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Sol–gel materials with trapped trinuclear class-II mixed-valence macrocyclic complexes that mimic their solution redox behaviour†

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The redox chemistry of mixed-valence $Co^{III}/Fe^{II}/Co^{III}$ complexes in solution and trapped in sol–gel matrices has been compared. Whereas the redox $S_2O_8{}^{2-}/OH^-$ reactivity cycling of the complexes $[\{L_nCo^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ physically immobilized into the pore network of TEOS-derived xerogels, where L_n represents a polyaza macrocycle, mimic perfectly the reactivity shown in solution without leaching of the complex to the reaction medium, all attempts to immobilize smaller and negatively charged dinuclear $[\{L_nCo^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^-$ related complexes have been found unsuccessful. A fine tuning of the pore size of the matrix, the electrostatic interactions between the matrix's surface and the complexes, as well as possible chemical adduct formation between the OR groups of the matrix and the cyanide ligands, seem to be responsible for the effects observed. The chemical preparation of the mixed-valence complexes inside the sol–gel matrix has also been tried by using a silylated modified L_n ligand with four hydrolysable-$Si(OEt)_3$ groups. Following the anchoring of the ligand to a TEOS-derived matrix, the initial formation of the L_nCo^{III} building block has been achieved, but diffusion of the negatively charged $[Fe(CN)_6]^{4-}$ species to the $\{L_nCo^{III}\}^{3+}$ centre is severely hindered unless high acidity is used. Nevertheless, under such acidic conditions the mixed-valence $[\{L_nCo^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^-$ compounds have been successfully formed inside the matrix and have been characterized by IR and UV-Vis spectroscopy. Despite this fact, the redox $S_2O_8{}^{2-}/OH^-$ reactivity cycling carried out on the latter materials has proved to be much more slow than for xerogels containing the trinuclear $[\{L_nCo^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ species physically trapped.

Introduction

Sol–gel materials have been extensively studied in the last decades and their properties have been reviewed.[1–12] One issue of particular interest is the possibility of using sol–gel procedures for trapping into solid materials compounds that display interesting properties when in solution. Actually, there are many organic, inorganic and organometallic compounds that show interesting physico-chemical properties that can be exploited for practical applications in solid-state devices, but primary preparative work usually restrict the study of their properties to those shown in solution. Material chemists working in the sol–gel field tend to focus their interest in the properties of the materials as a bulk, but attention is also paid in some cases to analyze the way in which the constraints imposed by the matrix affect the chemical properties of the compounds, in particular to the chemical reactivity.[13] In any case better understanding of the comparative behavior of compounds in solution and trapped into sol–gel materials is, no doubt, desirable.

We have been involved in recent years in the preparation of a series of mixed-valence Co^{III}/Fe^{II} cyano-bridged di- and trinuclear complexes. In these compounds the cobalt centre is encapsulated by a macrocyclic ligand of varying size and donor characteristics, while the iron unit is the hexacyanoferrate(II) ion (Chart 1).[14–19]

These Robin and Day class-II complexes[20] show interesting properties as far as their redox and MMCT bands are concerned. In particular, the reversible fading of the charge transfer bands appearing in the visible (*ca.* 500–550 nm) region of the spectrum on oxidation of the iron centre to Fe^{III}, suggested its possible use as electrochromic materials.[21] Although the values found for the extinction coefficients of these bands are, so far,[14] not suited for this application with the compounds already available,[22] they represent a first step towards the development of larger species with increased absorptivities. With regards to the solution redox behavior

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† Electronic supplementary information (ESI) available: Fig. S1. Changes of the UV-Vis spectrum of a sample of the immobilized $[\{L_{15}SiCo^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^-$ complex upon oxidation with a 0.1 M solution of $S_2O_8{}^{2-}$ at pH 3. Fig. S2: IR spectra of the CN bond stretching region for the immobilized $[\{L_{15}SiCo^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^-$ complex and that obtained upon oxidation, $[\{L_{15}SiCo^{III}(\mu\text{-NC})\}Fe^{III}(CN)_5]$. Fig S3: Nitrogen adsorption–desorption isotherm for the sample containing trapped *trans*-$[\{L_{15}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ complex. Fig. S4: BJH pore size distribution for a sample containing trapped *trans*-$[\{L_{15}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ and MP pore size distribution for the same sample. See DOI: 10.1039/b710963f

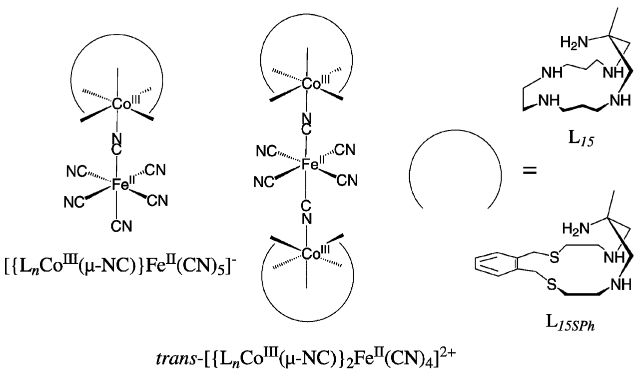


Chart 1

of these complexes, the outer-sphere oxidation of the dinuclear complexes demonstrated to be an excellent tool for proving the involvement of hydrogen-bonding in the process, with activation entropies and volumes having definite opposite signs.[23] The reduction of the oxidized dinuclear Co^{III}/Fe^{III} form has been found even more interesting, as these complexes are able to oxidize OH^- to H_2O_2 catalytically in the presence of external oxidants.[24] Interestingly the trinuclear $Co^{III}/Fe^{II}/Co^{III}$ series of compounds[19] show MMCT bands in practically the same position in the UV-Vis spectrum than their related dinuclear precursors, but their extinction coefficients are double those of the dinuclear complexes. That is, the charge transfer between each two metal units (Co^{III}/Fe^{II}) is essentially independent from the other, so that practical electrochromic properties can be expected for related compounds with higher metal nuclearities.

