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Multilayered networks built from polyoxometalates and cyanometalates

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ABSTRACT

We report the syntheses of ε-Keggin polyoxomolybdates capped by neodymium, samarium, europium and terbium and the corresponding multidimensional materials connected with hexacyanoferrate, $[PMo_{12}O_{37}(OH)_3\{Ln(H_2O)_5(Fe(CN)_6)_{0.25}\}_4]$ (Ln = Nd, Sm, Eu, and Tb). The single crystal X-ray diffraction measurement of the Ln = Nd system reveals a multilayered structure (orthorhombic, *P*mmn). The magnetic measurement showed that these four compounds exhibit paramagnetism due to each Ln^{III} centre. In addition, the electrochemistry shows the reversible Mo(V)/Mo(VI) redox behaviour.

1. Introduction

Multi-dimensional coordination compounds built around polyoxometalates (POMs) have been developed mostly during the last 15 years, and now come in a wide variety of structures. If some structures have been reported where the POM units are directly linked together via intermolecular oxo bridges [1], the systems where the link is ensured by transition metal complexes are by far the most common [2]. The properties of such materials depend essentially on the nature of metal and ligand used, the POMs usually playing the part of inert structuring agents, with the exception of some polyoxovanadates which are intrinsically magnetically active [2d,3]. Luminescence has for instance been achieved by using silver(I) [4] or lanthanide [5] centres, while networks built from POMs and amino complexes of first-row transition metals are particularly studied for their magnetic properties [6], including the recently reported first example of simultaneous spin-canting and metamagnetism in a copper(II) compound [7]. Catalysis is another popular application of both isolated and multi-dimensional POMs, and several POM networks have indeed been found to be active in electro- [8] or photocatalysis [8a,b,9] in spite of their mostly insoluble nature which generally limits their use in homogeneous catalysis. One of the most spectacular architectures, a three dimensional (3D) array featuring chiral helical channels, has been obtained by Wang and co-workers by the reaction of copper(II), proline and the $[\alpha\text{-}BW_{12}O_{40}]^{5-}$ Keggin anion in hydrothermal conditions [10].

Very recently, we reported the first multi-dimensional system built from a polyoxometalate and a hexacyanometalate as bridging metal complex, the multilayered $[\varepsilon\text{-}PMo_{12}O_{37}(OH)_3\{La(H_2O)_5(Fe(CN)_6)_{0.25}\}_4]$ network (**$\{PMo_{12}La_4Fe(CN)_6\}$**) [11]. Cyano-bridged metal assemblies have received much attention due to physical properties as diverse as high Curie temperature [12], photomagnetism [13], chemically sensitive magnetism [14], light-, electric-field- or temperature-induced phase transitions [15] and zero thermal expansion [16]. The lack of interest in studying cyanometalates in multi-dimensional POM chemistry may be explained firstly by the weak coordinating abilities, making them unable to overcome the charge repulsion from the negatively charged POMs, secondly by the instability under hydro- or solvothermal conditions, which are often a mandatory requirement for building metal–organic frameworks [17], including POM-based ones. Hence, our initial choice was a positively charged POM precursor derived from the ε-Keggin structure.

Among the five isomers (α to ε) of the well-known Keggin structure $\{XM_{12}O_{40}\}$, the ε isomer, derived from the standard α isomer by a formal 60° rotation of each of the four $\{M_3O_{13}\}$ units [18], is the least stable one and has so far never been observed in the absence of a stabilization by extra capping transition metals.[1] Klemperer and co-workers were the first to synthesize a $[(C_5Me_5Rh^{III})_8(\varepsilon\text{-}Mo^{V}{}_{12}O_{36})(Mo^{VI}O_4)]^{2+}$ cluster under hydrothermal conditions [19]. Müller et al. followed with the $[\varepsilon\text{-}H_2Mo^{V}{}_{12}O_{30}(\mu_2\text{-}OH)_{10}\{Ni^{II}$

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[1] An $[\varepsilon\text{-}Al^{III}{}_{13}O_4(OH)_{24}(OH_2)_{12}]^{7+}$ ion does indeed exist (G. Johansson, Arkiv Kemi 20 (1963) 305), though it may not be considered a POM by the standard definition ('transition metal oxide cluster').

