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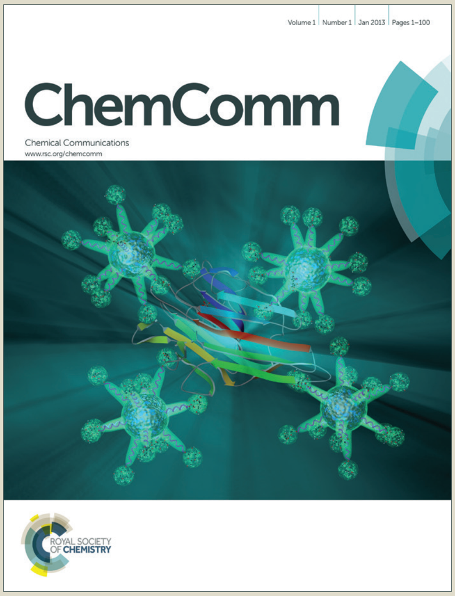

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Hydration-switchable charge transfer in the first bimetallic assembly based on $[Ni(cyclam)]^{3+}$ - magnetic CN-bridged chain $\{(H_3O)[Ni^{III}(cyclam)][Fe^{II}(CN)_6]\cdot 5H_2O\}_n$†

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An alternating bimetallic $\{(H_3O)[Ni^{III}(cyclam)][Fe^{II}(CN)_6]\cdot 5H_2O\}_n$ chain undergoes reversible dehydration at 40°C accompanied by electron transfer which leads to Ni^{II} - Fe^{III} in about 45% of metal centres. The hydrated dark blue form is a paramagnet while the dehydrated yellowish-green form shows ferromagnetic coupling between neighbouring Ni^{II} and Fe^{III}.

The search for new functional molecular materials is important for future technological developments. Systems showing bistability of electronic states, responsive to external stimuli like temperature, humidity or light are sought after as potential molecular sensors and switches. Good candidates for this purpose are bimetallic molecular materials characterized by reversible metal-to-metal charge-transfer (MMCT), in which electron transfer results in changes of magnetic and optical characteristics, especially cyano-bridged assemblies, where additionally effective magnetic interactions are mediated by the short bridge.[1] The rational design of CT materials requires control over redox potentials of two metal centres. It allows diverse possibilities of tuning by the use of different combinations of metal ions and the modification of their coordination environment, but at the same time it presents a serious challenge. Therefore charge-transfer switchable magnetic materials are rare. Only a few CN-bridged bimetallic assemblies exhibiting temperature-dependent phase transitions with the change of oxidation states and/or electron transfer under irradiation[2-7] have been reported. Most of them are based on $Co^{II/III}$ and $Fe^{II/III}$ redox couples,[2,3] rarely in combination with other metals: Mn,[4] W,[5,6] and Os.[7] Apart from temperature and light, the third factor that may induce electron transfer is the presence of guest molecules. Reversible response to sorption is essential for the construction of vapour-sensitive or multi-controllable magnetic switches. So far there are only sporadic reports on the charge-transfer effect induced or modified by the removal of the crystallization solvent,[3] and only one in which the reversibility of such process is well documented for the $Fe^{II/III}$-$W^{IV/V}$ redox pair.[5]

Redox properties of Ni are practically unexplored in the field of magnetic molecular materials, although partial electron transfer from Ni^{II} to Fe^{III} was observed in an irreversible annealing process of a Prussian blue analogue (PBA).[8] Apart from that case, Ni^{III} in bimetallic assemblies is encountered almost exclusively in square planar complexes with maleonitriledithiolate (mnt) ligand.[9] However, the $Ni^{II/III}$ couple is known to be active in catalytic processes and in systems of biological relevance.[10] The macrocyclic complex of Ni^{II} with the cyclam ligand (cyclam = 1,4,8,11-tetraazacyclotetradecane) can be oxidised to a relatively stable $[Ni(cyclam)]^{3+}$.[11] Although $[Ni(cyclam)]^{2+}$ is widely used in the construction of molecular magnetic materials as a linear building block[12,13,14] and it is known to form sorption-sensitive CN-bridged networks,[15] its oxidized form was characterized only in mononuclear complexes with different axial ligands. Here we report the first bimetallic compound based on $[Ni(cyclam)]^{3+}$ and its hydration-dependent charge-transfer properties.