In view of the promising properties of these compounds, we decided to investigate if the solution reactivity of these di- and trinuclear mixed-valence Co^{III}/Fe^{II} complexes can be transferred to solid materials. For this purpose, we selected to use sol–gel procedures, given the fact that this methodology has been successfully applied in recent years to prepare hybrid materials containing different types of metal complexes, either trapped into the matrix,[25–33] or covalently bound to it.[34–40] Some of us have demonstrated that these procedures can be used for preparing xerogels containing dinuclear macrocyclic metal complexes[41,42] retaining the major features of the chemical reactivity displayed by the complexes in solution. Here we report the first results obtained for materials containing the above mentioned mixed-valence complexes prepared using both strategies (trapping and covalent bonding), the focus of our interest dealing mainly with the analyses of the way in which the redox reactivity of the complexes is affected by the constraints imposed by the matrix. As these initial results indicate that most of the coordination chemistry of these compounds can be transferred to the solid phase, the possibility for the future development of electrochromic materials and silica-supported complexes as catalysts for the reaction producing H_2O_2 in alkaline medium cannot be disregarded.

Results and discussion

Reactivity of the complexes in solution

As the major goal of the present work was to determine to which extent the reactivity of the class-II mixed-valence complexes can be transferred from solution to solid materials, some brief comments about the solution chemistry of the complexes is needed before analyzing their behavior when trapped into sol–gel matrices. The complexes indicated in Chart 1 are prepared in solution *via* a stoichiometric substitution of the aqua ligand in $[Co(H_2O)L_n]^{3+}$ by $[Fe(CN)_6]^{4-}$ or $[\{L_nCo^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^-$ (Scheme 1, $L_n = L_{15}$).[14,18]

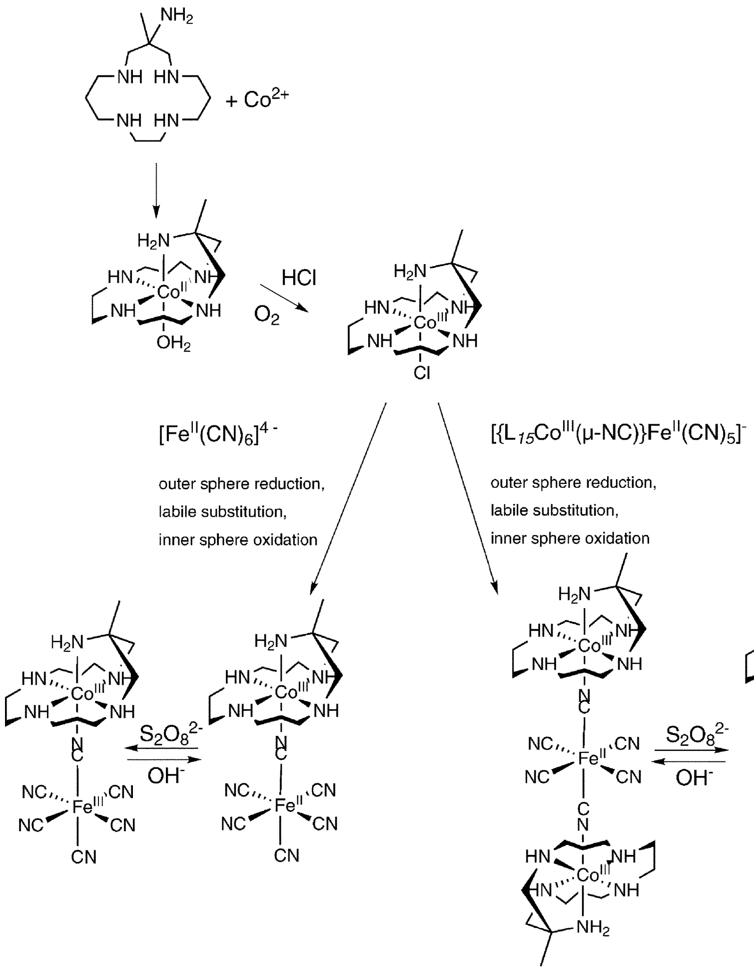
The preparative reaction is mechanistically not so simple, it is driven by an outer-sphere redox process, followed by a facile substitution on the Co^{II} labile complex formed, and further redox inner-sphere rearrangement.[43] The full process has been proved to be applicable to the preparation of the di- and trinuclear complexes shown in Chart 1.[19] In the latter cases, it is important to note that substitution of the aqua ligand in the $[Co(H_2O)L_n]^{3+}$ species by a cyanide nitrogen from a dinuclear $[\{L_nCo^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^-$ complex can become an accessible reaction path even when the redox potentials do not favor the process shown in Scheme 1.[15]

Although some of the complexes indicated in Chart 1 exist in different isomeric forms,[14,16,19,44] the absence of distinct reactivity patterns has already been established. The oxidation/reduction reactivity of the dinuclear parent complex $[\{L_{15}Co^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^-$ has been described previously,[23,24] and the reactivity of the trinuclear *trans*-$[\{L_{15}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ and *trans*-$[\{L_{15SPh}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ complexes was checked in a similar way. Thus, at pH = 3 addition of $S_2O_8^{2-}$ to a solution of the trinuclear complexes[19] leads to oxidation of the iron centre (Scheme 1, bottom) with the consequent depletion of the intense brown–purple color associated with the MMCT band due to the Robin and Day class-II behavior of the complexes (Fig. 1(a)). On increase of the pH to *ca.* 10 the spectrum returns to that of the original reduced $Co^{III}/Fe^{II}/Co^{III}$ complex, as seen in Fig. 1(b), in a matter of seconds.