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$(H_2O)_3\}_4]$ polyoxomolybdate prepared under usual bench conditions, exhibiting antiferromagnetic coupling between Ni^{II} centres, but not suitable for the elaboration of multi-dimensional networks because of its complete insolubility in any common solvent [20]. Dolbecq and co-workers isolated the first lanthanide-capped ε-Keggin polyoxomolybdate $[\varepsilon\text{-PMo}^{V}_8\text{Mo}^{VI}_4O_{36}(OH)_4\{La(H_2O)_4\}_4]^{5+}$ (**$\{PMo_{12}La_4\}$**) ten years ago [21] and studied its reaction with carboxylate ligands in order to build multi-dimensional materials [22]. The same group extended later that family of so-called POM-based metal–organic frameworks (POMOFs) by working with the Zn^{II} and Co^{II} analogues, under hydrothermal conditions [23], while Xu and co-workers have reported multilayered architectures built from an $\{\varepsilon\text{-GeMo}^{V}_8\text{Mo}^{VI}_4O_{40}Ni_4\}$ core and bidentate N-donor linkers [24]. In this paper, we present syntheses and characterizations of some **$\{\varepsilon\text{-PMo}_{12}Ln_4\}$** precursors (Ln = Nd^{III}, Sm^{III}, Eu^{III}, Tb^{III}) [25], followed by the reaction with hexacyanoferrate(II) as well as the characterization, electrochemical and magnetic properties of the resulting networks.

2. Experimental

2.1. Syntheses

All commercially available reagents were used as purchased without further purification.

2.1.1. Preparation of a 0.10 M solution of $[Mo_2O_4(H_2O)_6]^{2+}$ ions in 4M HBr (solution A)

$Na_2MoO_4{\cdot}2H_2O$ (3.87 g, 16 mmol) is dissolved in 80 mL of 4 M HBr before $N_2H_4{\cdot}H_2O$ (210 μL, 4.3 mmol) is added. The resulting solution is left stirring for 3 h at 80 °C, it progressively turns deep red. It is allowed to cool down to room temperature before further use.

2.1.2. $[\varepsilon\text{-PMo}_{12}O_{38}(OH)_2\{Nd(H_2O)_5\}_4]Br_3{\cdot}18H_2O$ ($\{PMo_{12}Nd_4\}$)

The synthesis is a variation on the procedure previously described by Sécheresse and co-workers for $[\varepsilon\text{-PMo}_{12}O_{36}(OH)_4\{La(H_2O)_4\}_4]^{5+}$ [21]. To 20 mL of solution A are added successively a solution of $Na_2MoO_4{\cdot}2H_2O$ (242 mg, 1.0 mmol) in 1 mL of water, a solution of $NaH_2PO_4{\cdot}2H_2O$ (66 mg, 0.42 mmol) in 4 mL of water and finally a solution of Nd_2O_3 (8.1 g, 24 mmol) in 40 mL of 4 M HBr. The pH of the resulting mixture is adjusted to 2.8 by addition of an 8 M NaOH solution, and is maintained at this value for another 30 min. The blue suspension is then filtered and the filtrate leaves to crystallize at room temperature. Small red prismatic crystals appear after one week. They are air-stable and can be washed carefully with a small quantity of cold water and cold ethanol. Yield: 184 mg (13%/P). FTIR spectrum (KBr pellets): ν (cm^{-1}) = 1000 (w), 991 (sh), 971 (s), 921 (s), 905 (sh), 819 (m), 774 (s), 744 (sh), 598 (m). *Anal.* Calc. for $Br_3H_{78}Mo_{12}Nd_4O_{78}P$: Br, 7.21; H, 2.36; Mo, 34.62; Nd, 17.35; P, 0.93. Found: Br, 7.46; H, 2.30; Mo, 32.64; Nd, 17.06; P, 0.41%.