The alternating bimetallic $\{(H_3O)[Ni^{III}(cyclam)][Fe^{II}(CN)_6]\cdot 5H_2O\}_n$ (**1**) chain is formed in the reaction between $[Ni^{III}(cyclam)]^{3+}$ and $[Fe^{II}(CN)_6]^{4-}$ in acidified H_2O-EtOH-MeCN solution in form of a dark blue polycrystalline precipitate. Needle-shaped crystals of **1** suitable for x-ray structure determination can be obtained by slow diffusion, however, simultaneous crystallization of small amounts of brown plates of the previously characterized 2D honeycomb-like $\{[Ni^{II}(cyclam)]_3[Fe^{III}(CN)_6]_2\cdot 22.5H_2O\}_n$ [12] network is observed. The reduction potential for the $[Ni(cyclam)]^{2+/3+}$ redox couple in neutral water solution is higher than that of $[Fe(CN)_6]^{4-/3-}$ although they both can be modified by the change of solvent and pH.[17] We have assessed relative redox potentials of both

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ions at different pH values and observed that with increasing solution acidity reduction potential increases for the $Fe^{II/III}$ couple and decreases for the $Ni^{II/III}$ one (Fig. S1, ESI†), causing an increased stability of $[Ni^{III}(cyclam)]^{3+}$ in the presence of $[Fe^{II}(CN)_6]^{4-}$. For this reason, compound **1** can also be obtained on different synthetic pathways (described in detail in ESI†) starting from the substrates of reversed oxidation states: $[Ni^{II}(cyclam)]^{2+}$ and $[Fe^{III}(CN)_6]^{3-}$ (Fig. S2, S3, ESI†).

Compound **1** crystallizes in the monoclinic system, space group C2/m (Table S1, ESI†). The structure (Fig. 1, S4, S5, ESI†) consists of chains of alternating Ni-cyclam and hexacyanoferrate units connected by CN bridges in trans positions. Both metal ions occupy special positions: Fe1 lies on the intercept of the mirror plane m (x ½ z) and two-fold axis 2 [½ y ½] and Ni2 on the intercept of the same mirror plane and axis 2 [0 y 0]. Consequently, the asymmetric unit comprises only one bridging and one terminal cyano group and one-fourth of the cyclam ligand. Metal centres are in an octahedral environment: Fe1 almost ideal (CShM for OC-6 = 0.002)[18] and Ni2 slightly distorted (CShM = 0.164), due to the elongation of axial bonds. The CN bridge is significantly bent with the Ni-N-C angle of 160.28°. The Ni-N distance in cyclam complex of 1.971 Å, is much shorter than it could be expected for Ni^{II} and characteristic for Ni^{III}.[16] The Ni-Fe chains run along [101] direction. The network contains two symmetry independent water molecules, with O1 located in a special and O2 in a general position. They are connected by a net of hydrogen bonds, in which all terminal CN ligands and all NH groups of cyclam are engaged (Fig. S6, ESI†). The charge of the chain is compensated by the presence of one proton, which can be distributed over 6 water molecules per formula unit, and therefore its exact location could not be established.

The presence of Ni in 1:1 molar ratio to Fe in **1** was confirmed by the SEM-EDS microanalysis (Ni atomic content *vs.* Fe in the range of 50.30-51.54% for 4 sampled areas), conducted in order to exclude the possibility of the formation of a polymorph of the $\{[Fe(cyclam)][Fe(CN)_6]\cdot 6H_2O\}_n$ chain.[13]

A thermogravimetric analysis of **1** (Fig. S7, ESI†) shows that five crystallization water molecules are released in two steps: 4 H_2O from room temperature to 50°C and the remaining one between 50 and 75°C. Above 120°C decomposition begins and H_3O^+ is released together with CN groups. When dried under reduced pressure or increased temperature (40ºC) **1** can be transformed into a monohydrate $\{(H_3O)[Ni(cyclam)][Fe(CN)_6]\cdot H_2O\}_n$, which we denoted as **1d**. The process is accompanied by the change of colour from dark blue to brownish-green and the loss of crystallinity, although the crystals seemingly retain their shape (Figure 2). Sample **1d** kept for several hours at 20°C and 100% humidity restores its original dark blue colour (Movie S1, ESI†) and water content (checked by gravimetric analysis). The rehydrated sample is denoted **1dh**.

Powder XRD study (Figure 3) shows that the pattern of the dehydrated form **1d** differs significantly from the pattern calculated from the single crystal data for **1**. The first peak at 2θ = 11.26° for **1**, which corresponds to reflections from (1 1 0) and (1 1 -1) planes, after dehydration is shifted to higher angles and splits into two components at 11.70° and 11.86°. It indicates the decreasing distance between the planes. The separation between the chains is defined by the interval between (1 1 -1) planes (7.84 Å), and we assume that with the loss of crystallization water it decreases by 0.39 Å (5%), more than the distance between (1 1 0) planes, which shortening by 0.30 Å (4%) is connected with the bending of CN-bridges. In the pattern of the rehydrated sample **1dh** all original peaks reappear, but small traces of the dehydrated form are still visible, showing that the rehydration process is not entirely reversible.

