Crystal Structures and Intercalation Reactions of Three-Dimensional Coordination Polymers $[M(H_2O)_2]_2[Mo(CN)_8]\cdot4H_2O$ (M = Co, Mn)

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Two coordination polymers $[M^{II}(H_2O)_2]_2[Mo^{IV}(CN)_8]\cdot4H_2O$ [M^{II} = Co (**1**), Mn (**2**)] were prepared as monocrystals and structurally characterised. These compounds crystallise in the tetragonal systems *I4/m* (**1**) and *I4/mcm* (**2**) and form three-dimensional networks containing channels occupied by two types of water molecules, i.e. coordinated to M^{II} and crystallised ones. The dehydration of these materials occurs topochemically to give $[M^{II}(H_2O)]_2[Mo^{IV}(CN)_8]$ compounds having an open metal coordination site on the M^{II} ions that may be accessible to coordination by other species and serve as a reaction site. The intercalation of water, ammonia and amines has been studied.

Introduction

One of the challenges of contemporary chemistry is the molecular design of materials to achieve specific properties. An interesting group of compounds that has attracted considerable attention from material chemists and crystal engineers is two- and three-dimensional coordination polymers able to absorb and/or desorb guest molecules, which exhibit potential applications in the areas of separation and catalysis.[1] A very successful approach to these materials involves the deliberate design by self-assembly of two- and three-dimensional host-guest supramolecular architectures containing relatively large channels, cavities, or windows. Zeolites, which contain channels and cavities because of rigid three-dimensional frameworks and clays, via intercalation between two-dimensional layers, are natural prototypes of such architectures and are currently used. However, it is relatively difficult to modify and derivatise them in a systematic way in comparison with coordination polymers. Numerous examples already exist of inorganic[2] and metal-organic[3,4] zeolite and clay mimics which reversibly incorporate small molecules or organic guests. The structural flexibility of the molecular frameworks and their different nature compared to zeolites and clays may provide novel complementary properties, for example, optical, electronic or magnetic for such "porous" materials.[5] Some of these coordination polymers act as hosts in intercalation reactions since a vacant site for coordination of others species may have been created.

In recent years, a large number of structurally characterised host-guest open framework solids have been obtained by a self-assembly of systems containing cyanometalate units as building blocks.[6−13] As a matter of fact, the multidimensional structure formed by the successive $-M-CN-M'-$ linkages affords a void with a shape and/or a size appropriate to the intercalation of a guest molecule in order to stabilise the crystal structure. This stabilisation can also be provided by the coordination of labile ligands at M′ (for instance, H_2O, NH_3, aliphatic and aromatic amines, etc.) which can be exchanged by intercalation. Two- and three-dimensional Hoffman-like frameworks containing linear and bent $[Ag(CN)_2]^-$ or $[Au(CN)_2]^-$ twofold coordination,[7] trigonal and pyramidal $[Cu(CN)_3]_2^-$ threefold coordination,[8] tetrahedral[9] $[Cd(CN)_4]^{2-}$ and square-planar[10] $[Ni(CN)_4]^{2-}$ fourfold coordination and also sixfold coordination[11] $[M(CN)_6]^{n-}$ building blocks, combined with a different metallic or organometallic coordination centre, have already been reported.

The eightfold-coordinated building blocks $[M(CN)_8]^{4-}$ (M^{IV} = Mo, W, Nb) offering eight bridging cyano ligands potentially able to form tightly connected architectures, have attracted some attention in recent years because of their magnetic[12f] and photomagnetic properties.[12a−12e] Nevertheless, structurally characterised polynuclear coordination polymers based on the use of $[M(CN)_8]^{4-}$ (M = Mo

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or W) as building blocks are still rare. In fact, as far as we are aware, structural reports of cyano-bridged $M^{II}M^{IV}$ (M = Mo or W) dimetallic compounds are very recent and concern the following examples: the chain $[\{Mn_2(L)_2(H_2O)\}]\{Mo(CN)_8\}]\cdot 5H_2O$,[12c] the two-dimensional mixed-valence compound $[\{Mn(L)\}_6\{Mo^{III}(CN)_7\}\{Mo(CN)_8\}_2]\cdot 19.5H_2O$[12d] {L = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene} and the three-dimensional compound $[Fe(H_2O)_2]_2[Mo(CN_8)]$.[12e] Furthermore, to the best of our knowledge, the intercalation behaviour of these compounds has never been studied. As a matter of fact, the $[M(CN)_8]^{4-}$ building block has also been employed in combination with the organometallic $[(CH_3)_3Sn]^+$ cation in order to design three-dimensional coordination polymers $[\{(CH_3)_3Sn\}_4M^{IV}(CN)_8]$ (M^{IV} = Mo, W) containing THF guest molecules in the channels.[13] However, after removal of the guest molecules by heating, no reabsorption of THF or absorption of others solvent molecules has been observed.

