] Prussian Blue derivatives have been widely studied due to their magnetic, charge storage and electrochromic properties,[3-8] and recently they have met new successes as sensors for cation recognition. Metal-cyanido frameworks have proven useful as ion-exchange materials, incorporating NH_4^+ and alkali metal cations within its lattice.[4,8-10] A high selectivity for Cs^+ has been observed. attributed to the excellent size-fitting into the structure cavity.

Examples of molecular PBA systems operating in solution are extremely scarce; the lack of robustness of these species in solution is associated to the substitutional lability of the metal ions involved. In fact, only a few examples of molecular metal-cyanido cages (cationic o neutral), capable of mimicking the cation-exchange behaviour observed for Prussian Blue Analogues in solid state, have been prepared.[11-14] Particularly, although Fe/Co,[15,16] Ru/Co,[17] and Rh/Co cubic cages,[18] have interesting results in K^+ and Cs^+ exchange processes, its use is hampered by its stability, limited to organic solvents. Thus, it is not surprising that the preparation of anionic, inert, water-soluble, and discrete mixed-valence compounds, capable of resisting non-mild solution conditions, represents a challenging goal. A recent perspective appeared that puts clearly in focus all these preparation, solubility and stability issues.[19]

In this line, some time ago, we succeeded in the preparation of discrete and very robust, cyanido-bridged Fe^{II}/Co^{III} complexes in a fast and straightforward manner. This mechanistically designed process involves a classical rate limiting outer-sphere redox rapidly followed by a substitution/inner-sphere redox reaction sequence.[20-28] The methodology allowed us the synthesis of aqueous and oxidation persistent (pH 1-12; $S_2O_8^{2}$ cyanido-bridged complexes.

Despite that functionalisation of these species in different environments has been explored, its rather “closed” unreactive structures did not allow for its incorporation to supporting systems.[29,30] We consequently moved to the use of Co^{III} synthons bearing tetradentated amine macrocycles and two substitutionally active positions that could act as building blocks for our redox assisted self-assembly reactions while leaving an empty coordination position for functionalisation. However, the use of the standard preparation protocol generated a discrete square $\{Fe^{II}{}_2Co^{III}{}_2\}^{2-}$ cyanido-bridged complex after chromatography work-up.[31,32] No significant amounts of the possible $Co^{III}/(Fe^{II})_2$ or $(Co^{III})_2/Fe^{II}$ species were detected, and the actuation of a complex self-assembly reaction in aqueous medium applies.[22]

Hence, our interest moved to the application of the above-mentioned redox-directed assembly to complexes of higher nuclearity and geometrical complexity, in order to produce robust water soluble discrete PBAs. Here, we present the use of the C_{3v} $\{Co^{III}(Me_3\text{-}Tacn)\}^{3+}$ (Me_3-Tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) building-block for this purpose. The system allowed us to obtain a PBA box due to the availability of three facial, substitutionally active, cobalt coordination sites (Scheme 1a).



Scheme 1.- Self-assembly of the $\{Fe^{II}{}_4Co^{III}{}_4\}$ system (*a*) and its DFT-calculated structure (*b*).

The overnight reaction of an aqueous solution of the sodium or potassium salts of $[Fe^{II}(CN)_6]^{4-}$ with $[Co^{III}(Me\text{-}Tacn)Cl_3]$ at pH 8 and 60 ºC produces a very dark solution that is loaded onto a Sephadex G25 column. An ill-defined initial dark grey band is eluted on washing with water; a neat purple band follows; its purification (see SI) yields solids for the salts of both alkaline cations.

The ^{1}H NMR spectra in D_2O show a very simple pattern in agreement with the formation of discrete high symmetrical (C_{3v}) species containing the $\{Co^{III}(Me\text{-}Tacn)\}$ moiety. The ICP analyses (Fe:Co ratio 1:1) of the samples, in combination with their ^{13}C NMR spectra (only two CN signals of similar intensity are observed) confirm the formation of a $\{Fe^{II}{}_4Co^{III}{}_4\}^{4-}$ cyanido-bridged cubic cages for both salts. Although, we have not been able to isolate a crystal suitable for XRD analyses, Spartan[33] has been used to optimise de structure proposed (Scheme 1b), which effectively shows a symmetrical cubic structure. Inspection of the ^{1}H and ^{13}C NMR (either in D_2O or Methanol-d_4 solution) signals of the sodium and potassium salts reveals slight differences in the chemical shifts (Figure 1a).