This reactivity is the same as that previously observed for the dinuclear complexes, peroxides being produced in the oxidation by the Fe^{III} centre during the cycling. For the dinuclear complexes, the study of the intimate reaction mechanism of this process has provided enough information to ascertain an important degree of hydrogen bonding during the oxidation process,[23] as well as the formation of cyano-related OH^- adducts during the reverse reduction reaction.[24] The reduction process is formally uphill from a thermodynamic point of view, and the above mentioned adducts represent the only way to provide the reactivity pathway observed. Further detailed comparative studies about the intimate mechanism operating for the trinuclear species in relation with their dinuclear precursors are currently underway.

Reactivity of the complexes in solid matrices prepared by sol–gel procedures

Having summarized the major features of the redox reactivity of the complexes in aqueous solution, the results obtained in solid matrices will be presented, with special emphasis on the preparation of the materials and the analysis of their redox behavior. We initially concentrated our interest in the preparation of materials containing the dinuclear Co^{III}/Fe^{II} $[\{L_{15}Co^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^-$ complex trapped into TEOS-



Scheme 1 Comparative reactivity.

derived xerogels (TEOS = tetraethyl orthosilicate). For this purpose, controlled amounts of aqueous solutions containing the complex were used to promote the hydrolysis of TEOS (see Experimental section). These attempts were unsuccessful, given the fact that most of the complex solution separates in a different phase during gelification, so lowering the complex concentration in the resulting materials. Furthermore, the weak color from the solids prepared in this way disappears completely when the materials are washed with water.

In view of these facts, and considering the interesting parallelism between the complex formation in solution and in silica gel matrices found for some other systems studied,[41,42] we decided to explore this preparation scheme on the mixed-valence complexes. The aim was to be able to reproduce within the matrix the step-by-step preparative process of the simpler dinuclear $[\{L_{15}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^-$ complex indicated in Scheme 1.[14,44–46] The use of the functionalized L_{15} ligand indicated in Chart 2, L_{15Si}, should allow, as for previously described systems,[41] its immobilization onto the silica gel matrix.

The preparation of the silylated ligand L_{15Si}, which contains four hydrolysable –Si(OEt)$_3$ groups, was carried out following the procedure described in the Experimental section. The use of this compound allowed the preparation of monolithic samples containing the macrocycle covalently bonded to the TEOS-derived silica matrix, providing a useful starting point to check the reactivity within the solid. Soaking the L_{15Si}-containing samples in an aqueous $CoCl_2$ solution at pH 9, and bubbling air for *ca.* 16 h, leads to a UV-Vis spectrum that shows the presence of a low spin, t_{2g}^6, Co^{III} amine complex (λ_{max} at *ca.* 500 and 350 nm). That is, the formation of the $\{L_{15Si}Co^{III}\}^{3+}$ complex moiety from the immobilized macrocycle and external Co^{II} can be achieved within the matrix, at least partially. As expected from both the high stability of macrocyclic Co(III) complexes and the covalent links between the macrocycle and the matrix, no significant color changes are observed upon repeated washing of the material with water. That is, the first two processes in Scheme 1 can be carried out within the solid matrix.

Following some initial unsuccessful attempts using neutral water solutions of $[Fe(CN)_6]^{4-}$, the generation of the dinuclear Co^{III}/Fe^{II} mixed-valence complex (Scheme 1, bottom left) inside the matrix could be achieved by using aqueous solutions of hexacyanoferrate(II) at a pH close to 1 ($HClO_4$). Under these conditions, the $[Fe(CN)_6]^{4-}$ anion is in its diprotonated {2−} form and the silica surface is beyond its isoelectric point,[13] thus allowing diffusion of the anion through the pore network. For monolithic samples prepared under these conditions a darkening of the samples occurred, leading finally to purple xerogels with an intense band in the visible region