2.1.3. $[\varepsilon\text{-PMo}_{12}O_{38}(OH)_2\{Sm(H_2O)_5\}_4]Br_3{\cdot}17H_2O$ ($\{PMo_{12}Sm_4\}$)

The same procedure as for **$\{PMo_{12}Nd_4\}$**, with exception of using 8.4 g of Sm_2O_3 instead of Nd_2O_3. Yield: 246 mg (18%/P). FTIR spectrum (KBr pellets): ν (cm^{-1}) = 1002 (sh), 987 (sh), 974 (m), 918 (s), 905 (sh), 819 (m), 773 (s), 736 (sh), 600 (m). *Anal.* Calc. for $Br_3H_{76}Mo_{12}O_{77}PSm_4$: Br, 7.19; H, 2.30; Mo, 34.56; P, 0.93; Sm, 18.05. Found: Br, 8.11; H, 2.34; Mo, 33.99; P, 0.50; Sm, 16.49%.

2.1.4. $[\varepsilon\text{-PMo}_{12}O_{38}(OH)_2(Eu(H_2O)_5)_4]Br_3{\cdot}16H_2O$ ($\{PMo_{12}Eu_4\}$)

To 10 mL of solution A are added successively a solution of $Na_2MoO_4{\cdot}2H_2O$ (121 mg, 0.5 mmol) in 0.5 mL of water, a solution of $NaH_2PO_4{\cdot}2H_2O$ (33 mg, 0.21 mmol) in 2 mL of water and finally a solution of Eu_2O_3 (4.2 g, 12 mmol) in 20 mL of 4 M HBr. The pH of the resulting mixture is adjusted to 3.5 by addition of an 8 M NaOH solution, and is maintained at this value for another 30 min. The blue suspension is then filtered and the filtrate leaves to crystallize at room temperature. Small red parallelepipedic air-stable crystals appear after one week. Yield: 146 mg (21% /P). FTIR spectrum (KBr pellets): ν (cm^{-1}) = 1002 (sh), 992 (sh), 968 (s), 927 (s), 905 (sh), 818 (m), 774 (s), 745 (sh), 599 (m). *Anal.* Calc. for $Br_3Eu_4H_{74}Mo_{12}O_{76}P$: Br, 7.22; H, 2.25; Mo, 34.68; P, 0.93, Eu, 18.31. Found: Br, 9.00; H, 2.31; Mo, 34.42; P, 0.58; Eu, 18.41%.

2.1.5. $[\varepsilon\text{-PMo}_{12}O_{38}(OH)_2(Tb(H_2O)_5)_4]Br_3{\cdot}16H_2O$ ($\{PMo_{12}Tb_4\}$)

Tb_2O_3 (2.2 g, 6 mmol) is dissolved in 5 mL of hot (80–90 °C) 4 M HBr, the resulting solution is allowed to cool down to room temperature (solution B). To 5 mL of solution A are slowly added successively a solution of $Na_2MoO_4{\cdot}2H_2O$ (61 mg, 0.25 mmol) in 250 μL of water, a solution of $NaH_2PO_4{\cdot}2H_2O$ (17 mg, 0.11 mmol) in 1 mL of water, and solution B. The pH of the resulting mixture is adjusted to 3.7 by addition of an 8 M NaOH solution, and is maintained at this value for another 30 min. The blue suspension is then filtered and the filtrate leaves to crystallize at room temperature. Small red parallelepipedic air-stable crystals appear after one week. Yield: 20 mg (5%/P). FTIR spectrum (KBr pellets): ν (cm^{-1}) = 1003 (sh), 998 (sh), 965 (s), 935 (s), 905 (sh), 810 (m), 766 (s), 730 (sh), 605 (m). *Anal.* Calc. for $Br_3Tb_4H_{74}Mo_{12}O_{76}P$: Br, 7.16; H, 2.23; Mo, 34.39; P, 0.96; Tb, 18.98. Found: Br, 6.97; H, 2.22; Mo, 34.87; P, 0.43; Tb, 18.61%.

