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ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012, Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Molecular iodine adsorption within Hofmann-type structures $M(L)[M'(CN)_4]$ (M = Ni, Co; M' = Ni, Pd, Pt): impact of their composition.

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ABSTRACT : A series of thermally stable Hofmann-type clathrate structures with the general formula $M(pz)[M'(CN)_4]$, where M and M' are bivalent metal ions $M^{II} = Ni^{II}$, Co^{II} , $M^{II} = Ni^{II}$, Pd^{II} , Pt^{II} , and pz is pyrazine bidentate ligand, was synthesized and investigated for the efficient entrapment of iodine (I₂) in solution and in gas phase. Iodine-containing clathrates thus prepared were analysed to determine the saturation capacity, thermal stability, guest-induced structural changes of the clathrate's lattice and the nature of the confined iodine according to the chemical composition of the host structure. An efficient confinement of about 1 I₂ per unit cell is observed for the series of clathrates with the Ni^{II} and Pd^{II} ions in the square planar position whatever the bivalent metal ion in the octahedral position. Specific responses in the lattice adjustment are detected for Co^{II} in the octahedral and Pd^{II} in the square planar positions.

1 Introduction

Nuclear power plants now require a reprocessing procedure of spent fuel to recover the 235 U and the 239 Pu for the Mixed OXide (MOX) fuel for power production.¹ The dissolution of the spent fuel in these plants is responsible for the production of radioactive iodine isotopes $(^{133}I_2, ^{131}I_2, ^{129}I_2, ^{125}I_2$ and others), which are dangerous for health due to their volatility, toxicity and their persistence in the environment.² Amongst them, the radioactive ${}^{129}I_2$ isotope represents a major concern due to its long half-lifetime of $1.5 \cdot 10^7$ years and the β , γ and X-ray emission.³ The nuclear industry pays a great deal of attention to the efficient and selective iodine capture during fuel reprocessing or in case of abnormal working conditions in order to minimize the environmental impact.⁴ The industrial iodine treatment employs usually two different methods: (i) caustic or acidic scrubbing solutions and (ii) direct chemisorption on silver-based materials.² The mostly used alkaline (caustic) scrubbing method relies on the treatment of out-gases with NaOH solutions and then precipitation of stable and insoluble NaI and NaIO₃ compounds. This technique is already used in the Reprocessing Facility of La Hague

in France, the Rokkashoko Reprocessing Plant in Japan and at Windscale and the Thermal Oxide Reprocessing Plant facility in the United Kingdom. Alternative scrubbing methods include, the Iodox process which employs hyperazeotropic nitric acid scrubbing solution to solubilise and oxidize iodine to $(IO_3)^2$ species with their further precipitation and encapsulation as Ba(IO₃) or the "Mercurex" process which uses a mercuric nitrate-nitric acid solution to precipitate insoluble HgI2 are currently used at pilot scale or applied in laboratory.⁴ These methods present several drawbacks such as the plant safety due to a high corrosiveness, a large quantity of produced liquid wastes demanding special treatment, a multi-step technology and the potential formation of nitrated organics. The second alternative method to scrubbing technology consists of employing solid silver-containing sorbents able to chemically adsorb iodine. For instance, the silver-containing zeolite mordenite⁵ has been used for many decades, but the iodine diffusion inside the zeolite is slow and limits the capture efficiency. Moreover the stability of silverexchange zeolite is poor and the preparation of such a material is expensive. In the recent years, the employment of new thermally stable nanoporous materials such as zeolites,⁶ zeolite-related

structures ("zeoballs")⁷ or different Metal-Organic-Frameworks $(MOFs)^{8-11}$ has been proposed as an alternative way for the selective entrapment of iodine in gas phase and in solution, and its storage. In particular, MOFs exhibit high iodine sorption efficiency due to their higher porosity in comparison with the zeolite-like materials. We can cite the three-dimensional $[Cu^{II}(btz)]_n$ MOF⁸ (with H₂btz = 1,5bis(5-tetrazolo)-3-oxapentane) able to absorb 0.5 I₂/Cu^{II}, a series of aluminum carboxylate-based functionalized MOFs (MIL-100) with a maximum capacity of 0.71 I₂/Al for MIL-100-NH₂,⁹ as well as the Zn^{2+} -based zeolitic imidazolate framework (ZIF-8)¹⁰ and $[Cu_3(btc)_2]_n$ (btc = 1,3,5-benzene tricarboxylate) MOF¹¹ able to capture volatile iodine respectively up to 0.76 I₂/Zn and 1.1 I₂/Cu. Recently, we reported a preliminary study on the use of another promising nanoporous coordination polymer belonging to the family of Hofmann-like clathrates for the efficient and reversible capture of iodine in gas phase and in solution.¹² This work encouraged us to extend our investigations to iodine adsorption in other Hofmanntype frameworks and pursue the effort in the fundamental understanding of the iodine sorption mechanism.

Hofmann clathrates represent a large family of materials which have been studied since the 20th century for their large flexibility and their potential applications.¹³ The term *clathrate* (from Latin *clathratus*, "enclosed by the cross bars of a grating") was introduced by the crystallographer H. M. Powell in 1948 to describe the property of certain compounds to retain small sized molecules inside the porosity of its own crystal lattice, by weak van der Waals forces.¹⁴ The first Hofmann clathrate of general formula Ni^{II}(CN)₂·NH₃·G (G = guest molecule) able to accomodate small host molecules, such as benzene, thiophene, furane, pyrrole inside a host lattice with a complex stoichiometry has been described by A. Hofmann and F. Küspert in 1897.¹⁵ Starting from this date, numerous analogous named *Hofmann-type* clathrates of general formula $M(L)_n[M'(CN)_4] \cdot xG$,¹⁶ where M and M' are transition metal ions, L is an organic ligand and G are host molecules have been investigated in view of various applications such as sensors for specific molecules,¹⁷ the storage of gaseous compounds for the energy¹⁸ or for the sequestration of pollutants.¹⁹ The nature of the transition metal ions and ligands highly influences the lattice symmetry, the pore size and then the size and the nature of the guest molecules that can be incorporated. As reported in literature,²⁰ a large set of bivalent metal ions, such as Mn^{II}, Fe^{II}, Ni^{II}, Co^{II}, Cu^{II}, Zn^{II} and Cd^{II} can occupy the octahedral site M due to the high stability of the octahedral complexes. From a chemical point of view,²¹ these metallic centres are coordinated to the six nitrogen from the cyano ligands through a σ bonding. The relatively strong bridging cyanides bonds M'-CN-M ensure a high thermal stability for these compounds. The square-planar M' site, which is coordinated through a σ bonding and a π back donation to the C side of the four CN⁻ ligands, offers less possibility for modulation. Stable square planar geometries are typical for cations having a d⁸ configuration such as Ni^{II}, Pd^{II} and Pt^{II} and for the ligands with low steric hindrance and behaving as π -acceptors, as in the case of cyanides. Due to these reasons, the building blocks $[M'(CN)_4]^{2-}$ (M = Ni, Pd, Pt) can only be used in order to preserve a tetragonal lattice (space groups P4/m or P4/mmm).²² The largest variety has been observed for the ligand L, since it may be either a monodentate ligand, such as ammonia,¹⁵ water,²³ pyridine or imidazole,²⁴ or a bidentate one, such as pyrazine (pz),²⁵ 4,4'-bipyridine (bpy),²⁶ bipyridyl acetylene (bpac),²⁷ 4,4'azopyridine (azpy),²⁸ ethylendiammine (en),²⁹ 1,2-ethanedithiol etc.³⁰ The bidentate ligands ensure higher thermal stability thanks to the resulting three-dimensional structures of the coordination networks. The ligand L mainly controls the pore size, which allows the introduction and the retention of a specific size of molecules. In this line of thought, the research on Hofmann-type clathrates have

targeted different applications.¹⁷⁻¹⁹ For instance, the spin transition properties combined with the accommodation of different type of molecules in the cages of Fe^{II}-containing host structures, such as Fe^{II}(L)[M'(CN)₄] (with L = pz, azpy or bpac and M' = Ni^{II}, Pd^{II} or Pt^{II}), opened the possibility to use Hofmann-type clathrates as sensors for specific molecules. Notably, Letard and Kepert and coll.^{17b} and Real^{17a,c} and Kitagawa and coll.^{17c,d} introduced a large set of gas species (O₂, N₂, CO₂, CS₂, SO₂) and solvents or large molecules²⁷ inside Fe^{II}(pz)[M^{II}(CN)₄] (M = Ni, Pt) or Fe^{II}(bpac)[Ni^{II}(CN)₄], respectively. Another interesting application of the Hofmann-type clathrates lies with the hydrogen storage¹⁸ or for the CO₂ sequestration.¹⁹