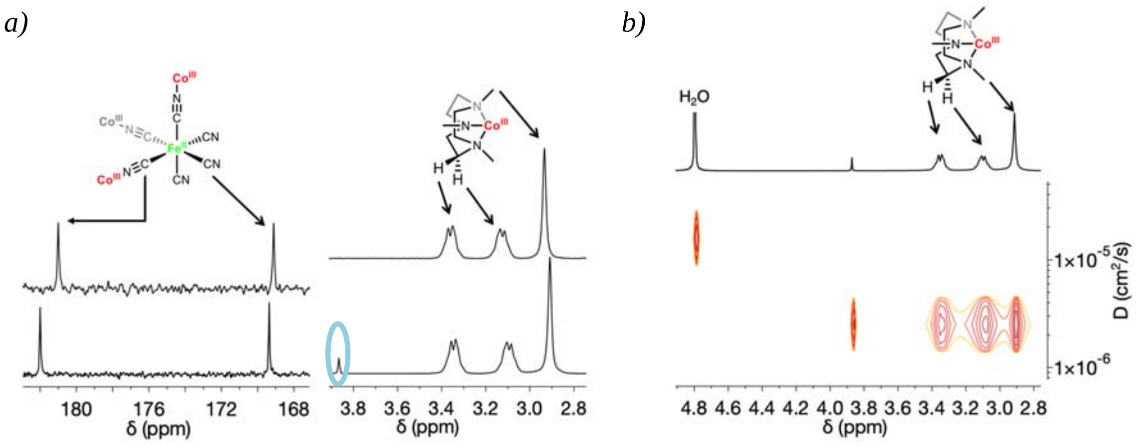


Figure 1.- *a)* ^{1}H and ^{13}C (cyanide zone) NMR D_2O spectra of the sodium and potassium salts of the $\{Fe^{II}_4Co^{III}_4\}^{4-}$ cube. *b)* DOSY NMR spectrum of the sodium salt of the $\{Fe^{II}_4Co^{III}_4\}^{4-}$ cube.

The species assembled using $Na_4[Fe(CN)_6]$ shows an additional unexpected signal at 3.87 ppm in D_2O (4.00 ppm in Methanol-d_4) integrating two protons (Figure 1a, circled) and with no correlation with any carbon atom, as indicated by HSQC. A DOSY experiment shows an identical value of the diffusion coefficient for all signals (Figure 1b), which strongly suggests that the signal can be assigned to an encapsulated water molecule within the sodium $\{Fe^{II}_4Co^{III}_4\}^{4-}$ cage. Interestingly, the chemical shift of the protons ascribed to the encapsulated water indicates a lower acidity than that of the free solvent, which is also related with the lack of deuterium scramble. Although the encapsulation of water molecules,[14] and the existence of $\{Na\text{-}OH_2^{+}\}$ encapsulated pairs have been confirmed by X-ray analysis in different solid PBAs,[8,10] to the best of our knowledge, this is the first time where the confinement effect of a water molecule is detected in aqueous solution.

Furthermore, the HRMS-ESI spectrometry peaks correspond to $\{Fe^{II}_4Co^{III}_4\}^{4-}$ cubic cages associated with at least a $\{Na\text{-}OH_2\}^{+}$ cationic pair or a sodium or potassium cation (when potassium salts were used); no void cubes are detected (see SI, Figure S2 and S3). Accordingly, the IR spectra (Figure S4) show a slightly different H-O-H bending signal at *ca.* 1740 cm^{-1}.

The ^{13}C NMR spectrum of an equimolar mixture of the sodium and potassium cubes only shows the signals of the potassium species (Figure S5), which is relevant in view of the ion-exchange reactivity of other PBAs.[10,17,18] Similarly, the ^{1}H NMR experiment shows the progressive disappearance of the resonance at 3.87 ppm (Figure S6). After 4 hours at room temperature, the complete release of the encapsulated water, exclusive of the sodium cage, is observed. The same results are obtained when an excess of KCl is added to an aqueous solution of the sodium cage. No reverse potassium to sodium ion-exchange was observed on adding an excess of $NaClO_4$ to the potassium cube. Despite that some PBAs possess unique Cs^{+} selectivity,[10,15,17,18] our cube shows a clear preference for K^+. No spectroscopic changes have been observed upon addition of caesium salts to any of the cages, a feature that could be attributed to the relatively small size of the $\{Fe_2Co_2\}$ faces of the cube (see SI).