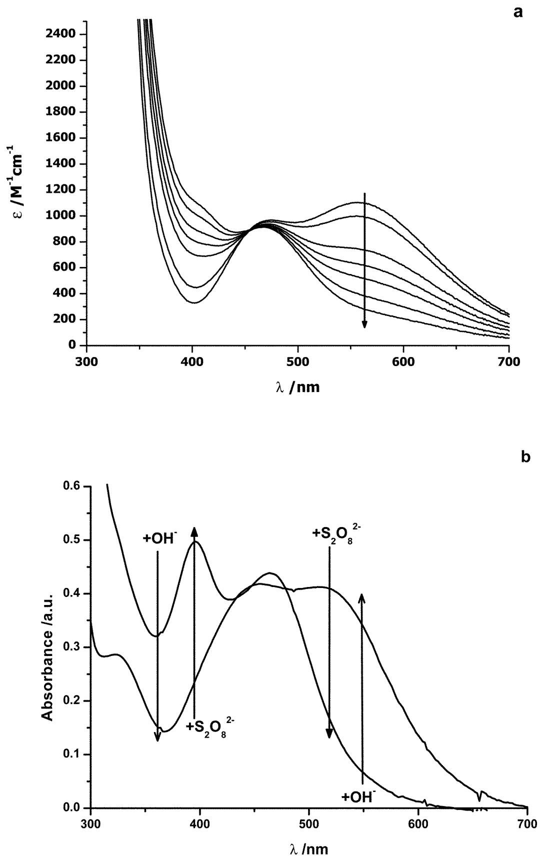


Fig. 1 (a) Changes in the UV-Vis spectra of a pH 3 solution of the trinuclear complex *trans*-$[\{L_{15SPh}Co^{III}(\mu\text{-}NC)\}_2Fe^{II}(CN)_4]^{2+}$ on addition of peroxodisulfate. Total depletion of the band takes place in *ca.* 60 min at room temperature and $[S_2O_8^{2-}]$ 0.05 M. (b) Reversible changes in the UV-Vis spectrum of a 4.5×10^{-4} M solution of *trans*-$[\{L_{15}Co(\mu\text{-}NC)\}_2Fe^{II}(CN)_4]^{2+}$ on oxidation with peroxodisulfate at pH 3 and further increase to pH 10.

(560 nm), corresponding to the MMCT signal of the expected mixed-valence $[\{L_{15Si}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^-$ compound. The fact that formation of the mixed-valence complex could be only achieved in acidic solutions is in agreement with previous reports showing that diffusion of charged species, as $[Fe(CN)_6]^{4-}$, through the pore network of xerogels is more conditioned by the interactions with the matrix than by the pore size.[47,48] Once achieved the formation of the mixed-valence complex, further reactivity tests were carried out to explore the possibility of oxidizing the Fe^{II} centre in a way similar to that found in solution. Although soaking the samples in an aqueous solution of $S_2O_8^{2-}$ at pH 7 gives no changes in color, when the pH is lowered to 2 an important loss of color on standing for long periods, *ca.* 48–72 h (Fig. S1, ESI†), is observed. The bleaching of the MMCT band occurs under these conditions by oxidation of the Fe^{II} centre by the peroxodisulfate anion, but it only takes place once the dinuclear complex has been protonated to its cationic $[\{L_{15Si}Co^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_3(CNH)_2]^+$ form,[23] more suitable for interaction with the dianionic $S_2O_8^{2-}$ oxidant.

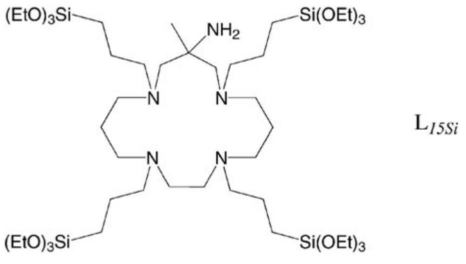


Chart 2

The cyanide bond stretching region of the IR spectra of the samples containing the immobilized dinuclear mixed-valence complex, as well as its oxidized form, were also collected (Fig. S2, ESI†). In both samples the existence of two main CN stretching frequencies at 2130 and 2080 cm^{-1} agree very well with the values observed for equivalent non-immobilized complexes.[17,19] In the spectra, nevertheless, a new signal at lower energies (1980 cm^{-1}) is also evident, and can probably be related to an adduct formation of the cyanide ligands with the OR groups of the matrix. The relative intensity of this signal is much higher for samples containing the oxidized complex $[\{L_{15Si}Co^{III}(\mu\text{-}NC)\}Fe^{III}(CN)_5]^0$, as expected from the higher polarizing characteristics of the Fe^{III} centre. In this respect, reduction studies carried out on this family of complexes in solution agree very well with the adduct formation capability of this Fe^{III} oxidized form.[24] After reaching the oxidized $[\{L_{15Si}Co^{III}(\mu\text{-}NC)\}Fe^{III}(CN)_5]^0$ state, recovery of the MMCT band *via* OH^- reduction of the iron centre could be only partially achieved after soaking the xerogels for very long periods (one to two weeks) at pH 10–11, and this occurs with partial dissolution of the sample. Thus, it is clear that a cycling of the complex in a way similar to that indicated in Fig. 1 could not be completed. Probably the approach of the anionic OH^- species to the neutral complex is highly disfavored by the existence of an anionic-surface (isoelectric point at pH 2)[13] in the matrix.

Given the unsuccessful attempts to carry out a complete transfer of the solution behavior of the dinuclear mixed-valence complexes to silica gel matrices, either using physical immobilization or covalent bonding to the matrix, we decided to try physical trapping of the larger and positively charged trinuclear complexes, *trans*-$[\{L_{15}Co^{III}(\mu\text{-}NC)\}_2Fe^{II}(CN)_4]^{2+}$ and *trans*-$[\{L_{15SPh}Co^{III}(\mu\text{-}NC)\}_2Fe^{II}(CN)_4]^{2+}$ (see Chart 1). In this case, monolithic samples containing trapped complexes could be prepared as described in the Experimental section and no bleaching occurred during prolonged soaking. The reactivity cycles indicated in Fig. 1 and Scheme 1 (bottom right) could be repeated for days without apparent loss of the trapped complex, as indicated by the absence of any of the intense UV-Vis signals of the complex in the mother-liquor. Both the size and basic character of the pore network in the matrix formed can be easily held responsible of this differentiating factor with respect to materials containing the dinuclear-trapped solids. The UV-Vis spectra of these trinuclear species trapped in the silica gel matrices perfectly match those obtained in aqueous solution (Fig. 2) indicating that the nature of the immobilized complexes corresponds exactly to the compounds in solution.