In this context, this paper is devoted to the synthesis and the crystal structures of two three-dimensional networks based on the $[Mo(CN)_8]^{4-}$ building block and M^{II} = Co, Mn metal ions. The title compounds were prepared for the first time as single crystals and their crystal structures were resolved. The presence of labile ligands coordinated to an M^{II} ion, i.e., H_2O molecules, opens the possibility for substitution reactions. In principle, this strategy should offer a means of incorporating various guest molecules in the network and thus modulate both structural and physical properties of these compounds.

Results and Discussion

Synthesis and Crystal Structures of $[M(H_2O)_2]_2[Mo(CN)_8]\cdot 4H_2O$ (M = Mn, Co)

The slow diffusion in an H-shaped tube of two 10^{-4} M aqueous solutions containing $K_4[Mo(CN)_8]\cdot 2H_2O$[10] and $[M(H_2O)_6](NO_3)_2$, allows yellow (M^{II} = Mn) or orange (M^{II} = Co) crystalline plates to be obtained. The complexes have been fully characterised by elemental analyses, IR spectroscopy, and X-ray crystallography (Table 1).

Infrared C−N stretches for both compounds [2144 (s) cm^{-1}] are shifted to higher frequencies than those of $K_4[Mo(CN)_8]\cdot 2H_2O$ [2125 (s), 2102 (s) cm^{-1}], clearly showing a coordination of all the CN groups to M^{II}.

The X-ray crystallographic study at 160 K reveals that these compounds $[M(H_2O)_2]_2[Mo(CN)_8]\cdot 4H_2O$ [M = Co^{II} (**1**), Mn^{II} (**2**)] have three-dimensional structures. Although, these two compounds are not strictly isostructural, the organisation of the three-dimensional structures and their cell parameters are similar. The compounds crystallise in a tetragonal system with space groups *I*4/*m* for **1** and *I*4/*mcm* for **2**. The structures possess one molybdenum (Mo^{IV}) site and one M^{II} (M^{II} = Co or Mn) site. Eight −C−N−M linkages surround the Mo atom forming a perfect square antiprism environment, as shown in Figure 1. Thus, the geometry of $[Mo(CN)_8]^{4-}$ unit is changed from the dodecahedral one in the starting $K_4[Mo(CN)_8]\cdot 2H_2O$ compound[14] to square-antiprismatic in the final products. It should be noted that such a geometrical rearrangement is characteristic for two- and three-dimensional compounds containing $[M(CN)_8]^{4-}$ units which have already been reported.[12,13] The Mo−C bond lengths are equal to 2.160(7) and 2.168(6) Å for **1** and 2.153(4) Å for **2**. The C−N bond lengths are equal to 1.145(9), 1.141(9) Å for **1** and 1.150(5) Å for **2**. Four N−C−Mo linkages and two water molecules in the *trans* configuration surround the M^{II} sites (Figure 1). The sites adopt a perfect octahedral environment. The M−N bond lengths are equal to 2.124(6), 2.158(6) Å for **1** and 2.207(3) Å for **2**. The M−O1 and M−O2 bond lengths are equal to 2.051(9) and 2.099(8) Å for **1** and 2.283(8) and 2.231(8) Å for **2**, respectively. It should be noted that all of the Mo−C−N bonded angles are close to 180° [Mo−C1−N1 175.2(6)°; Mo−C2−N2 174.3(5)° for **1** and