The sodium to potassium exchange process was time-resolved by UV-Vis (Figure 2a). Results indicate that the process is not in equilibrium even when a large excess of Na^+ is present (Figure 2b triangles, no intercept), and that the limiting value obtained under flooding $[NaClO_4] = 1.0$ M conditions corresponds to the rate constants determined at very low, uncontrolled, ionic strength (Figure 2b, circles).

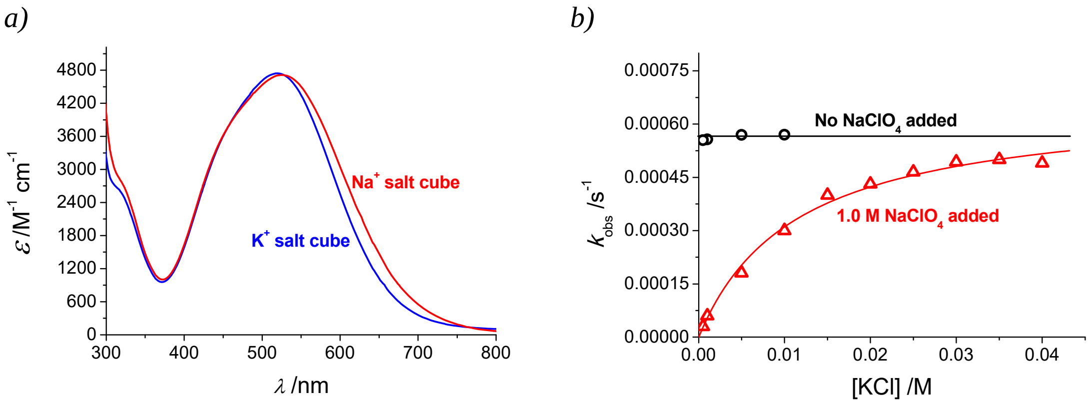


Figure 2.- *a)* Electronic spectra of the prepared $\{Fe^{II}{}_4Co^{III}{}_4\}^{4-}$ cubic cages in water. *b)* [KCl]-dependence at 25 ºC in aqueous solution of the sodium-to-potassium cation exchange of the sodium cube; circles correspond to non-flooded ionic strength reaction conditions and triangles to $I = 1.0$ M ($NaClO_4$).

The robustness shown by the new cages in aqueous medium (expected from the extremely inert LS $t_{2g}{}^6$ Oh configurations), prompted us to carry out a series of solution studies of processes that involve pH and redox activity; Figure 3a collects the UV-Vis spectrum of the sodium salt in water at different acidities. The energy and intensity of the bands in water or alkaline medium corresponds to the presence of $[Fe^{II}(CN)_6]^{4-}$ (320 nm) and $\{Co(N)_6\}^{3+}$ (340 nm and 475 nm) chromophores,[34] overlapped with an intense new band at 525 nm (4710 $M^{-1}cm^{-1}$) associated with a MMCT band between Co^{III} and Fe^{II} centres.[22,35,36] Its nature was confirmed by a bathochromic shift on decreasing the polarity of the solvent (Figure S7).[37] Acidification of the sample leads to an increase of the energy of the band, due to the protonation of the terminal nitrile units attached to the iron centres, which decreases their negative charge.[31,38,39] Slight differences remain between the electronic spectra of the sodium and potassium salts of the $\{Fe^{II}{}_4Co^{III}{}_4\}^{4-}$ cage on acidification, indicating the permanence in the protonated box of either $\{Na\text{-}OH_2{}^+\}$ or K^+. The reversible acid-base titration of an aqueous solution of the sodium cube by UV-Vis spectroscopy was also conducted;[25] results indicated the presence of three pK_a values (2.3, 1.8, 0.93) in the acidity range up to 1.0 M $HClO_4$, in line with those determined for the same family of complexes.[23,31] The spectral changes (Figure S8) agree well with those in

Figure 3a. Solutions had to be kept at the 10 mM level to insure solubility of the protonated species, and data corresponding to the K^+ shows a larger error due to this fact; only two pK_a values (2.2 and 1.2) could be determined.