In this respect the IR spectra of the monolithic samples are strikingly informative about the nature of the complex–matrix linkage. Surprisingly, in contrast with the spectra of the

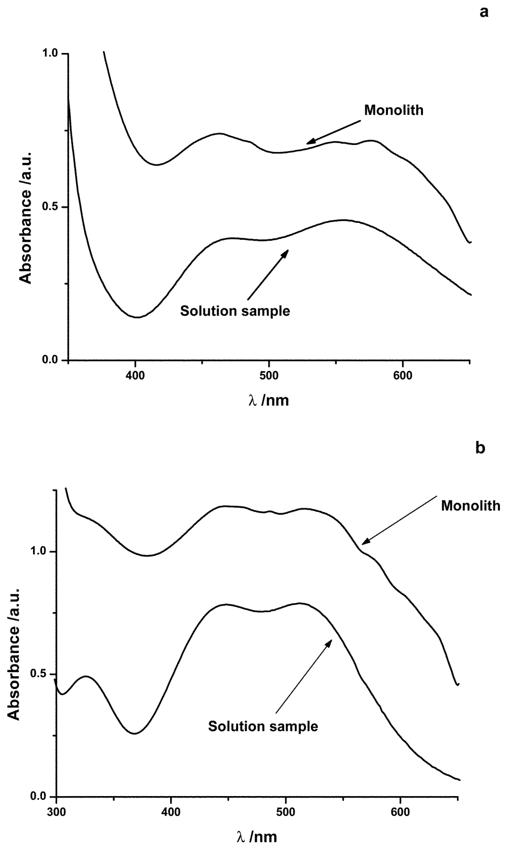


Fig. 2 UV-Vis spectra of the trinuclear complexes studied, (a) *trans*-$[\{L_{15SPh}Co^{III}(\mu\text{-}NC)\}_2Fe^{II}(CN)_4]^{2+}$ and (b) *trans*-$[\{L_{15}Co^{III}(\mu\text{-}NC)\}_2Fe^{II}(CN)_4]^{2+}$ in aqueous solution and trapped in silica gel matrices.

trinuclear complex in solution or dispersed in KBr and also with the behavior of the xerogels containing the related dinuclear complexes commented above,[1] no CN stretching bands are observed for these materials. The large extinction coefficient of the CN stretching signals at *ca.* 2000–2100 cm^{-1} should have made them visible in the spectra of the samples even at the 1% concentration estimated for the complexes inside the monoliths. Actually, the indicative CN stretching signals in the 2150–2050 region of the IR spectra of samples of the solid complexes dispersed in KBr at concentration of only 0.01% are still visible. Thus, only the existence of interactions of the cyano ligands with the OR groups in the matrix, already detected for the above described dinuclear complexes, can explain the disappearance of the signals in the IR spectra of the xerogels. The resulting adduct species, already held responsible for some of the solution reactivity of the complexes,[24,49–51] can, *de facto*, transform the character of the cyanide bond from triple to double,[52] thus causing a shift of the stretching frequencies at lower energies. The high electron-withdrawing characteristics of two $\{L_{15Ph}Co^{III}\}^{3+}$ attached to the same iron centre should now enable a resulting quasi-double character of the CN bond leading to a shift of stretching band to the 1600 cm^{-1} region (compared with 1930 cm^{-1} for the dinuclear complexes), where the absorption of the matrix does not allow for its observation. Some preliminary studies of this adduct chemistry in solution of this type of trinuclear complexes agree with this fact.[53]

Soaking monolithic samples of *ca.* 5 × 5 × 5 mm of the xerogels containing less than 1% of any of the trinuclear complexes indicated above, in a solution 0.01 M in HCl and 0.1 M in $Na_2S_2O_8$ produced the changes in visible spectrum indicated in Fig. 3(a) with depletion of the MMCT signal in the 540–570 nm region, which clearly indicates oxidation of the iron centres.[18,23] Not surprisingly, oxidation occurs more slowly than in solution because of the required slow diffusion of the oxidant through the pore network to reach the trapped Fe^{II} centre of the cationic $\{2+\}$ species. Oxidation is completed in 3–4 h, and the resulting final spectra lack the characteristic MMCT band of the mixed-valence complex. It is also very interesting to note that the intense absorption at 420 nm (see Fig. 1(b)) typical of the $[Fe^{III}(CN)_6]^{3-}$ moiety is not observed in the spectra of the xerogels after treatment with $Na_2S_2O_8$. Cleaning the sample and soaking it in a 0.01 M NaOH solution produced the reappearance of the MMCT band, as shown in Fig. 3(b). Successive treatments with $S_2O_8^{2-}$ and OH^- can be repeated without any significant decay in the reproducibility of the spectral changes observed, *i.e.* the