As a part of our research, we recently proposed a Ni^{II}(pz)[Ni^{II}(CN)₄] structure for the insertion of molecular iodine.¹² The advantage of using the Hofmann-type structures consists especially in: (i) the high thermal stability of the host structure (up to 400 °C) as well as its chemical robustness towards hydrolysis, (ii) the excellent storage density of 1 I₂ per unit cell, which is comparable to the performance of most of the MOFs, (iii) the ability to the iodine capture both, in gas and solution, and (iv) the possibility to fully regenerate the structure by heating above 200 °C without any deterioration of the host framework. In the present work, we broadened our study on the iodine sorption to Hofmann clathrates analogues to emphasise how the building blocks nature influences the iodine sorption. In this aim, we limited ourselves to some compositions that met the following criteria: i) easiness of the clathrates' preparation with commercially available products and aerobic conditions, and *ii*) high crystallinity and same space group as the reference structure $Ni^{II}(pz)[Ni^{II}(CN)_4] \cdot 2H_2O$ to allow a better comparison. Thus, the present article describes the synthesis and the investigation of the iodine adsorption properties for a series of Hofmann-type frameworks $\dot{M}^{II}(pz)[\dot{M}^{,II}(CN)_4]$, where $M = Ni^{II}$, $Co,^{II} M' = Ni^{,II}$, Pd^{II} , Pt^{II} and pz =pyrazine. A particular emphasis is given on the understanding of the sorption mechanism as a function of the clathrate composition.

2 Experimental Section

2.1 Synthesis

All compounds used in the present experimental work, $Ni^{II}(NO_3)_2 \cdot 6H_2O$, $Ni^{II}(BF_4)_2 \cdot 6H_2O$, $Co^{II}(NO_3)_2 \cdot 6H_2O$, $K_2[Ni^{II}(CN)_4]$, pyrazine and solid iodine (99%) were purchased from Sigma-Aldrich or from Alfa-Aesar for $K_2[Pd^{II}(CN)_4]$ and $K_2[Pt^{II}(CN)_4]$ and employed without further purification. All reactions were carried out under aerobic conditions, with analytical grade solvents.

Synthesis of the clathrates M(L)[M'(CN)₄]·2H₂O.

The host structures M(L)[M'(CN)₄]•2H₂O were precipitated as microcrystalline powders, by adapting the previously published procedure.¹² In a typical synthesis, 3 mmol of the salt $M(NO_3)_2 \cdot 6H_2O$ or $M^{II}(BF_4)_2 \cdot 6H_2O$ (M = Ni^{II}, Co^{II}) were dissolved in a mixture of 20 ml of bidistilled water and 20 ml of methanol under stirring. Then, 3 mmol of the pyrazine were dissolved in a mixture of 20 ml of water and 20 ml of methanol and added to the first solution. Finally, 3 mmol of the tetracyanometallate salt $K_2[M'(CN)_4]$ (M' = Ni^{II}, Pd^{II} or Pt^{II}) were dissolved in 10 ml of distilled water and dropwise added to the reaction mixture, with instantaneous precipitation of a powder. The powders were recovered by centrifugation at 10000 rpm for 5 min and thoroughly washed three times with bi-distilled water and twice with methanol. Washing steps with acetone were also necessary to grind easily the solid to a fine powder. The powders were vacuum dried. The so-prepared powders presented as water clathrates, or hydrates, *i.e.* with water as guest molecules in the pores. The composition modulations that were

taken into account in the present work are (with respective calculated and found elemental analyses):

Ni^{II}(pz)[Ni^{II}(CN)₄]·2H₂O (violet powder). Anal. Calcd: C, 28.45; N, 24.89; Ni, 34.79. Found: C, 28.69; N, 25.26; Ni, 35.12.

Co^{II}(pz)[Ni^{II}(CN)₄]·2H₂O (pink powder). Anal. Calcd: C, 28.44; N, 24.88; Ni, 17.45; Co, 17.39. Found: C, 28.51; N, 25.21; Ni, 17.48. Co, 17.59.

Ni^{II}(pz)[Pd^{II}(CN)₄]·2H₂O (violet powder). Anal. Calcd : C, 24.95; N, 21.84; Ni, 15.26; Pd, 27.55 Found: C, 24.23; N, 22.07; Ni, 14.45; Pd, 26.53.

A deviation higher than 0.3% is obtained for this compound compared to expected values. Further analysis (EDX) showed that low amounts of KBF₄ salts may be present as the impurity for this compound (Ni/F = 2.8 and Ni/K = 11 that corresponds to less to *ca*. 3 wt% of KBF₄).

Ni^{II}(pz)[Pt^{II}(CN)₄]·2H₂O (violet powder). Anal. Calcd: C, 20.27; N, 17.73; Ni, 12.39; Pt, 41.17. Found: C, 20.26; N, 18.05; Ni, 12.77; Pt, 40.77.

 $Co^{II}(pz)[Pd^{II}(CN)_4]$ - $2H_2O$ (pink powder) : Anal. Calcd: C, 24.91; N, 21.80; Co, 15.28; Pd, 27.61. Found: C, 25.34; N, 21.98; Co, 15.54; Pd, 28.08.

In order to remove all trace of solvents all compounds were thermally activated at 80 °C under primary vacuum. For most of the compositions, except Ni^{II}(pz)[M''(CN)₄] with M'' = Pd^{II}, Pt^{II}, the removal of the guest water was accompanied by a change of colour, for instance, from violet to grey for Ni^{II}(pz)[Ni^{II}(CN)₄], from pink to violet-blue for Co^{II}(pz)[M'(CN)₄] (M' = Ni^{II}, Pd^{II}).

Iodine capture from cyclohexane solutions.

Iodine kinetic and isotherm investigations were performed on the thermally activated clathrates. Kinetic sorption tests were made at room temperature by detecting the decrease in the iodine concentration in cyclohexane (from an initial value of $3.5 \cdot 10^{-3}$ M) with a transmission UV-VIS spectrometer at different times, 5, 10, 20, 30, 60 and 180 min. For all materials except Ni^{II}(pz)[Pt(CN)₄], the absorbance of the iodine solution decreases rapidly and becomes constant after ~2 hours, indicating that the equilibrium is reached. For the platinum containing compound the equilibrium is achieved after 12 hours. For the adsorption isotherms, different iodine concentrations in the range $10^{-5} - 7 \cdot 10^{-2}$ M in cyclohexane were selected to determine the amount trapped by UV-VIS spectroscopy, as a function of the equilibrium concentration. Note that the iodine solubility limit in cyclohexane is close to $8 \cdot 10^{-2}$ M, so that it was not possible to use higher concentrations. The clathrates were kept 12 hours (to reach the equilibrium in all cases) at room temperature in dynamic contact with cyclohexane iodine solutions. The amount of the iodine absorbed in the materials was determined by measuring the residual concentration of iodine in solution by UV-VIS spectroscopy at the end of the experiment and confirmed by chemical analysis performed on the resulting solids. For all adsorption tests, we chose a powder-to-volume ratio of 0.332 mmol per 1 ml i.e: for a fixed volume of 20 ml, we used 20 mg of $Ni^{II}(pz)[Ni^{II}(CN)_4]$ (or $Co^{II}(pz)[Ni^{II}(CN)_4])$, 25 mg of Ni^{II}(pz)[Pd^{II}(CN)₄] (or Co^{II}(pz)[Pd^{II}(CN)₄]) and 29 mg of $Ni^{II}(pz)[Pt^{II}(CN)_4]$. For the synthesis of I₂-loaded clathrates with maximal iodine loading, the $7 \cdot 10^{-2}$ M iodine cyclohexane solutions were used. After 12 h of dynamic contact, the clathrates were filtered off, thoroughly washed with pure cyclohexane in order to eliminate the physisorbed iodine on the grain surfaces and vacuum dried.