The magnetic susceptibility for the hydrated sample **1** (Fig. 4) gives $\chi T = 0.45$ cm^{3}K/mol, which is close to the theoretical value of 0.41 expected for low-spin (LS) Fe^{II} with $s = 0$ and Ni^{III} with $s = ½$, $g = 2.1$. For the sample dried at 312 K in vacuum (**1d**), χT reaches 1.03 cm^{3}K/mol at room temperature. From the possible electronic transitions, the configuration LS Fe^{III} with $s = ½$, $g = 2.0$ and Ni^{II} with $s = 1$, $g = 2.2$ gives the closest χT value of 1.59. Using these the theoretical χT values, the fraction of Ni^{II}-Fe^{III} in the dried phase **1d** is estimated at *ca.* 50%. The significant increase of χT below 100 K for the dried sample is consistent with the presence of the ferromagnetic exchange interaction along Fe-Ni chains, contrary to the hydrated sample where zero spin at the Fe site blocks magnetic interactions. The sharp maximum in χT at 5 K marks the ordering of **1d** phase, which is better visible in ZFC/FC measurements (Fig. S8, ESI†). For the rehydrated sample **1dh** the high-temperature value of χT drops down to 0.57 indicating that the charge transfer leading back to Ni^{III}-Fe^{II} takes place, however not completely, with 12% of Ni^{II}-Fe^{III} still present. In the χT plot of **1dh** an additional peak at 14 K appears, which coincides with the maximum for Ni-Fe based Prussian blue analogue.[8] For the sample dried again in the same procedure, which we denoted as **1dhd**, the high-temperature χT value rises back to 1.03 cm^{3}K/mol and the peak observed for **1dh** at 14 K reappears, proving that the rehydration process causes gradual decomposition of **1**, probably connected with the release of cyclam ligand and the formation of Ni-Fe PBA. This supposition is further supported by characteristic features of ZFC/FC curves (Fig. S8, ESI†).

The magnetization measured at 1.8 K for samples **1** and **1d** (Fig. S9, ESI†) increases slowly and does not reach constant value at the maximum applied field of 70 kOe. For the hydrated phase **1** the highest magnetization value of 1.30 μ_B is close to the expected saturation for Ni^{III} with $s = ½$, $g = 2.1$. For the dehydrated phase **1d** magnetization reaches 2.03 μ_B which is consistent with the fraction of Fe^{III}-Ni^{II} of 46%.

Mössbauer ^{57}Fe spectra for samples **1** and **1d** (Fig. 5 and S10, ESI†) corroborate with the magnetic measurement results. For **1** only one doublet with small quadrupole splitting (QS) is observed, confirming the presence of LS Fe^{II}. For **1d** additional components with large QS appear, which can be attributed to LS Fe^{III}. The fraction of Fe^{III} in **1d** can be estimated at about 40% (Table S2, ESI†), which is in reasonable agreement with magnetic susceptibility results.

The UV-Vis diffuse reflectance spectra (Fig. S11, ESI†) reflect the change of colour upon dehydration. For **1** very broad and strong peak between 500 and 1000 nm is present, which can be attributed to metal-to-metal charge-transfer. After dehydration this peak almost disappears leaving only a broad shoulder. The possibility of light-induced charge-transfer was studied, however, no change in magnetic susceptibility was observed under irradiation with the light of 785 nm wavelength. In the CN-stretching region of IR spectra several peaks, which shift significantly to higher frequency upon dehydration, can be observed (Fig. S12, ESI†). The strengthening of CN bonds is connected with the change of oxidation states of metals and braking of H-bonds upon the loss of water.

In conclusion, we have obtained the first bimetallic assembly based on $[Ni^{III}(cyclam)]^{3+}$ and observed its unusual charge transfer properties. The CN-bridged $(H_3O)[Ni^{III}(cyclam)][Fe^{II}(CN)_6]\cdot 5H_2O$ (**1**) chain undergoes reversible dehydration in the temperature range of 20-40°C, accompanied by gradual decomposition. The process results in the modification of structure and change of oxidation states of about 50% of the metal centres from Ni^{III}-Fe^{II} to Ni^{II}-Fe^{III}. It is reflected by the change of colour and magnetic susceptibility, as well as low temperature magnetic behaviour.