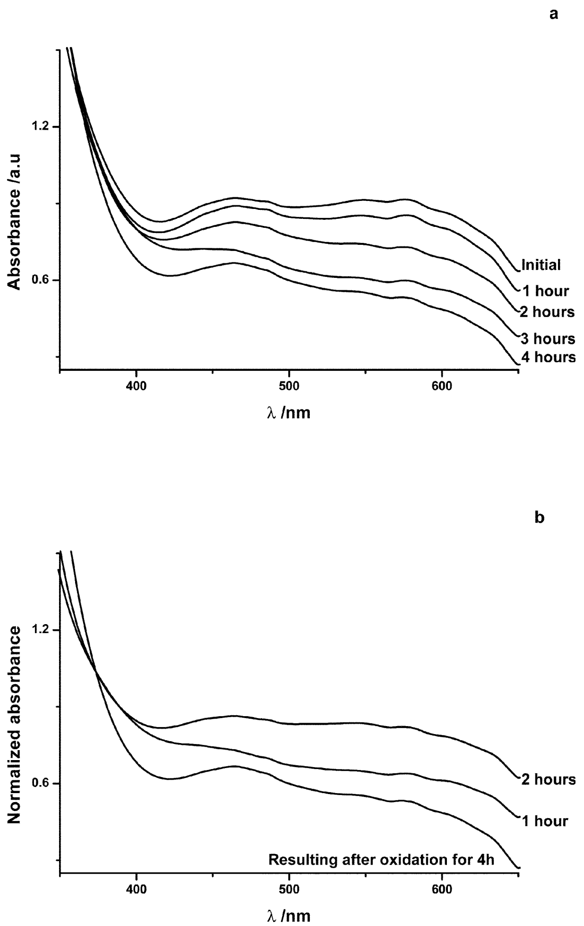


Fig. 3 Changes in the UV-Vis spectrum of a 5 × 5 × 5 mm block of silica gel containing less than a 1% of *trans*-$[\{L_{15SPh}Co^{III}(\mu\text{-}NC)\}_2Fe^{II}(CN)_4]^{2+}$. (a) When soaked in a 0.1 M solution of $Na_2S_2O_8$ at pH 2 (HCl). (b) When the resulting block is rinsed and soaked in a 0.01 M NaOH solution.

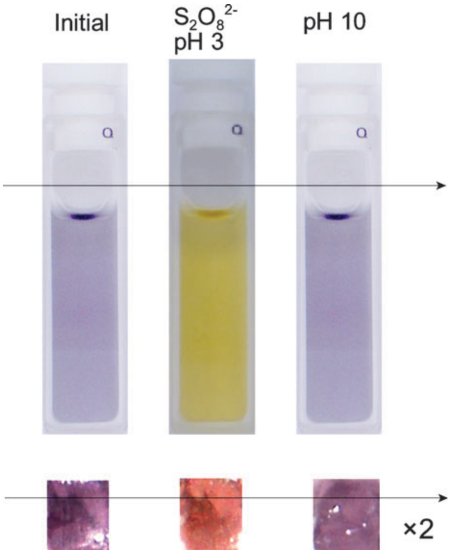


Fig. 4 Comparative reactivity in solution (top) and silica gel trapped (bottom) of the redox cycling of the *trans*-[{$L_{15SPh}Co^{III}$(μ-NC)}$_2$-$Fe^{II}(CN)_4$]$^{2+}$ complex. The spectra of the solution samples are those shown in Fig. 1(a), while the silica gel trapped samples spectra correspond to those indicated in Fig. 3.

reactivity cycle in Scheme 1 can be now completed and repeated in a reproducible way.[54] The above mentioned absence of the band at 420 nm corresponding to the oxidized [$Fe^{III}(CN)_6$]$^{3-}$ moiety, can be easily related with the absence of any cyanide stretching signals in the IR spectra. If the triple bond character of the cyanide groups has been *partially* converted to double by adduct formation,[50] the LMCT band at 420 nm should be disturbed to lower energy, given the electronic pumping into the cyanide ligand carbon from the oxygen of the OR groups of the matrix. As a result, the oxidized *trans*-[{L_nCo^{III}(μ-NC)}$_2Fe^{III}(CN)_4$]$^{3+}$ forms show only the weak bands corresponding to the Co^{III} chromophore, plus the dominant intense LMCT band of the iron centre shifted to a lower energy region of the spectrum. A red shift should be observed for the system when compared with the aqueous solution (Fig. 4).

Porosity study of the monolithic samples prepared

In view of the promising properties of the materials described above, a detailed adsorption study was carried out on samples of materials containing the trapped trinuclear complexes, as well as for a blank sample prepared with the same procedure for comparative purposes. For the samples containing trapped complexes, the shape of the nitrogen adsorption isotherms show a hysteresis loop and fit to the type IV IUPAC classification (Fig. S3, ESI,†for the case of the gel containing the trinuclear L_{15} complex).[55] The analysis of these isotherms by the BET method[56] leads to the values of the specific pore volume (V_{BET}) and specific surface area (S_{BET}) included in Table 1, from which an average value of the pore diameter (d_{BET}) can be calculated, provided a cylindrical shape is assumed.

From the point of view of the chemical properties of these materials the pore size distribution, which determines the capability of chemical species to diffuse through the pore network and to exchange with an external solution, is rather relevant. The size of the mesopores was analyzed using the BJH method[57] and the results (see Table 1 and Fig. S4(a), ESI†) indicate that both samples contain a rather uniform distribution of pore sizes with a maximum for a pore diameter of *ca.* 3.5 nm. This value is significantly larger than the molecular size of the trinuclear complexes; so that the complex ions trapped at these sites would be able to diffuse almost free of any interaction and it can be reasonably assumed that they would be released during the washing of the samples.

As the size of the mesopores exceeds that of the chemical species involved in the redox processes described above, microporosity evidence was checked by the t-plot method.[58] The results in Table 1 confirm the existence of micropores, whose size distribution was analyzed using both the MP[59] and the Horvath–Kawazoe (HK)[60] methods. As an example, Fig. S4(b) (ESI†) shows the results obtained by applying the MP method to the sample doped with the L_{15} complex.