Iodine capture in gas phase.

The gas phase iodine sorption tests were also performed on the thermally activated clathrates. For this, we used hermetically closed containers having two connected compartments. 0.332

mmol of a given dehydrated powdered host clathrate were placed in one compartment and 800 mg of solid iodine in a second one. We kept the closed container at 80 °C with homogeneous heating in an oil bath for 3 days in order to enhance the diffusion of the sublimated iodine inside the host structure. Once the system is cooled down, we removed the I₂-loaded clathrate and thoroughly washed with pure pentane with a soxhlet for 24 hours to eliminate the excess of the physisorbed iodine. The amount of iodine absorbed in the materials was determined from thermogravimetric analyses.

Desorption tests and cycling ability.

The iodine desorption from the host clathrates was performed by heating the solid at 200 °C under primary vacuum for 2 hours. For the Ni^{II}(pz)[Ni^{II}(CN)₄] and Ni^{II}(pz)[Pd^{II}(CN)₄] structures, we carried out 3 full cycles of adsorption-desorption process, both in solution and in vapours.

2.1 Characterization methods

The UV-VIS spectra in transmission mode for the detection of the residual concentration of iodine in cyclohexane were recorded on a SPECOORD 210 UV-VIS spectrometer. For the spectra in reflectance mode on the solid samples, a Perkin Elmer Lambda 35 spectrometer with integration sphere was used. A reference background was registered with BaSO₄ (white powder, 100% reflectance). The Infrared spectra in transmission mode for all materials were recorded in a dried KBr matrix on a Nicolet Model 510P spectrophotometer. The in-situ IR spectroscopic analyses for the adsorption of water on the Hofmann-type networks were performed on an Equinox55 (Bruker) spectrometer. For both techniques a background without the sample was recorded. Raman spectroscopic analyses were performed in reflectance mode for all materials on the solid samples with a LabRAM ARAMIS IR² (Horiba Jobin Yvon). Two lasers were employed to record the spectra: laser Helium Neon (HeNe), with $\lambda = 633$ nm and power 440 μ W, and laser D473, with $\lambda = 473$ nm and power 1.3 mW. X-Ray Powder Diffraction patterns (XRPD) for all materials were obtained over the interval $2\theta = 5.90$ range at room temperature with the Panalytical XPERTPro diffractometer mounted in a Debye-Sherrer configuration and equipped with a Cu K α or Cu K α_1 radiation. For the bulk Hofmann-type networks without iodine the XRPD patterns were measured in a 0.5 mm capillary, after sieving the powder with a 45 µm steel sieve. For the iodine-loaded materials, for which the introduction in the capillary was difficult, a planar configuration with fixed sample and rotating diffraction angle was preferred. The XRPD data were obtained with a long exposure of 12 hours (1000 s per step of 0.16°). The Miller planes of the Hofmann-type structures were indexed by simulating with the X-ray powder patterns with Mercury software, by using Crystallographic Information Files (CIFs) available in the literature for the analogue structure Fe^{II}(pz)[Pt^{II}(CN)₄].¹⁷ The unit cell parameters for the empty and iodine loaded solids were determined by a whole pattern fitting using the LeBail method (see SI).³¹ Elemental analyses were performed by the Service Central d'Analyse (CNRS, Villeurbanne, France). TGA analyses were performed by using a thermal analyser STA 409 Luxx (Netzsch) on the range 25 - 1000 °C at the speed 5 °C/min under air. The TGA coupled mass spectroscopy for the iodine-loaded materials was carried out on a Setsys Evolution 16-18 (Setaram) provided of the Calisto software combined with a mass spectrometer Hiden Analytical QGA with software MASsoft 7 Professional. SEM/EDX microscopy was performed on a FEI Quanta FEG 200 instrument. The powders were deposited on an adhesive carbon film and analysed under high vacuum. The quantification of the heavy elements was carried out with the INCA software, with a dwell time of 3 µs.

The electrical conductivity of the samples was recorded at 80 °C by Complex Impedance Spectroscopy (CIS) with a Novocontrol dielectric alpha analyzer, in the $10^{-2} - 10^{6}$ Hz frequency range. In order to prevent any destruction of the clathrate structure under an applied external pressure, conductivity measurements were not carried out on pellets prepared from compressed powder. The powder was thus introduced between two gold-coated electrodes in parallel plate capacitor configuration with an annular Teflon spacer for insulation. Prior to experiments, the empty materials were in situ treated at 200 °C for 2 hours under dried nitrogen flux, in order to ensure that the residual solvent molecules are fully removed. For the iodine loaded materials, the in situ treatment was limited to 80 °C to avoid any departure of the iodine guest as pointed out by TGA analysis. CIS gives access to the real part of the ac conductivity, which results, in many cases from the superposition of Maxwell Wagner Sillars, $\sigma_{MWS}(\omega, T)$, the dc conductivity, $\sigma_{dc}(T)$, and the polarization conductivity, $\sigma_{pol}(\omega, T)$ (Equation 1):

$$\sigma_{ac}(\omega, T) = \sigma_{MWS}(\omega, T) + \sigma_{dc}(T) + \sigma_{pol}(\omega, T)$$
(1)

where ω is the electric field angular frequency and T the temperature. Basically, *dc* conductivity corresponds to long-range redistribution of charges, *i.e.* ionic or electron transport, while the polarisation contribution arises from local rearrangement of charges or dipoles causing dipolar reorientation and thus resulting in the intrinsic bulk polarization. Maxwell Wagner Sillars polarisation is due to the accumulation of charges at the sample/electrodes interface and also depends on extrinsic parameters, such as the sample shape.

The crystal structures of the Hofmann-type clathrates $M(pz)[M'(CN)_4]$ (M = Ni, Co; M' = Pd, Pt) were built using a computational assisted structure determination approach³² starting with the Ni(pz)[Ni(CN)₄] structure model we previously reported.¹ The Ni atoms were subsequently substituted by the diverse cations and the unit cell parameters were imposed to that successfully indexed by XRPD for the I2 loaded samples (Table 1). All these structure models were then geometry optimized by maintaining fixed the experimental unit cell parameters and by using for all atoms of the frameworks the generic Universal Force Field (UFF)³³ for the van der Waals parameters and the partial charges extracted from the charge equilibration qEq method.34 The Ewald summation was employed to evaluate the electrostatic interactions while the van der Waals interactions (represented by a classical 12-6 Lennard-Jones (LJ) potential) beyond 14 Å were neglected. The resulting structures were further refined at the Density Functional Theory level using the PW91 GGA density functional³⁵ and the double numerical basis set containing polarization functions on hydrogen atoms (DNP)³⁶ available in the DMol³ code.³⁷ The absolute I₂ adsorption isotherms for all these so-built structures were computed up to 1 bar at 25°C using Grand Canonical Monte Carlo (GCMC) simulations with the CADSS code.38 The I2 molecule was represented by a diatomic uncharged LJ model (I-I bond remaining fixed at 2.66 Å) with potential parameters taken from the UFF force field.³³ Such a nonreactive force-field for I₂ implies that the calculations consider in a first approximation that iodine remains in its molecular state in the whole range of concentration. The I2-framework interactions were described by a repulsion-dispersion LJ term. The corresponding LJ parameters were calculated using the mixing Lorentz-Berthelot combination rules. The GCMC simulations considered a simulation box of 64 (4 \times 4 \times 4) unit cells with typically 2 \times 10⁸ Monte Carlo steps and a cut-off distance of 14 Å for the short-range interactions. The I₂ adsorption enthalpy was calculated at low coverage for all the structures using the revised Widom's test particle method.³⁹ The preferential location of I2 was further analysed at the saturation by a carefully analysis of the configurations generated at 1 bar.

3 Results and Discussion

A Synthesis of Hofmann-like clathrates $M(pz)[M'(CN)_4]$ (M = Ni^{II}, Co^{II} and M' = Ni^{II}, Pd^{II}, Pt^{II}) and pz =pyrazine.