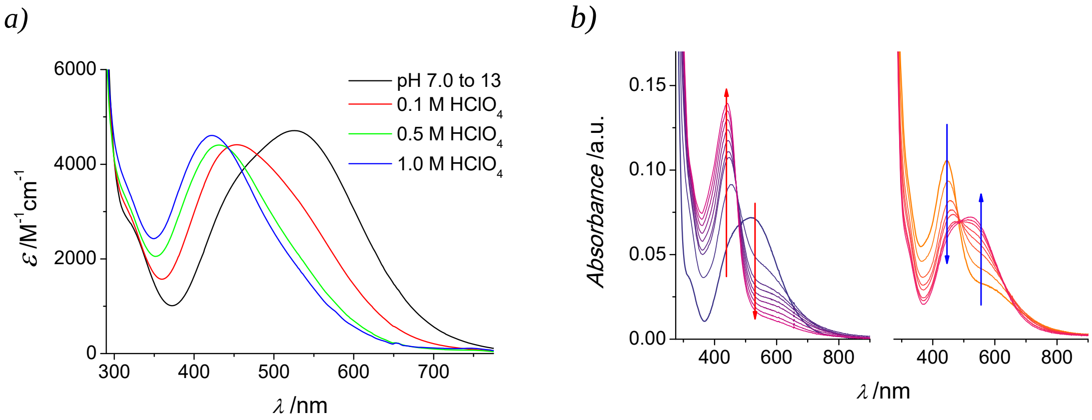


Figure 3.- *a)* Acidity-dependent electronic spectra of the sodium salt of the $\{Fe^{II}_4Co^{III}_4\}^{4-}$ cage. *b)* Spectral changes obtained addition of a large amount (10^3 fold) of sodium peroxodisulfate to an aqueous solution of the same cage (left) and further addition of NaOH solution (right).

As a whole, the extreme robustness of the new cube in acidities between 0.5 M NaOH and 1.0 M $HClO_4$ is established. Surprisingly, comparing with complexes of the same family,[20,22,31,38] addition of small amounts of $Na_2S_2O_8$ to the sample does not produce the depletion of the MMCT band. Only if ratios larger than 1:500 are used, depletion of this MMCT band occurs, with the expected increase in the intensity at 420-440 nm due to the $[Fe^{III}(CN)_6]^{3-}$chromophore (Figure 3b). Repetitive column chromatography of these oxidised samples produces the reappearance of the reduced cubic species. The same effect is observed after addition of NaOH to the final solution obtained after oxidation (Figure 3b); clearly, the well-established water oxidation process by the new $\{Fe^{II}_4Co^{III}_4\}^{4-}$ is operative and competitive at low peroxodisulfate concentrations even at neutral pH.[32,40]

The CV characterisation of the samples was conducted in 0.1 M aqueous KCl or $NaClO_4$ (depending on the cage); two blocks of waves are observed, one at negative and one at positive potentials. At negative potential (corresponding to the four $Co^{III/II}$ couples) two irreversible non-resolved signals are observed (Figure S9), while at positive potential (attributed to the $Fe^{III/II}$ couples)[22,24,31] the CV is much more defined. For the potassium salts, the CV consists of a set of four fully reversible signals in the expected range of potential values (Figure 4a). Surprisingly, the CV of the sodium salt is much more complex (Figure 4b), showing high degree of irreversibility (see Figure S10).

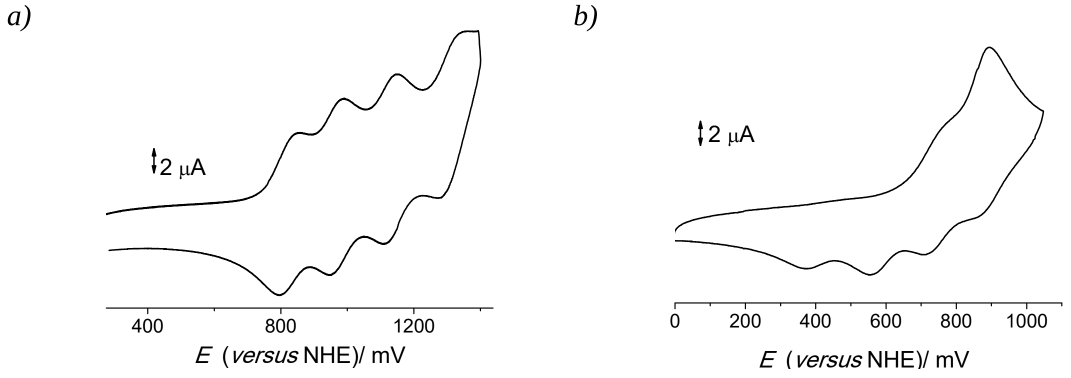


Figure 4.- CV of the Fe^{III}/Fe^{II} signals of the potassium (*a*) and sodium (*b*) salts of the $\{Fe^{II}{}_4Co^{III}{}_4\}^{4-}$ cage.