The micropore size distribution obtained for samples containing both complexes is very similar, with a well defined maximum at a diameter of *ca.* 0.7 nm, close to the molecular size of the trinuclear complexes. From the X-ray crystal structure data available for the complexes,[19,61] the shape of the trinuclear $Co^{III}/Fe^{II}/Co^{III}$ complexes can be approximately described as being cylindrical (see Scheme 1) with a length of 1.7 nm and a diameter that changes with the nature of the macrocycle (0.65 nm for the L_{15} complex and 0.86 nm for the L_{15SPh} complex). It is clear, as expected, that the size of the guest complex influences the network structure and the complex ions trapped at the micropore network would not be able to diffuse out of the monolithic samples, but remain accessible to reagents of smaller molecular size, thus allowing a reactivity quite similar to that found in solution. It is interesting to note that in a previous study, it was found that a macrocyclic binuclear Cu(II) complex could be also trapped within the pore network of sol–gel materials given its excellent fit between the sizes of the complex and the pores.[42] Furthermore, leaching of the macrocycle was observed during successive reactivity cycles, given the fact that these lead to a decrease in the size. For the case of the materials studied in the present work, the stability and kinetic properties of the trinuclear complexes make complex decomposition negligible during the reactivity test, so hindering possible leaching and gaining a better reproducibility between cycles.

For the blank material without any trapped trinuclear complexes, the nitrogen adsorption–desorption isotherm indicated the absence of mesopores in the sample, although it has micropores of the same size as those found for the samples containing trapped complexes (Table 1). The porosity of the neat sample is definitively larger and the results indicate that, although mesoporosity appears to be induced by the presence of the complexes trapped, the presence of micropores is reduced in the material containing the immobilized compounds. It seems clear that the impossibility of the preparation of analogous materials containing trapped dinuclear [$Fe^{II}(CN)_5$]$^-$ complexes would be related to their worse template effect of the network, allowing them to diffuse out of the micropore network. Key factors, such as the interaction

Table 1 Summary of textural data for the samples containing trapped trinuclear mixed-valence complexes

	Trapped complex		
	$[\{L_{15}Co^{III}(\mu\text{-}NC)\}_2Fe^{II}(CN)_4]^{2+}$	$[\{L_{15SPh}Co^{III}(\mu\text{-}NC)\}_2Fe^{II}(CN)_4]^{2+}$	Blank monolith
BET			
S_{pore}/m^2 g^{-1}	240	70	458
V_{pore}/cm^3 g^{-1}	0.16	0.05	0.25
D_{pore}/Å)	27	33	25
BJH			
S_{meso}/m^2 g^{-1}	181	58	47
V_{meso}/cm^3 g^{-1}	0.13	0.05	0.03
$D_{meso}{}^a$/Å	29	36	29
t-plot			
S_{micro}/m^2 g^{-1}	82	27	160
V_{micro}/cm^3 g^{-1}	0.04	0.01	0.06
External surface/m^2 g^{-1}	159	43	246
HK			
$D_{HK}{}^b$/Å	7.5	7.3	6.6
MP			
$D_{hydr}{}^c$/Å	6.6	7.2	6.6

[a] Maximum in the distribution of mesopore diameter. [b] Median value. [c] Maximum in the distribution.

between the CN groups and the silica network revealed by the IR studies indicated before, must be probably required for an effective immobilization of any of the complexes. Furthermore, it is important to note that the previously described[42] trapped dinuclear species, as well as the trinuclear species *trans*-$[\{L_nCo^{III}(\mu\text{-}NC)\}_2Fe^{II}(CN)_4]^{2+}$ (L_n = L_{15}, L_{15SPh}) complexes, are positively-charged, whereas the dinuclear $[\{L_nCo^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^-$ compounds are anionic. Clearly, electrostatic interactions with the basic groups in the pore network during the gelification process are also essential for an effective trapping of the complex.

Conclusions

Summarizing, the redox reactivity of mixed-valence trinuclear complexes of the type *trans*-$[\{L_nCo^{III}(\mu\text{-}NC)\}_2Fe^{II}(CN)_4]^{2+}$ has been compared in solution and in immobilized silica gel matrices. Although the times required for the redox cycling of the complexes shown in Scheme 1 in the solid materials is longer, due to inherent diffusion-controlled conditions, the reactivity pattern is parallel in the two cases. Fig. 4 presents the comparative reactivity in solution and silica gel trapped for *trans*-$[\{L_{15SPh}Co^{III}(\mu\text{-}NC)\}_2Fe^{II}(CN)_4]^{2+}$ complex. Evidence has been obtained indicating that, although trapping of these complexes is evident by physical (size) constraints, there are also contributions from chemical interactions between the coordinated CN groups and the functional groups in the matrix. Attempts to prepare xerogels containing trapped the related $[\{L_nCo^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^-$ dinuclear complexes were unsuccessful, probably a combination of the negative charge on these species and their smaller size reduce their capability to be trapped into the TEOS pore network. The *construction* of these dinuclear mixed-valence complexes in the matrix has, nevertheless, been achieved *via* preliminary immobilization of a silylated macrocyclic ligand. In this case, though, the negative charge of the immobilized $[\{L_nCo^{III}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^-$ dinuclear complex prevents an easy redox $S_2O_8{}^{2-}/OH^-$ cycling as that observed for the trapped cationic trinuclear derivatives.

Experimental

Materials

The ligands L_{15} and L_{15SPh}, as well as their mixed-valence dinuclear and trinuclear complexes, have been prepared according to the methods described in the literature.[14,15,17,19] Whenever the complexes were obtained as a mixture of isomeric forms no further purification and separation was carried out, given the inexistence of distinct reactivity patterns for the different isomers.[19,44] All other reagents and solvents were obtained from commercial sources and used without further purification.