The synthesis of a series of the Hofmann-type clathrates was performed by reaction between M(NO₃)₂·6H₂O or M(BF₄)₂·6H₂O salts ($M^{II} = Ni^{II}$, Co^{II}) with a tetracyanometallate $K_2[M'(CN)_4]$ (M^{II} , = Ni^{II} , Pd^{II} , Pt^{II}) precursor and a bidentate pyrazine ligand in a water/methanol mixture, by adapting the synthesis for $Fe^{II}(pz)[Ni^{II}(CN)_4]$ ·2H₂O published by Niel *et al.* (see Experimental Section).¹⁷ The hydrated compounds $M(pz)[M'(CN)_4] \cdot 2H_2O$ (M = Ni^{II}, Co^{II} and M' = Ni^{II}, Pd^{II}, Pt^{II}, pz = pyrazine) were obtained as microcrystalline powders (Fig. 1, Fig. S1, Electronic Supporting Information (ESI)) and characterized by spectroscopy and X-Ray Powder Diffraction (XPRD). Infrared (IR) spectroscopy confirmed the presence of the M'-CN-M coordination mode by the relevant cvanide stretching vibrations observed in the 2165 - 2186 cm⁻¹ range, which are shifted to higher wavenumbers in comparison with the respective tetracyanometallate precursors (initially at 2121 cm⁻¹ for $K_2[Ni^{II}(CN)_4]$; 2134 cm⁻¹ for $K_2[Pd^{II}(CN)_4]$ and $K_2[Pt^{II}(CN)_4]$; Table 1, Fig. S2, ESI).^{12, 17} The same feature is observed with $\delta(M')$ -CN), which is initially situated at 416 cm⁻¹ and at 400 cm⁻¹ for $K_2[Ni^{II}(CN)_4]$ and $K_2[M^{II}(CN)_4]$ (M = Pd, Pt) tetracyanometallate precursors respectively and which is blue shifted $(422 - 471 \text{ cm}^{-1})$ after coordination of the cyanometallate toward the bivalent transition metal (Table 1, Fig. S2, ESI). The coordination of the pyrazine ligand to M^{II} is also confirmed by the occurrence of the $\delta(M-N_{pz})$ bands at 485 cm⁻¹ for Ni^{II}-N_{pz} and at 474 cm⁻¹ for Co^{II}-N_{pz} (Fig. S2, ESI). The reference values were measured experimentally from the related metal-pyrazine complexes. Note that IR spectra for Co^{II}-based compounds in the octahedral position show shifts of the $v(C\equiv N)$ and $\delta(M-N_{pz})$ modes toward lower wavenumbers in comparison with the Ni-based ones. This observation supports a weaker coordination of Co^{II} to cyanometallate moieties than Ni^{II}. On the contrary, the replacement of the square planar Ni^{II} with Pd^{II} and Pt^{II} in $[M'(CN)_4]^{2-}$ induces the shift of the v(C=N) vibrations modes toward higher wavenumbers (Table 1), while the IR mode $v(M-N_{nz})$ did not change since it was not affected by M'.

XRPD analysis indicates that all obtained compounds are isostructural to the previously reported Fe^{II}(pz)[Pt^{II}(CN)₄] analogue (Fig. 2).¹⁷ Lebail analysis carried out to model the XRPD data demonstrated that the materials crystallize in a tetragonal *P4/m* space group with the cell parameters summarized in Table 1 (see Lebail refinements, ESI). Note that: (*i*) the use of the Co^{II} results in a slightly larger unit cell with respect to the Ni^{II} cation, since the coordination strength M^{II} - ligand for Ni^{II} is higher than for Co^{II}, and (*ii*) the Ni^{II}(pz)[Pd^{II}(CN)₄]·2H₂O and Ni^{II}(pz)[Pt^{II}(CN)₄]·2H₂O compounds show a slightly larger unit cell with respect to Ni^{II}(pz)[Ni^{II}(CN)₄]·2H₂O due to an increase of the *back donation* M'→C≡N⁻ in the range Ni^{II} < Pd^{II} < Pt^{II}.

TGA curves for all compounds indicate a start for the water molecules loss at 100 °C, but the temperature of the complete water remove depends on the metal ions nature (Fig. S3, ESI). A treatment at 80 °C under primary vacuum for 8 h was chosen for a complete dehydration of the host structures. The XRPD analyses performed on both, hydrated and dehydrated compounds, led to a perfect overlap of the patterns with no relevant lattice change upon water removal, as it was previously reported by Niel *et al.*¹⁷ Note also that all compounds exhibit an excellent thermal stability up to 350 – 450 °C (Table 1). The decomposition temperatures show that the compounds with $M^{II} = Ni^{II}$ present a better stability upon heating in comparison with the Co^{II}-based ones, that is in agreement with the weaker coordination of Co^{II} in the octahedral position to the cyanometallate moiety also observed by IR. On the contrary, the replacement of the square planar Ni^{II} with Pd^{II} and Pt^{II} gave

increased thermal stabilities: for instance up to 425 and 450 °C for respectively $Ni^{II}(pz)[Pd^{II}(CN)_4]$ and $Ni^{II}(pz)[Pt^{II}(CN)_4]$ instead of 400 °C for $Ni^{II}(pz)[Ni^{II}(CN)_4]$. Several attempts have been performed in order to determine the porosity and the surface area of our materials with He. Unfortunately, these attempts failed due to the very long equilibrium time (several days without equilibrium achieved) and the very low pressure to realise.



Fig. 1. Photographs of the $M(pz)[M^{1}(CN)_{4}] \cdot 2H_{2}O$ powders ($M = Ni^{II}$, Co^{II} and $M' = Ni^{II}$, Pd^{II} , Pt^{II}) before (top) and after iodine entrapment (bottom).



Fig. 2. X-Ray powder diffraction patterns for $M(pz)[M'(CN)_4]$ ($M = Ni^{II}$, Co^{II} and $M' = Ni^{II}$, Pd^{II} , Pt^{II} and pz = pyrazine) before and after maximal iodine adsorption in cyclohexane solution.

B Iodine entrapment in liquid and gas phases.

The thermally activated host structures were used for the adsorption of iodine both, in cyclohexane solution and in gas phase (see Experimental Section). Cyclohexane was used as a solvent since we were interested in the interaction with the molecular I_2 (*i.e.* no dissociative charge transfer with the solvent). Kinetic studies were performed at an iodine concentration of $3 \cdot 10^{-3}$ M in order to determine the equilibrium time and the reaction order. For these experiments, the host materials (powder-to-volume ratio of 0.332 mmol per 1 ml of solution) were shaken with 20 ml of the iodine solution in cyclohexane for different time periods up to 12 h and the residual concentration of iodine in solution was measured by using UV-VIS electronic spectroscopy. All kinetic curves were fitted with a pseudo-second order model⁴⁰ (Fig. 3) following the formula:

$$Q = \frac{kQ_e t}{1 + kQ_e^2 t},$$

where Q (mmol.g⁻¹) is the amount of entrapped iodine at time t (min), Q_e is the entrapped amount at equilibrium $(t \to \infty)$ and k (g.mmol⁻¹.min⁻¹) is the kinetic constant. The curves show that the iodine capture is quite rapid for all compounds with the equilibrium reached after 2 hours except Ni^{II}(pz)[Pt^{II}(CN)₄], for which the process is quite longer with $t_{eq} = 12h$ (Table 2). Note also that the kinetic constants for the clathrates with M^{II} = Co are slightly higher with respect to Ni^{II}-based ones (Table 2).



Fig. 3. Iodine sorption kinetic curves in a cyclohexane solution for $M^{II}(L)[M^{\prime II}(CN)_4]$ ($M = Ni^{II}$, Co^{II} and $M^{\prime} = Ni^{II}$, Pd^{II} , Pd^{II} and pz = pyrazine) at room temperature. The solid line represents the fit with the pseudo-second order model.