It is clear that the presence of a $\{Na\text{-}OH_2\}^+$ pair,[8,10] strongly interacting when compared with a simple spherical K^+, within the $\{Fe^{II}{}_4Co^{III}{}_4\}^{4-}$ cubic box, produces important electronic distribution changes in the assembly. This can be observed in the ^{13}C NMR spectrum (Figure 1a), where the in-cage cyanido carbon shifts show significant differences. The MMCT band in the electronic spectrum (Figure 3a), related with the degree of coupling between iron and cobalt centres in the $\{Fe^{II}{}_4Co^{III}{}_4\}^{4-}$ cage for these *Class II* mixed-valence compounds,[37] is also revealing. [36,41-43]

In conclusion, the mechanistically driven self-assembly of simpler $\{Fe^{II}{}_{1,2}Co^{III}{}_{1,2}\}^{2-}$ mixed valence complexes has been applied to the formation of a new $\{Fe^{II}{}_4Co^{III}{}_4\}^{4-}$ anionic cage. The compound shows a remarkable pH stability in aqueous solution, and can be reversibly oxidised with peroxodisulfate to its neutral $\{Fe^{III}{}_4Co^{III}{}_4\}$ form, which produces H_2O_2 reverting to the original reduced compound in a sort of catalytic process. The cage behaves as a molecular, robust, and water soluble PBA, which encapsulates $\{Na\text{-}OH_2\}^+$ pairs and K^+ cations, the latter with a clear preference. The electrochemical properties of its sodium and potassium salts have been found dramatically dependent on the encapsulated units. The new compound prepared represents, to the best of our knowledge, the prime of the proposed models for Prussian Blues, given its anionic character that enables mimicking encapsulation processes by electrostatics and not only by hydrophilic-hydrophobic interactions.

Supporting Information Available: Experimental procedures for the preparation and characterisation of the compounds. MS, IR, NMR and UV-Vis spectral data, Spartan-DFT optimised structures and cyclic voltammograms or the new complexes prepared.

Acknowledgements Financial support from the Spanish Ministerio de Ciencia e Innovación (project CTQ2015-65707-C2-1-P (MINECO/FEDER) is acknowledged.

REFERENCES

1.- Aguila, D.; Prado, Y.; Koumousi, E. S.; Mathoniere, C.; Clerac, R. Switchable Fe/Co Prussian blue networks and molecular analogues. *Chem. Soc. Rev.* **2016,** *45*, 203-224.

2.- de Tacconi, N. R.; Rajeshwar, K.; Lezna, R. O. Metal Hexacyanoferrates:ΓÇë Electrosynthesis, in Situ Characterization, and Applications. *Chem. Mater.* **2003,** *15*, 3046-3062.

3.- Sato, O.; Einaga, Y.; Fujishima, A.; Hashimoto, K. Photoinduced Long-Range Magnetic Ordering of a Cobalt–Iron Cyanide. *Inorg. Chem.* **1999,** *38*, 4405-4412.

4.- Asai, M.; Takahashi, A.; Tajima, K.; Tanaka, H.; Ishizaki, M.; Kurihara, M.; Kawamoto, T. Effects of the variation of metal substitution and electrolyte on the electrochemical reaction of metal hexacyanoferrates. *RSC Adv.* **2018,** *8*, 37356-37364.

5.- Boudjema, L.; Mamontova, E.; Long, J.; Larionova, J.; Guari, Y.; Trens, P. Prussian Blue Analogues for the Separation of Hydrocarbons in Humid Conditions. *Inorg. Chem.* **2017,** *56*, 7598-7601.

6.- Kraft, A.; Rottmann, M. Properties, performance and current status of the laminated electrochromic glass of Gesimat. *Sol. Energ. Mat. Sol. C.* **2009,** *93*, 2088-2092.