2.1.6. $[\varepsilon\text{-PMo}_{12}O_{37}(OH)_3\{Nd(H_2O)_5(Fe(CN)_6)_{0.25}\}_4]{\cdot}12H_2O$ ($\{PMo_{12}Nd_4Fe(CN)_6\}$)

$\{PMo_{12}Nd_4\}$ (60 mg, 0.018 mmol) synthesized as described above is dissolved in 30 mL of methanol, then a solution of $Na_4Fe^{II}(CN)_6{\cdot}10H_2O$ (10 mg, 0.02 mmol) in 30 mL of water is added dropwise over 90 min. A red-brown precipitate slowly appears; after the end of the addition the resulting suspension is let stirring for another 15 min. The powder is filtered, thoroughly washed with water and then with methanol. Yield: 50 mg (87% /Mo). FTIR (KBr pellets): ν (cm^{-1}) = 2065 (s), 2018 (s), 988 (sh), 968 (m), 925 (s), 905 (sh), 810 (m), 767 (s), 690 (w), 589 (m). *Anal.* Calc. for $C_6H_{67}FeMo_{12}N_6Nd_4O_{72}P$: C, 2.26; H, 2.12; Fe, 1.75; Mo, 36.09; N, 2.63; Nd, 18.08; P, 0.97. Found: C 2.34, H, 2.31, Fe, 1.55; Mo, 33.26; N, 2.51; Nd, 17.51; P, 0.31%. Air-stable single crystals (red platelets) and suitable for X-ray diffraction grow by slow diffusion of a **$\{PMo_{12}Nd_4\}$** solution in methanol and a $Na_4Fe^{II}(CN)_6{\cdot}10H_2O$ solution in water in a H-shaped tube carefully filled with a 1:1 water/methanol mixture.

2.1.7. $[\varepsilon\text{-PMo}_{12}O_{37}(OH)_3\{Sm(H_2O)_5(Fe(CN)_6)_{0.25}\}_4]{\cdot}12H_2O$ ($\{PMo_{12}Sm_4Fe(CN)_6\}$)

The same procedure as for **$\{PMo_{12}Nd_4Fe(CN)_6\}$,** with the exception of using **$\{PMo_{12}Sm_4\}$** instead of **$\{PMo_{12}Nd_4\}$**. Yield: 43 mg (74% /Mo). FTIR spectrum (KBr pellets): ν (cm^{-1}) = 2063 (s), 2015 (s), 1000 (sh), 968 (m), 929 (s), 811 (m), 770 (s), 690 (w), 591 (m). *Anal.* Calc. for $C_6H_{67}FeMo_{12}N_6O_{72}PSm_4$ (found): C, 2.24; H, 2.10; Fe, 1.74; Mo, 35.81; N, 2.61; P, 0.96; Sm, 18.71. Found: C, 2.19; H, 2.04; Fe, 1.49; Mo, 37.90; N, 2.30; P, 0.60; Sm, 18.26%.

2.1.8. $[\varepsilon\text{-PMo}_{12}O_{37}(OH)_3\{Eu(H_2O)_5(Fe(CN)_6)_{0.25}\}_4]{\cdot}12H_2O$ ($\{PMo_{12}Eu_4Fe(CN)_6\}$)

The same procedure as for **$\{PMo_{12}Nd_4Fe(CN)_6\}$**, with the exception of using **$\{PMo_{12}Eu_4\}$** instead of **$\{PMo_{12}Nd_4\}$**. Yield: 36 mg (61% /Mo). FTIR spectrum (KBr pellets): ν (cm^{-1}) = 2062 (s), 2017 (s), 970 (m), 930 (s), 814 (m), 774 (s), 680 (w), 594 (m). *Anal.* Calc. for $C_6H_{71}Eu_4FeMo_{12}N_6O_{74}P$: C, 2.21; H, 2.20; Eu, 18.66; Fe, 1.71; Mo, 35.24; N, 2.58; P, 0.95. Found: C, 2.17; H, 2.25; Eu, 18.39; Fe, 1.35; Mo, 34.90; N, 2.05; P, 0.46%.

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