Fig. 4. Iodine adsorption isotherms in a cyclohexane solution for $M(pz)[M'(CN)_4]$ ($M = Ni^{II}$, Co^{II} and $M' = Ni^{II}$, Pd^{II} , Pt^{II} and pz = pyrazine) at room temperature. The solid line represents the fit with the Langmuir model.

For a complete characterization of the iodine uptake, sorption isotherms were obtained by the iodine capture in cyclohexane solution at increasing iodine concentrations in the solubility range (*i.e.* under $8 \cdot 10^{-2}$ M *i.e.* 21 g.L⁻¹). The entrapped amount *vs* equilibrium concentration curves were fitted with the Langmuir model⁴¹ since all show the trend of the I-type isotherm which is typical, according to the IUPAC conventions, for monolayer-limited adsorptions (Fig. 4). This model is described by the following formula:

$$\frac{Q_e}{Q_{max}} = \frac{KC}{1+KC},$$

where Q_e (mmol.g⁻¹) is the amount of entrapped iodine at equilibrium concentration *C* (mol.L⁻¹), Q_{max} (mmol.g⁻¹) is the maximal capacity at the saturation and *K* is the Langmuir constant (l.mol⁻¹).

All isotherms present a concave trend with a steep increase at low concentration indicating a relatively high affinity for iodine. The maximal adsorption capacity (Q_{max}), which is indicative of the efficiency of the compounds to capture I₂ determined from the plateau of the isotherm is in the range 2.86 - 3.28 mmol.g⁻¹ (76 - 83 wt %), which corresponds to the adsorption of 1 mole of I₂ per mole of clathrate for all compounds, except Ni^{II}(pz)[Pt^{II}(CN)₄] (Table 2). The latter shows a maximal capacity of 1.14 mmol.g⁻¹ (29 wt %) corresponding to 0.5 mole of I₂ per mole of compound. The Q_{max} values obtained from the isotherm fitting with the Langmuir model are very similar for all solids as summarised in Table 2. The amount of the captured iodine by the host structures was confirmed by the TGA analysis performed for the compounds with the maximal iodine loading (Fig. S4, ESI).

The iodine adsorption isotherms simulated for $M^{II}(pz)[M^{,II}(CN)_4]$ $(M^{II} = Ni^{II}, Co^{II}$ and $M^{,III} = Ni^{II}$, Pd^{II}) are reported in Fig. 5. All are of Langmuir-type in shape and the absolute uptakes at saturation, *i.e.* 1 I₂ molecule per unit cell, are in very good agreement with the experimental data (Fig. 4). We observe that the nature of the M^{II} and $M^{,III}$ metal slightly affects the overall isotherm profile with only small changes at the initial stage of adsorption. This latter point is consistent with the similar adsorption enthalpies predicted by GCMC calculations, *i.e.* -50.2, -48.0 and -50.5 kJ/mol for $Co^{II}(pz)[Ni^{II}(CN)_4]$, $Ni^{II}(pz)[Ni^{II}(CN)_4]$ and $Ni^{II}(pz)[Pd^{,II}(CN)_4]$ respectively.



Fig. 5. Iodine adsorption isotherms simulated at 298 K for $M^{II}(pz)[M^{3II}(CN)_4]$ $(M^{II} = Ni^{II}, Co^{II} and M^{3II} = Ni^{II}, Pd^{II})$. The inset represents the data for the low pressure domain represented in semi-logarithm scale.

The iodine capture by the Hofmann clathrates was also investigated in gas phase. For this, the thermally activated compounds were exposed to I₂ vapour at 80 °C (iodine vapour pressure about 1 kPa) in a closed adsorption chamber during 72 h. The I₂ uptake from the gas phase determined from TGA curves is in the range 2.32 - 3.32mmol.g⁻¹ (or 59 – 84 wt%) for M^{II}(pz)[M^{II}(CN)₄] (M = Ni, Co, M' = Ni, Pd), that corresponds to 0.8 moles of I_2 per mole of Ni^{II}(pz)[Ni^{II}(CN)₄] and 1 moles of I_2 per mole of others clathrates (Fig. 6, Table 2). Only Ni^{II}(pz)[Pt^{II}(CN)₄] shows a lower capacity equal to 1.14 mmol.g⁻¹ (or 29 wt%) corresponding to 0.5 moles of I_2 per mole of compound (Fig. 6, Table 2), similarly to the iodine loading in solution. Thus, the amount of the captured iodine is comparable in gas phase and in solution, but the kinetics in the gas phase are much slower: 3 days in gas phase versus 2 h in cyclohexane solution.

Note that the slightly lower capacity of $Ni^{II}(pz)[Ni^{II}(CN)_4]$ in gas phase in comparison with the one in cyclohexane may be explained by its particular affinity with water, which enters in competition with iodine during the adsorption process in gas phase. In order to confirm this hypothesis, the iodine capture was performed in gas phase in the presence of water (see ESI). A 37% decrease (0.5 I₂/ unit cell) of the iodine uptake at saturation was observed for Ni^{II}(pz)[Ni^{II}(CN)₄], while Co^{II}(pz)[Ni^{II}(CN)₄] maintains a relatively high maximal capacity of 0.8 I₂/unit cell. It was indeed detected by spectroscopic analyses that the Ni²⁺-containing structures form more stable complexes with adsorbed water than the Co²⁺-containing ones (see ESI).



Fig. 6. TGA curves for a series of Hofmann clathrate hosts $M(pz)[M'(CN)_4] \cdot I_2$ ($M = Ni^{II}$, Co^{II} and $M' = Ni^{II}$, Pd^{II} , Pt^{II} , pz = pyrazine) and $Ni(pz)[Pt(CN)_4] \cdot I$ obtained by iodine loading in gas phase.



Fig. 7. Mass-spectroscopy curves for $M(pz)[M^{2}(CN)_{4}]\cdot I_{2}$ ($M = Ni^{II}$, Co^{II} and $M^{2} = Ni^{II}$, Pd^{II} , Pt^{II} , pz = pyrazine) and $Ni(pz)[Pt(CN)_{4}]\cdot I$ obtained by iodine loading in gas phase showing the iodine desorption.

	Space group	<i>a; b</i> [Å]	C [Å]	Volume of the unit cell [Å ³]	v(C≡N) [cm ⁻¹]	$\begin{array}{c} \delta(\text{M-CN}) \\ [\text{cm}^{\text{-1}}] \end{array}$	T_{dec} °C
Ni ^{II} (pz)[Ni ^{II} (CN) ₄]·2H ₂ O	P4/m	7.17	7.03	362.1	2174	444	400
$Ni^{II}(pz)[Ni^{II}(CN)_4]\cdot I_2$	P4/m	7.26	7.00	369.1	2165	442	400
Co ^{II} (pz)[Ni ^{II} (CN) ₄]·2H ₂ O	P4/m	7.22	7.15	373.1	2167	442	350
Co ^{II} (pz)[Ni ^{II} (CN) ₄]·I ₂	P4/m	7.15	6.89	353.3	2178	465	350
Ni ^{II} (pz)[Pd ^{II} (CN) ₄]·2H ₂ O	P4/m	7.33	7.03	378.7	2188	428	425
Ni ^{II} (pz)[Pd ^{II} (CN) ₄]·I ₂	Pmmm	7.43; 7.22	7.04	377.8	2178	428	425
Co ^{II} (pz)[Pd ^{II} (CN) ₄]·2H ₂ O	P4/m	7.38	7.14	398.8	2179	422	350
$Co^{II}(pz)[Pd^{II}(CN)_4]\cdot I_2$	Pmmm	7.32; 7.16	6.98	366.0	2183	428	350
Ni ^{II} (pz)[Pt ^{II} (CN) ₄]·2H ₂ O	P4/m	7.32	7.02	376.8	2186	471	450
Ni ^{II} (pz)[Pt ^{II/IV} (CN) ₄]·I ⁻	P4/m	7.17	6.97	358.9	2186; 2200	469	450

Table 1. Structural characteristics of a series of Hofmann-type clathrates $M(pz)[M'(CN)_4]$ (M = Ni^{II}, Co^{II} and M' = Ni^{II}, Pd^{II}, Pt^{II}).