Instruments

UV-Vis solution spectra were recorded on a Cary50 instrument in 1 cm path length cells in the 1×10^{-4} M scale, according to the published extinction coefficients.[14,19] The electronic spectra on the silica gel trapped complexes were recorded on a TIDAS J&M instrument equipped with fiber optics and focusing lenses. Infrared spectra were recorded from chips of the monolithic samples fixed in the laser path of a Nicolet 5700 FTIR instrument. NMR spectra were recorded with a Varian Unity 400 instrument. The adsorption isotherms experiments were carried out on a Micromeritics model Tristar 3000 instrument by the *Superfície específica BET* service of the *Serveis Cientificotècnics* of the *Universitat de Barcelona*. BET, BJH, MP and HK method calculations were carried out using the built-in ASP 2010 software.

Synthesis of the silylated macrocycle L_{15Si}

A mixture of 0.80 g (2×10^{-3} mol) of L_{15}, 1.27 g (15×10^{-3} mol) of Na_2CO_3 and 2.0 cm^3 (8×10^{-3} mol) of $Cl(CH_2)_3Si(OEt)_3$ in 200 cm^3 of acetonitrile was refluxed for 24 h under an argon atmosphere and then stirred for further 24 h maintaining the inert atmosphere. After elimination of the solvent under reduced pressure, 100 cm^3 of hexane and 100 cm^3 of diethyl ether were added; the resulting white precipitate was filtered off. The organic solution was evaporated under reduced pressure, leading to the isolation of L_{15Si}

as an oily liquid (0.96 g, 34% yield). NMR spectra in CD_3CN (ppm): δ_H 3.80 (q, 24 H, $C\mathit{H}_2$–CH_3), 3.58 (t, 8 H, N–C-H_2–CH_2–CH_2–Si), 2.4–3.2 (overlapped unresolved multiplets for the $C\mathit{H}_2$ groups in the macrocyclic ring), 1.84 (m, 8 H, N–CH_2–$C\mathit{H}_2$–CH_2–Si), 1.18 (t, 36 H, CH_2–$C\mathit{H}_3$), 1.12 (s, 3 H, H_2N–C–$C\mathit{H}_3$) and 0.72 (m, 8 H, N–CH_2–CH_2–$C\mathit{H}_2$–Si); δ_C 57.7, 51.5, 47.8, 46.8, 28.4 and 24.4 (carbons in the macrocycle); 58.3 ($\mathit{C}H_2$–CH_3), 49.5 (N–$\mathit{C}H_2$–CH_2–CH_2–Si), 26.6 (N–CH_2–$\mathit{C}H_2$–CH_2–Si), 17.9 (CH_2–$\mathit{C}H_3$) and 7.7 (N–CH_2–CH_2–$\mathit{C}H_2$–Si).

Preparation of the xerogels

For the preparation of the materials containing trapped metal complexes, 21 cm^3 of TEOS (tetraethyl orthosilicate) were mixed with 5 cm^3 of water and 0.5 cm^3 of 0.1 M HCl, the mixture is stirred and warmed to 60 °C for 15 min. An aqueous solution of the dinuclear, or trinuclear, mixed-valence complex (30 mg of complex in 3 cm^3), 10 cm^3 of dimethylformamide and 10 cm^3 of ethanol were then added. The resulting mixture was stirred for one hour and then transferred to plastic cuvettes and left to gel in an oven at 40 °C for two weeks. For the dinuclear $[\{L_{15}Co^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^-$ complex most of the added compound separates from the gel during the aging period, so that the resulting xerogels are only weakly colored, becoming colorless upon washing with water. For the trinuclear *trans*-$[\{L_nCo^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ (L_n = L_{15}, L_{15SPh}) complexes, monolithic samples of material of *ca.* 10 × 5 × 5 mm and showing the color typical of the complex were obtained. The color of these samples remains after washing thoroughly with water. Before using the xerogels for the reactivity or adsorption studies, they were left to stand in an oven at 70 °C for two weeks.

Blank monolithic TEOS samples were obtained using the same procedure but without the addition of the complex solution.

For the preparation of xerogels derived from the Si-containing macrocycle, 1.2 g of L_{15Si} were dissolved in 40 cm^3 of a mixture of ethanol and acetonitrile (1 : 1) and added to a mixture of TEOS (31 cm^3) and water (12 cm^3) previously warmed up to 60 °C. A volume of 0.3 cm^3 of 0.1 M HCl was then added to promote hydrolysis, and the resulting mixture was stirred for 1 h at 60 °C. The resulting solution was then transferred to plastic cuvettes and left to gel in an oven at 40 °C. After three weeks, monolithic samples of *ca.* 10 × 5 × 5 mm were obtained. These samples were washed with water and then left to stand in the oven at 70 °C for ten days before their use in the reactivity studies.

For xerogels containing trapped or covalently bound metal complexes, the concentration of the complex was estimated from the electronic spectra of the solutions obtained from the total destruction in alkaline solution of the monolithic samples. Although this is a gross estimation, it provides a value approximate enough for the purpose of the present work.

Reactivity tests carried out with the xerogels

The reactivity tests described in the RESULTS AND DISCUSSION section were carried out by immersing one or more monolithic pieces of the selected xerogel in a solution of the desired reagent in water, the pH being adjusted with 0.1 M solutions of HCl and NaOH. The samples were maintained into the solution for the time required for completing the corresponding reaction, which is easily monitored by the observed color changes. Once completed the reaction, the solid samples were washed three times with water to remove any excess of weakly trapped reagent.

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