We have shown for the first time that the redox properties of the $Ni^{II/III}$ couple can be employed in the construction of molecular materials exhibiting bistability of electronic states based on metal-to-metal charge-transfer. More importantly, the use of the cyclam complex, which for the Ni ion is stable under a wide range of conditions, contrary to its rather fragile Co and Fe counterparts,[19] uncovers new exiting prospects. As we have shown before, $[Ni(cyclam)]^{2+}$, due to its predictable linear-linker geometry, small size and weak intermolecular interactions, can be used to build flexible networks, which respond to the sorption of small molecules with structural and magnetic changes.[15] The discovery of its oxidized form as a building block opens up the possibility of rational design of materials in which charge-transfer and sorption properties are merged. The Ni-Fe chain that we present in this work is the first member of an emerging family of $Ni^{II/III}$-based CT-active assemblies - potential candidates for vapour-sensitive switches and multi-switchable materials. The results of our preliminary experiments show that a range of assemblies with similar dehydration-controlled electron transfer can be obtained by combining $[Ni(cyclam)]^{3+}$ with other metals.

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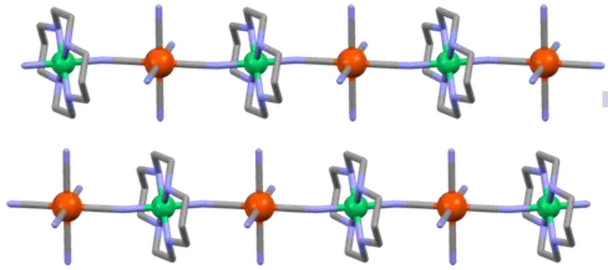

Fig. 1. Structure fragment of **1**; Fe - red balls, Ni - green balls, C - grey sticks, N - blue sticks; hydrogen atoms and water molecules omitted for clarity.

Fig. 2. Photographs of the dehydrated (**1d**) and rehydrated (**1dh**) crystals.

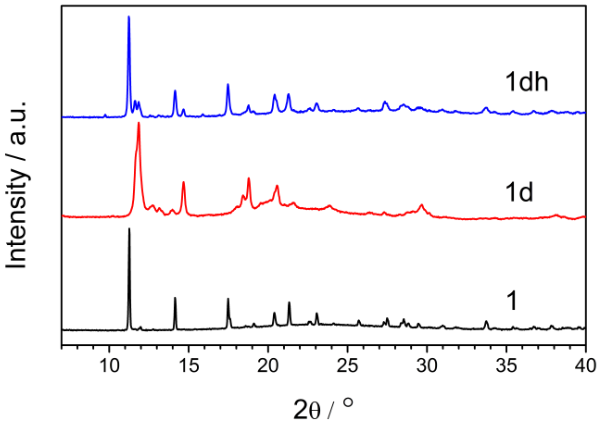

Fig. 3. Powder XRD patterns for samples: as synthesized (**1**), dried (**1d**) and rehydra
(**1dh**).

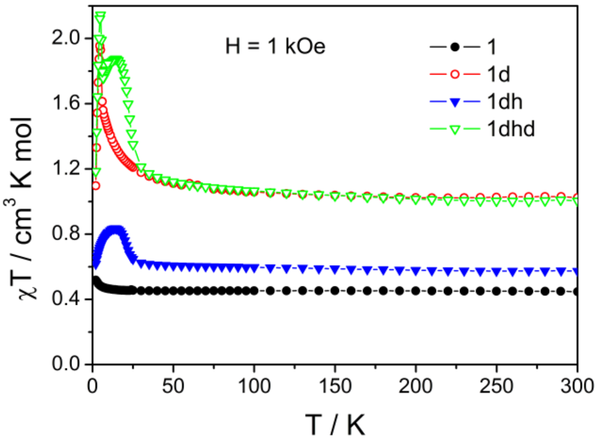

Fig. 4. Magnetic susceptibility for repeated dehydration-rehydration sequence of 1.

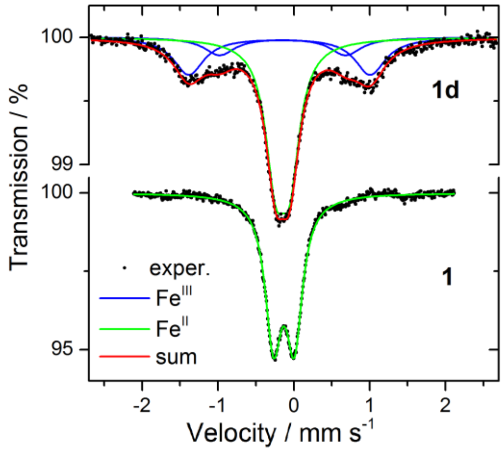

Fig. 5. ^{57}Fe Mössbauer spectra of **1** and **1d** measured at 80 K with fitted doublet components.

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