The mass spectroscopy associated with the TGA analyses showed that the captured iodine (in solution and in gas phase) can be thermally released from the hosts in the range 180 - 230 °C (peak's maxima), except iodine loaded Ni^{II}(pz)[Pt^{II}(CN)₄] exhibiting the peak at 340 °C (Fig. 6, Fig. 7, Table 2, Fig. S4, ESI). This observation highlights different natures of captured iodine by the Niversion compared to the other metals. Note that in the previously investigated MOF materials the desorption temperature for molecular iodine (around 150 – 200°C) is much lower⁴¹ than the desorption temperature of polyiodides (at around 300 °C).¹⁰ Ni^{II}(pz)[Pt^{II}(CN)₄] is indeed expected to adsorb polyiodides species while the adsorption in the other forms is limited to molecular iodine.⁴²

In order to get more insight into the iodine sorption mechanism and the nature of the absorbed iodine, the investigated Hofmann-type clathrates with maximal iodine loading were characterized by means of vibrational spectroscopy and XRPD. All FT-IR spectra of samples $M(pz)[M'(CN)_4] \cdot I_2$ (M = Ni, Co and M' = Ni, Pd) after iodine loading in solution or in gas phase indicate that the cyanide stretching vibration v(CN) slightly shifts upon iodine insertion indicating an interaction between the iodine and the cyano group of the tetracyanometallate moiety (Table 1, Fig. S2, SI). Three main tendencies may be clearly evidenced: (i) the v(CN) mode decreases for the Ni^{II}-containing hosts due to a weak transfer of the electron density from π -bonding orbital of the cyano ligand to the σ^* antibonding orbital of iodine, (*ii*) the v(CN) mode slightly increases for Co^{II}-based hosts probably due to the intensification of the $\sigma(Co^{II}-NC)$ bonding through weak interactions of cyanide ligand with iodine molecule, and (iii) a little shift of the band v(M -N_{pyrazine}) is detected indicating only a small effect on the coordination with pyrazine. Note that no change in the oxidation state of the metal ions in $M(pz)[M'(CN)_4] \cdot I_2$ (M = Ni, Co and M' = Ni, Pd) after iodine loading was observed by XPS experiments (Fig. S5, SI), which clearly indicates an absence of redox processes involving metal centres. The iodine sorption by Ni(pz)[Pt(CN)₄] induces the change of the platinum oxidation state from Pt^{II} to Pt^{IV} as previously reported for the isostructural compound.⁴² Indeed, the confinement of iodine molecules in these clathrates is achieved through the formation of weak interactions with both pyrazine and coordinated cyanometallates moieties. This was further confirmed by a very similar preferential arrangement of I₂ evidenced by GCMC simulations in the clathrates series as illustrated in Fig. 8. In all cases, the iodine molecules are homogeneously distributed in the middle of the channels leading to relatively weak interactions with both the cyano groups and the pyrazine (interacting distances ranging from 3.4 to 3.6 Å) consistent with the conclusion gained from the analysis of the FT-IR spectra.

Raman spectra of all iodine loaded clathrates M(pz)[M(CN)₄]·I₂ (M = Ni, Co, M' = Ni, Pd) show two peaks in the spectral window 100 -200 cm⁻¹ (Fig. 9 and Fig. S6, SI). The first large peak occurs at 163 -168 cm⁻¹ and the position of this peak is only slightly shifted as a function of the clathrate composition. The second peak situated in the 105 - 116 cm⁻¹ range is more sensitive to the nature of the metal ion involved in the cyanometallate moiety (Ni or Pd): the peak for $M(pz)[Pd(CN)_4] \cdot I_2$ (115, 116 cm⁻¹) is shifted toward higher wavenumbers in comparison with M(pz)[Ni(CN)₄]·I₂ (104, 108 cm⁻ ¹). The interpretation of Raman spectra of the confined iodine and polyiodides is quite difficult and fairly controversial in the literature. The stretching frequency of free iodine in the solid state is at about 180 cm⁻¹ (v_1 mode) and shifts to lower wavenumbers (around 170 cm⁻¹) when iodine interacts with a species that can donate electron density into its σ^* antibonding orbital.^{43, 44} The higher the interaction strength, the low the force constant and the more the v_1 mode decreases. In the case of iodide formation, the symmetric and the asymmetric stretching of I_3 classically appear as strong peaks at 150 cm⁻¹ and 103 cm^{-1.45} However, some studies report these Raman frequencies at 167 and 110 cm⁻¹ with a presence of weak peaks at 143 and 114 cm^{-1.46} The situation is more complicated for I_5^- , which can be found in V- or L- shaped configurations. They present three peaks at 110(w), 144(m) and 167(s) cm⁻¹ for the former and at 106(w), 135(m) and 167(s) cm⁻¹ for the later.⁴⁷ Note however that the intensity of the low-frequency peak is weak in both configurations. In this line of thought, the two main peaks observed in Raman spectra of the iodine loaded clathrates may be attributed to the v_1 symmetric mode of confined molecular iodine in the cages for the low frequency band $(163 - 168 \text{ cm}^{-1})$ and the presence of the polyiodides species, such as I_3^{-} { I_1^{-} , I_2 } together with the I_2 molecule for the low frequency band $(105 - 116 \text{ cm}^{-1})$.⁴⁸ Their formation is possible, but in small quantity, since they are probably due to the presence of few lattice defects in the clathrate networks because : (i) no change in the oxidation state of the cyanometallate moieties is observed by XPS analysis, (ii) the results from mass spectroscopy clearly indicates a desorption of molecular iodine and (iii) no chemical reasons for an important iodide formation are offered by the clathrate system because no redox process is occurring with the metal ions of the cyanometallate moiety and no adduct formation with a charge transfer involving the pyrazine ligands strongly coordinated to metal ions were observed.

	t _{eq} [h]	K _{kin}	Q _{max} [mmol.g ⁻¹]	<i>Q_{max}</i> [mol.mol ⁻¹]	Q _{max} [mol.g ⁻¹] in gas	T _{desorp} [°C]	ν(I-I) [cm ⁻¹]	ν(I-I-I) [cm ⁻¹]	ν(Pt ^{IV} -I) [cm ⁻¹]	Change in V _{unit celle} , %
Ni ^{II} (pz)[Ni ^{II} (CN) ₄]·I ₂	2	0.14	3.32	1.0	0.8	150	168	104	-	+ 2
Co ^{II} (pz)[Ni ^{II} (CN) ₄]·I ₂	2	0.28	3.28	1.0	1.0	180	163	108	-	-5
$Ni^{II}(pz)[Pd^{II}(CN)_4]\cdot I_2$	2	0.15	2.97	1.0	1.0	140	167	115	-	negligible
$Co^{II}(pz)[Pd^{II}(CN)_4]\cdot I_2$	2	0.29	2.86	1.0	1.0	170	165	116	-	-5
Ni ^{II} (pz)[Pt ^{II/IV} (CN) ₄]·I ⁻	12	0.04	1.14	0.5	0.5	250	-	-	129	-5





Fig. 8. Preferential arrangement of I_2 in $M^{II}(pz)[M^{*II}(CN)_4]$, including $Co^{II}(pz)[Ni^{II}(CN)_4]$ (a) and $Ni^{II}(pz)[Pd^{II}(CN)_4]$ (b), obtained by MC simulations at 298 K for a loading of 1 mol/clathrate mol (representation in the ac plane). Color code: light blue, Ni; green Co; magenta Pd; grey, C; dark blue, N, brown, I. The distances are reported in Å for I_2/CN (blue) and I_2/pz (red).