7.- Skunik-Nuckowska, M.; Bacal, P.; Kulesza, P. J. Charge storage and capacitance-type properties of multi-walled carbon nanotubes modified with ruthenium analogue of Prussian Blue. *J. Solid State Electr.* **2015,** *19*, 2753-2762.

8.- Song, J.; Wang, L.; Lu, Y.; Liu, J.; Guo, B.; Xiao, P.; Lee, J. J.; Yang, X. Q.; Henkelman, G.; Goodenough, J. B. Removal of Interstitial H2O in Hexacyanometallates for a Superior Cathode of a Sodium-Ion Battery. *J. Am. Chem. Soc.* **2015,** *137*, 2658-2664.

9.- Matsuda, T.; Kim, J.; Moritomo, Y. Symmetry Switch of Cobalt Ferrocyanide Framework by Alkaline Cation Exchange. *J. Am. Chem. Soc.* **2010,** *132*, 12206-12207.

10.- Zhang, N.; Kawamoto, T.; Jiang, Y.; Takahashi, A.; Ishizaki, M.; Asai, M.; Kurihara, M.; Zhang, Z.; Lei, Z.; Parajuli, D. Interpretation of the Role of Composition on the Inclusion Efficiency of Monovalent Cations into Cobalt Hexacyanoferrate. *Chem. Eur. J.* **2019,** *25*, 5950-5958.

11.- Nihei, M.; Ui, M.; Hoshino, N.; Oshio, H. Cyanide-Bridged Iron(II,III) Cube with Multistepped Redox Behavior. *Inorg. Chem.* **2008,** *47*, 6106-6108.

12.- Heinrich, L.; Berseth, A.; Long, R. Molecular Prussian Blue analogues: synthesis and structure of cubic Cr4Co4(CN)12 and Co8(CN)12 clusters. *Chem. Commun.* **1998,** 1231-1232.

13.- Li, D.; Clèrac, R.; Roubeau, O.; Harté, E.; Mathonière, C.; Le Bris, R.; Holmes, S. M. Magnetic and Optical Bistability Driven by Thermally and Photoinduced Intramolecular Electron Transfer in a Molecular Cobalt–Iron Prussian Blue Analogue. *J. Am. Chem. Soc.* **2008,** *130*, 252-258.

14.- Gu, Z. G.; Liu, W.; Yang, Q. F.; Zhou, X. H.; Zuo, J. L.; You, X. Z. Cyano-Bridged FeIII2CuII3 and FeIII4NiII4 Complexes: Syntheses, Structures, and Magnetic Properties. *Inorg. Chem.* **2007,** *46*, 3236-3244.

15.- Jiménez, J. R.; Tricoire, M.; Garnier, D.; Chamoreau, L. M.; von Bardeleben, J.; Journaux, Y.; Li, Y.; Lescouzec, R. A new {Fe4Co4} soluble switchable nanomagnet encapsulating Cs+: enhancing the stability and redox flexibility and tuning the photomagnetic effect. *Dalton Trans.* **2017,** *46*, 15549-15557.

16.- Garnier, D.; Jiménez, J. R.; Li, Y.; von Bardeleben, J.; Journaux, Y.; Augenstein, T.; Moos, E. M. B.; Gamer, M. T.; Breher, F.; Lescouëzec, R. K–{[FeII(Tp)(CN)3]4[CoIII(pzTp)]3[CoII(pzTp)]}: a neutral soluble model complex of photomagnetic Prussian blue analogues. *Chem. Sci.* **2016,** *7*, 4825-4831.

17.- Hsu, S. C. N.; Ramesh, M.; Espenson, J. H.; Rauchfuss, T. B. Membership Rules for a Molecular Box: The Admission Process and Protection Provided to Guest Molecules. *Angew. Chem.* **2003,** *42*, 2663-2666.

18.- Boyer, J. L.; Ramesh, M.; Yao, H.; Rauchfuss, T. B.; Wilson, S. R. Redox-Switched Complexation/Decomplexation of K+ and Cs+ by Molecular Cyanometalate Boxes. *J. Am. Chem. Soc.* **2007,** *129*, 1931-1936.

19.- Uchida, S. Frontiers and progress in cation-uptake and exchange chemistry of polyoxometalate-based compounds. *Chem. Sci.* **2019,** *10*, 7670-7679.