Different conclusions maybe done considering Ni(pz)[Pt(CN)4] after iodine encapsulation. Its FTIR spectrum shows two vibrations for the CN⁻ ligands, at 2186 and 2200 cm⁻¹. The first one is unchanged in comparison with the iodine free clathrate and it may be attributed to the bridging Pt^{II} - CN - Ni^{II} vibration, while the second one is assigned to the presence of the Pt^{IV} - CN - Ni^{II} bond highlighting the partial change of the oxidation state of Pt. The Raman spectrum of iodine loaded Ni^{II}(pz)[Pt^{II}(CN)₄] is also different in comparison with other Hofmann clathrates and demonstrates the presence of a single band at 129 cm⁻¹ characteristic of v(Pt^{IV}-I). This result is in agreement with the previously published work on the synthesis of $Fe(pz)[Pt^{IIIV}(CN)_4] \cdot I^{.42}$ In such a compound, 50 % of the Pt^{II} sites were oxidized to Pt^{IV} by the iodine and an oxidative addition of two reduced iodides onto the PtIV occurred with the concomitant formation of the covalent bond PtIV-I observed in gas phase and in solution. This different nature of the inserted iodine explains the low absorption kinetic observed for this compound involving chemisorption mechanism and low maximal capacity of 0.5 I₂ per clathrate as well as higher desorption temperature in comparison with others investigated clathrates.

In order to further confirm this conclusion, the ionic conductivity of the empty and the iodine saturated $Ni^{II}(pz)[Ni^{II}(CN)_4]$ and Ni^{II}(pz)[Pt^{II}(CN)₄] samples was measured (Fig. 10a, b). The low values of the polarization conductivity combined with the absence of the dc conductivity signal indicates that both $Ni(pz)[Ni(CN)_4]$ and $Ni(pz)[Pt(CN)_4]$ are insulator. This implies the absence of electrical charges diffusing into the bulk or at the surface of the empty solid. The scenario drastically differs for Ni^{II}(pz)[Ni^{II}(CN)₄]·I₂: σ_{ac} increases at low frequency by 5 orders of magnitude compared to the signal recorded for the empty solid. This is related to the presence of a dc plateau associated with the long-range transport of charge carriers created during the iodine trapping. This observation suggests that the diffusion process is assisted by the iodine molecules, the charge transport being propagated via the association of the iodine molecules along the tunnel pores.^{12b} The same electric behaviour was obtained for $Co^{II}(pz)[Ni^{II}(CN)_4] \cdot I_2$ and $Ni^{II}(pz)[Pd^{II}(CN)_4] \cdot I_2$ (Fig. S7, SI). This is consistent with the similar I_2 /host interaction and I_2 arrangements as evidenced by GCMC simulations. On the opposite, an unexpected trend was observed for the Pt-based clathrate, for which the electrical signal remains unchanged upon iodine adsorption (Fig. 10b). This suggests that the motion of the guest species is hindered and that there is no further charge carrier propagation within the porous solid. This observation is consistent with the creation of the Pt^{IV}-I species, resulting from the oxidative reaction evidenced for Ni^{II}(pz)[Pt^{II}(CN)₄]·I₂.⁴²



Fig. 9. Raman spectra for $M(pz)[M'(CN)_4]\cdot I_2$ ($M = Ni^{II}$, Co^{II} and $M' = Ni^{II}$, Pd^{II} , Pt^{II} , pz = pyrazine) and $Ni(pz)[Pt(CN)_4]\cdot \Gamma$ obtained by iodine loading in cyclohexane solution.



Fig. 10. Real part of the conductivity as a function of the frequency, recorded at 80 °C for the empty (dashed line) and the iodine loaded (solid line) $Ni^{II}(pz)[Ni^{II}(CN)_4]$ (a) and $Ni^{II}(pz)[Pt^{II}(CN)_4]$ (b).

Finally, the XRPD of $M^{II}(pz)[M'^{II}(CN)_4] \cdot I_2$ (M = Ni^{II}, Co^{II} and M' = Ni^{II}, Pd^{II}) and Ni(pz)[Pt^{II/V}(CN)_4] \cdot I samples after contact in solution

and in gas phase shows slight modifications: the general shift to lower values of 100 and 200 and a slight shift to higher angles of 001 and 002 peaks (Fig. 1, Fig. S8, ESI, Lebail refinements in ESI : Fig. S14-S23). The obtained lattice parameters and the unit cell volumes are reported in Table 1. The unit cell for $Ni^{II}(pz)[Ni^{II}(CN)_4] \cdot I_2$ remains tetragonal (*P4/m*), but it undergoes a slight expansion with a small increase (*i.e.* 0.084 Å) of the *a* and *b* cell parameters along the tetracyanonickelate planes and thus, an increase of the unit cell volume by 2% after iodine loading. For the $Co^{II}(pz)[Ni^{II}(CN)_4] \cdot I_2$ compound, the XRPD clearly indicates that the lattice adaptation is different, since we could detect a more significant shift of the diffraction peaks: all Miller planes (001), (002), (100) and (200) are shifted to higher angles and a slight shift for planes (110) and (111) is detected as well. The Lebail refinement indicates that the cell parameters decrease (i.e. 0.265 Å for c and 0.066 Å for a and b parameters) inducing a unit cell contraction by 5% upon iodine uptake (Table 1).

The XRPD pattern of Ni^{II}(pz)[Pd^{II}(CN)₄]·I₂ shows the appearance of a new peak at $2\theta = 25^\circ$, which is exclusively visible when the host structure is filled with iodine. It may be interpreted as a change from a tetragonal to an orthorhombic lattice with a new peak associated with the splitting of the 200 reflexion in 200 and 020 after iodine uptake. Note that the unit cell volume before and after the iodine insertion did not change: the increase of the parameter a was indeed accompanied by the decrease of b and c and their product remained extremely close to the initial volume of 378 Å³. The change of the space group from a tetragonal to an orthorhombic is also observed in the case of $Co^{II}(pz)[Pd^{II}(CN)_4] \cdot I_2$. The unit cell volume undergoes a contraction by 8% upon iodine insertion. Also, a new peak occurred at $2\theta = 25^{\circ}$ indicating a change of the unit cell upon iodine uptake from tetragonal to orthorhombic. By comparison with the previous studies, we could consider this complex lattice adaptation as the overlapping of two contributions: the contraction of the unit cell is the typical response when the Co^{II} occupies the octahedral position and the change of space group is the typical lattice adaptation that is detected when the square planar [Pd^{II}(CN)]²⁻ is employed. Notably, the IR mode v(C=N) shifted to higher values, following the same trend as Ni^{II}(pz)[Pd^{II}(CN)₄] \cdot I₂, where interactions between I₂ and the cyanide ligand induces the intensification of $\text{Co}^{\text{II}}\text{-NC}\,\sigma$ bonding. The oxidative addition that occurred in the case of Ni^{II}(pz)[Pt^{II}(CN)₄] after iodine treatment provokes a contraction of the unit cell, as the XRPD and LeBail refinement indicates. Indeed, the partial oxidation from $\mathsf{P} t^{\mathrm{II}}$ to $\mathsf{P} t^{\mathrm{IV}}$ induces a depopulation of the weakly antibonding orbitals of the CN with a consequent bond strengthening.

In order to summarize the effect of the lattice adaptation on the iodine loading, the typical iodine Raman signals in the range 80-200 cm⁻¹ as well as the desorption temperatures determined by TGA-mass spectroscopy are plotted versus respective unit cell volumes of Hofmann clathrates (Fig. 11). This analysis shows that a nearly linear relationship exists for both, the Raman band of confined iodine and its desorption temperature *vs.* the unit cell volume. The smallest unit cell exhibited by $Co(pz)[Ni(CN)_4]$ ·I₂ demonstrates the larger Raman blue shift and the higher desorption temperature. Thus, it may be considered as the best candidate for the selective entrapment of iodine.

On the opposite end, we find $Ni(pz)[Pd(CN)_4] \cdot I_2$ with the largest unit cell, the weakest Raman blue shift and the lowest desorption temperature.





Fig. 11. Plotting of desorption temperatures and Raman stretching mode of the confined iodine as function of the final unit cell volume at maximal capacity and (grey inset) evolution of the unit cell volume from the empty host structure to the filled structure.

C Reversibility of the iodine sorption.

The desorption and iodine loading reversibility were investigated for $M(pz)[M'(CN)_4]\cdot I_2$ (M = Ni, Co and M' = Ni, Pd) Hofmann clathrates. For this, the fully I₂ loaded materials (obtained in solution or in gas phase) were heated during 2 h at 300 °C under a continuous flow of argon inducing total removing of I₂ from the frameworks and giving the empty clathrates. The FTIR spectroscopy data (Fig. S2, SI) as well as PXRD (Fig. S9, SI) obtained after the heat treatment gave perfectly overlapping spectra and patterns as the ones before iodine loading indicating the possibility of a full regeneration. On the contrary, the iodine desorption for Ni(pz)[Pt^{II/IV}(CN)₄]·I⁻ performed at 400 °C is accompanied by the compound's decomposition. This fact excludes any possibility of a full regeneration of the structure, consistent with a charge transfer, *i.e.* an oxidative reaction between Pt and I₂.