20.- Bernhardt, P. V.; Macpherson, B. P.; Martínez, M. Discrete Dinuclear Cyano-Bridged Complexes. *Inorg. Chem.* **2000,** *39*, 5203-5208.

21.- Bernhardt, P. V.; Bozoglián, F.; Macpherson, B. P.; Martínez, M. Tuning the metal to metal charge transfer energy of cyano-bridged dinuclear complexes. *Dalton Trans.* **2004,** 2582-2587.

22.- Bernhardt, P. V.; Bozoglián, F.; Macpherson, B. P.; Martínez, M. Molecular mixed-valence cyanide bridged Co^{III}-Fe^{II} complexes. *Coord. Chem. Rev.* **2005,** *249*, 1902-1916.

23.- Bernhardt, P. V.; Bozoglián, F.; González, G.; Martínez, M.; Macpherson, B. P.; Sienra, B. Dinuclear Cyano-Bridged Co^{III}/Fe^{II} Complexes as Precursors for Molecular Mixed Valence Complexes of Higher Nuclearity. *Inorg. Chem.* **2006,** *45*, 74-82.

24.- Bernhardt, P. V.; Martínez, M.; Rodríguez, C. Molecular Co^{III}/Fe^{II} Cyano-Bridged Mixed-Valence Compounds with High Nuclearities and Diversity of Co^{III} Coordination Environments: Preparative and Mechanistic Aspects. *Inorg. Chem.* **2009,** *48*, 4787-4797.

25.- Basallote, M. G.; Bernhardt, P. V.; Calvet, T.; Castillo, C. E.; Font-Bardía, M.; Martínez, M.; Rodríguez, C. Mechanistic aspects of the chemistry of mononuclear Cr^{III} complexes with pendant-arm macrocyclic ligands and formation of discrete Cr^{III}/Fe^{II} and $Cr^{III}/Fe^{II}/Co^{III}$ cyano-bridged mixed valence compounds. *Dalton Trans.* **2009,** 9567-9577.

26.- Bernhardt, P. V.; Martínez, M.; Rodríguez, C. Outer-Sphere Redox Reactions leading to the Formation of Discrete Co^{III}/Fe^{II} pyrazine-Bridged Mixed Valence Compounds. *Eur. J. Inorg. Chem.* **2010,** 5621-5629.

27.- Bernhardt, P. V.; Martínez, M.; Rodríguez, C.; Vazquez, M. Discrete Rh^{III}/Fe^{II} and $Rh^{III}/Fe^{II}/Co^{III}$ Cyanide-Bridged Mixed Valence Compounds. *Inorg. Chem.* **2011,** *50*, 1429-1440.

28.- Cáceres, C.; Martínez, M.; Rodríguez, C.; Dreyse, P.; Ortega, V.; Isaacs, M. Electrochemical coating of [*trans* -L 14 Co III CNFe II (CN) 5]Na on ITO / Au electrode and its electrocatalytic properties towards nitrite reduction. *J. Electroanal. Chem.* **2014,** *722-723,* 1-6.

29.- Basallote, M. G.; Bozoglián, F.; Fernandez-Trujillo, M. J.; Martínez, M. Sol-Gel Materilas with Trapped Trinuclear *Class-II* Mixed-Valence Macrocyclic Complexes that Mimic their Solution Redox Behaviour. *New J. Chem.* **2008,** *32*, 264-272.

30.- Bernhardt, P. V.; Boschloo, G. K.; Bozoglián, F.; Hagfeldt, A.; Martínez, M.; Sienra, B. Tailoring mixed-valence CoIII/FeII complexes for their potential use as sensitizers in dye sensitized solar cells. *New J. Chem.* **2008,** *32*, 705-711.

31.- Alcázar, L.; Aullón, G.; Ferrer, M.; Martínez, M. Redox-Assisted Self-Assembly of a Water-Soluble Cyanido-Bridged Mixed Valence $\{Co^{III}/Fe^{II}\}_2$ Square. *Chem. Eur. J.* **2016,** *22*, 15227-15230.

32.- Alcázar, L.; Bernhardt, P. V.; Ferrer, M.; Font-Bardia, M.; Gallen, A.; Jover, J.; Martínez, M.; Peters, J.; Zerk, T. J. Kineticomechanistic Study of the Redox pH Cycling Processes Occurring on a Robust Water-Soluble Cyanido-Bridged Mixed-Valence {CoIII/FeII}2 Square. *Inorg. Chem.* **2018,** *57*, 8465-8475.

33.- *Spartan'18,* version v.1.4.0; Wavefunction,Inc.: Irvine, CA, USA, 2019

34.- Lever, A. B. P. *Inorganic Electronic Spectroscopy;* Elsevier: Amsterdam, 1984.

35.- Pérez-Tejada, P.; López-Pérez, G.; Prado-Gotor, R.; Sánchez, F.; González-Arjona, D.; López-López, M.; Bozoglián, F.; González, G.; Martínez, M. Electrolyte effects on the intervalence transition within discrete binuclear cyano-bridged complexes. An estimation of activation free energy from static, optical and electrochemical data. *Inorg. Chim. Acta* **2006,** *359*, 149-158.

36.- Bernhardt, P. V.; Macpherson, B. P.; Martínez, M. The influence of cis/trans isomerism on the physical properties of a cyano-bridged dinuclear mixed valence complex. *J. Chem. Soc. , Dalton Trans.* **2002,** 1435-1441.

37.- The estimated electronic coupling (H_{ab} = 4900 cm-1) and the degree of delocalisation (a = 6.6 %) in aqueous neutral solution agree with those determined for similar cyanido-bridged *Class II* Fe^{II}/Co^{III} complexes (reference 35).

38.- Bernhardt, P. V.; Bozoglián, F.; Macpherson, B. P.; Martínez, M.; González, G.; Sienra, B. Discrete cyanide bridged mixed-valence Co/Fe complexes: outer sphere redox behaviour. *Eur. J. Inorg. Chem.* **2003,** 2512-2518.

39.- Bozoglián, F. *PhD Thesis* **2006,** *Universitat de Barcelona*.

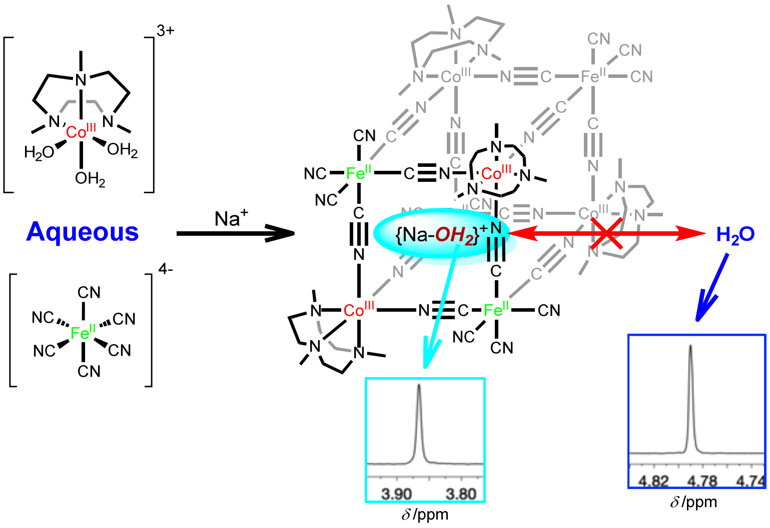
40.- Bernhardt, P. V.; Bozoglián, F.; Macpherson, B. P.; Martínez, M.; Merbach, A. E.; González, G.; Sienra, B. Oxidation of Mixed-Valence Co^{III}/Fe^{II} Complexes Reversed at High pH: A Kinetico-Mechanistic Study of Water Oxidation. *Inorg. Chem.* **2004,** *43*, 7187-7195.

41.- Creutz, C. Mixed Valence Complexes d^5-d^6 Metal Centers. *Prog. Inorg. Chem.* **1983,** *30*, 1-73.

42.- Marcus, R. A. Electron Transfer Reactions in Chemistry: Theory and Experiment. *Angew. Chem. , Int. Ed.* **1993,** *32*, 1111-1121.

43.- Robin, M. B.; Day, P. Mixed Valence Chemistry-A Survey and Classification. In *Advances in Inorganic Chemistry and Radiochemistry*, 10 ed.; Emeléus, H. J., Sharpe, A. G., Eds.; Academic Press: 1968; pp 247-422.

TOC



The facile assembly of a new mixed-valence, encapsulating, robust and water soluble (-Co^{III}-NC-Fe^{II}-CN-)$_4$ cube has been achieved using the enhanced lability of inert Co^{III} synthons triggered by outer-sphere redox processes.