The cycling ability of clathrates was tested on two examples, $Ni(pz)[M'(CN)_4]\cdot I_2$ (M' = Ni, Pd), by repeating the adsorptiondesorption process in solution and in gas overall three times. Comparable capacities for the third cycle were obtained for both compounds. PXRD patterns after three cycles of iodine entrapment in both conditions and after respective desorption indicate good structural stability and complete recovery of the host framework (Fig. S10, ESI).

4 Conclusion

The synthesis of a series of hydrated Hofmann-type clathrates $M^{II}(pz)[M^{\cdot II}(CN)_4]\cdot 2H_2O$ (M = Ni^{II}, Co^{II} and M' = Ni^{II}, Pd^{II}, Pt^{II}) was performed with the aim to investigate the iodine adsorption in the gas and liquid phases. The obtained coordination frameworks were characterized by spectroscopy and XRPD which prove that all obtained compounds are isostructural to the previously reported Fe^{II}(pz)[Pt^{II}(CN)_4] analogue and crystallize in a tetragonal system with a *P4/m* space group. These frameworks present cavities of 7 Å diameter tailored for insertion of molecular iodine with size of 5 Å. This fact and the good thermal stability of the networks in the temperature range 350 – 400 °C makes them interesting candidates for the iodine capture. Note however that the thermal stability of Co^{II}-based compounds was found slightly lower in comparison to the Ni^{II}-based one due to the weaker coordination of the former metal ion to the cyanometallate moiety. On the contrary, the

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tetracyanopalladate and tetracyanoplatinate precursors guarantee higher stability in comparison to the tetracyanonickelate.

The thermally activated series of clathrates were used for the iodine capture experiments in gas phase and in cyclohexane solution. In cyclohexane, the kinetic for these materials is very rapid with an equilibrium time of 2 hours except Ni^{II}(pz)[Pt^{II}(CN)₄] for which the process is quite longer with the equilibrium attained after 12 hours. All isotherms exhibited a steep increase at low concentrations and a plateau at maximal capacity, indicating an excellent affinity and a type I profile (adsorption of a monolayer). The maximal adsorption capacity is of 1 mole I₂ per mole of clathrate giving the final formula of $M^{II}(pz)[M'^{II}(CN)_4] \cdot I_2$ for $M = Ni^{II}$, Co^{II} and $M' = Ni^{II}$, Pd^{II} . This observation is in good agreement with the optimal uptake predicted by Monte Carlo simulations. For the gas phase, the kinetics are slower (12 h), but the adsorption capacity is close to that of the liquid phase. In addition, in the gas phase, water enters in competition with iodine during the adsorption process reducing the sorption capacity of $Ni^{II}(pz)[Ni^{II}(CN)_4]$ (0.8 mole of I_2 per unit cell) due to its particular affinity with water. However others clathrates retain their capacity (1 mole of I2 per unit cell) in gas phase. The large presence of water steam had an unfavourable effect on the storage capacity especially for the structures containing Ni²⁺ cations, rather than Co^{2+} . Note that the iodine adsorption capacities in both, solution or in the gas phase observed for $M^{II}(pz)[M^{,II}(CN)_4] \cdot I_2$ for M = Ni^{II} , Co^{II} and $M' = Ni^{II}$, Pd^{II} are comparable to what has already been observed for certain MOFs materials: 1.5 I₂ / Cu for the Cu-btc, $0.5 I_2$ / Cu for the [Cu^{II}(btz)]_n, 0.75 I₂ / Al for the MIL-101-NH₂ and 1.1 I_2 / Zn for the ZIF-8.⁸⁻¹¹

The combined spectroscopic characterisations and conductivity measurements as well as the thermogravimetric analysis coupled with Mass spectrometry shows that the iodine is predominantly captured in its molecular I₂ form independently on gas or liquid phases for $M^{II}(pz)[M^{\cdot II}(CN)_4] \cdot I_2$ (with $M = Ni^{II}$, Co^{II} and $M' = Ni^{\cdot II}$, Pd^{II}) frameworks. However, the formation of polyiodides, and more likely I_3^{-} species, resulting from the presence of some lattice defects in the clathrate frameworks, are likely formed in small quantity, as revealed by the low conductivity values.

It is also noticeable that the lattice adaptation upon the iodine insertion is different according to the nature of the employed building blocks and it influences the starting desorption temperature of I₂ out of the host structure. The small adaptation of the unit cell in the structure Ni^{II}(pz)[Ni^{II}(CN)₄] was interpreted as the effect of a relatively weak interaction between the guest and the cyanides and the pyrazine ligands as evidenced by Monte Carlo simulations. For this structure, iodine was successfully confined up to 150 °C (at atmospheric pressure). The use of $[Pd^{II}(CN)_4]^2$ in Ni^{II}(pz)[M'(CN)_4] triggers a change of space group from P4/m (tetragonal) to Pmmm (orthorhombic). The volume of the unit cell however does not significantly change after insertion of iodine and the iodine desorption started at the lowest observed temperature i.e. 140 °C due to a weaker confinement. The use of Co^{II} in the octahedral position gives a stronger interaction bringing to a relevant reduction of the unit cell upon iodine insertion. The nature of this interaction is interpreted as a relatively weak charge transfer between the guest iodine and the metal ion. Co^{II}(pz)[Ni^{II}(CN)₄] at maximal storage capacity exhibits the smallest unit cell and iodine was desorbed at 180 °C, *i.e.* at higher temperature with respect to the analogue structures containing physisorbed iodine. The opposing effects of using Pd²⁺ and Co²⁺ on the lattice adaptation could be concurrently observed for the case of Co^{II}(pz)[Pd^{II}(CN)₄]: the ability of this structure to confine iodine was very close to Ni^{II}(pz)[Ni^{II}(CN)₄]. Hence, the Co^{II}(pz)[Ni^{II}(CN)₄] was finally recognized as the best candidate for the selective entrapment of iodine.

A totally different mechanism is observed for the Ni^{II}(pz)[Pt^{II}(CN)₄] clathrate that underwent an oxidative addition with iodine. The clathrate shows much longer equilibrium time of 12 h and lower capacity of 0.5 moles I₂ per mole of clathrate that can be explained by the chemisorption mechanism and formation of Ni^{II}(pz)[Pt^{II/IV}(CN)₄]·I⁻ complex.

Finally, TGA-mass spectroscopy indicates that the I₂ molecules confined in $M^{II}(pz)[M'^{II}(CN)_4]$ ·I₂ for $M = Ni^{II}$, Co^{II} and M' = Ni^{II}, Pd^{II} may be thermally released between 130 and 200 °C according to the compositions before decomposition of the host structures. The study of the desorption process indicated that a full regeneration by thermal treatment of the structures was achieved and that the structures performed a good resistance to cycling processes with a good maintainability of the high sorption capacity.

Acknowledgements

The authors thank the ANR (ANR-AA-RMNP-003-01), University of Montpellier and CNRS for financial support. We also thank D. Granier, S. El Ghazi (PAC Chimie Balard, Montpellier), E. Celasco (Politecnico di Torino) for respectively XRPD, electrical and XPS measurements. G.M. thanks Institut Universitaire de France for its support.

Notes and references

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[†] Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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Graphical Abstract



Iodine Adsorption within Hofmann Clathrates M(pz)[M'(CN)₄] with $M^{2+} = Ni^{2+}$, Co^{2+} ; $M'^{2+} = Ni^{2+}$, Pd^{2+} , Pt^{2+}

Hofmann-type clathrate frameworks $M^{II}(pz)[M^{,II}(CN)_4]$ (pz = pyrazine, M = Ni, Co, M' = Ni, Pd, Pt) are able to efficiency and reversibly capture iodine in gas phase and in solution.