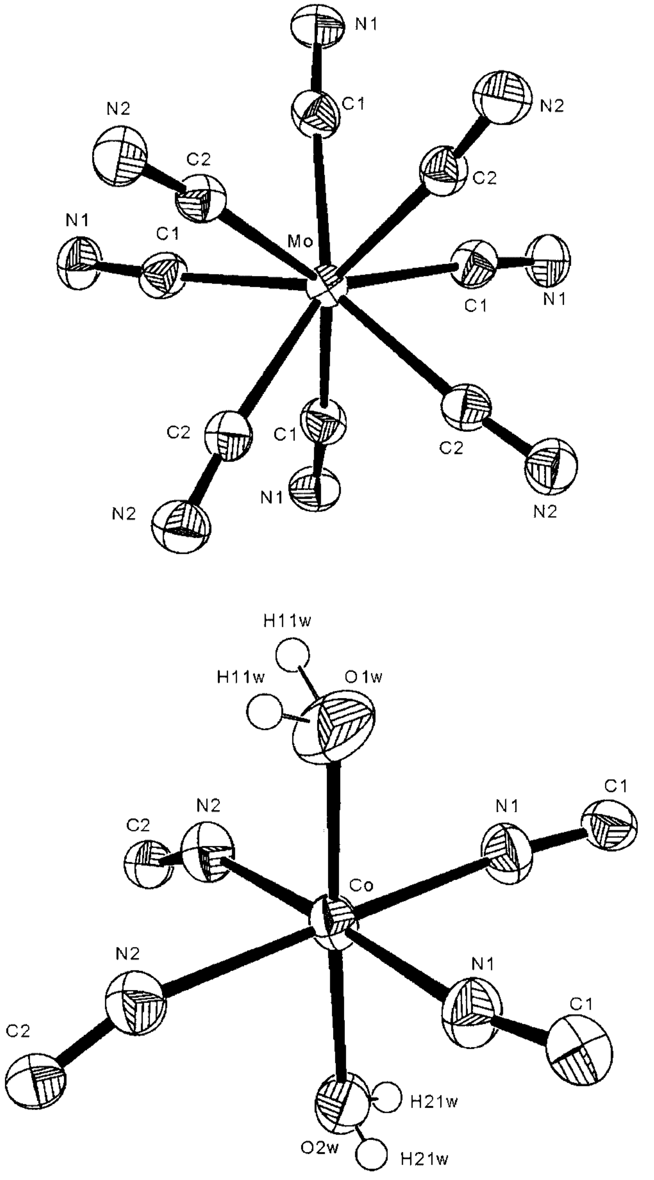

Figure 1. ORTEP drawing of local coordination environment of Mo and Co sites for compound **1**

178.5(3)° for **2**], while the M−N−C bonded angles deviate significantly from 180° [165.9(6)°, 155.2(6)° for **1** and 162.5(3)° for **2**].

The structural arrangement may be described as a centrosymmetrical {MoC2N2MN2C2}$_2$ lozenge motif which is linked to four other identical motifs by C2N2 bridges to form corrugated grid-like sheet layers, as shown in Figure 2 for **1**. The three-dimensional organisation may be described as interconnected perpendicular layers parallel to {[110], [111]} and {[011], [010]} planes. Each Mo atom belongs to two perpendicular layers and is a node of the three-dimensional network. This arrangement results in channels running along the *c* axis occupied by coordinated and crystallised water molecules as shown in a whole view of the structure of **1** viewed in the *ab* plane (Figure 3).

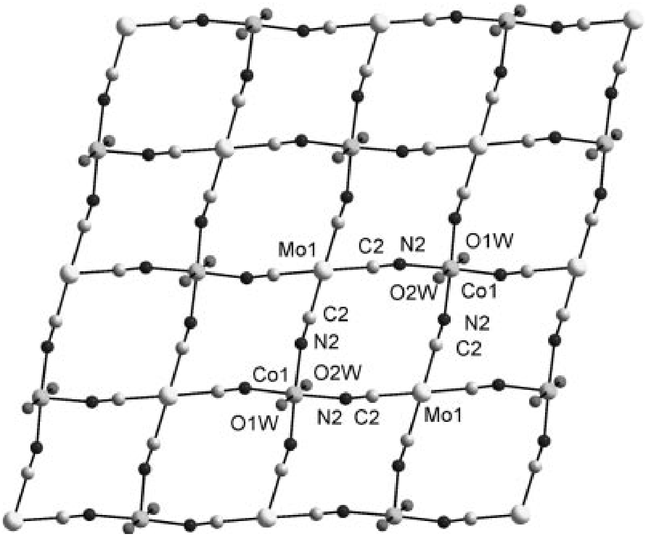

Figure 2. A view of the structure in the {[110], [111]} plane, showing a corrugated grid-like plan for compound **1**; hydrogen atoms are omitted for clarity

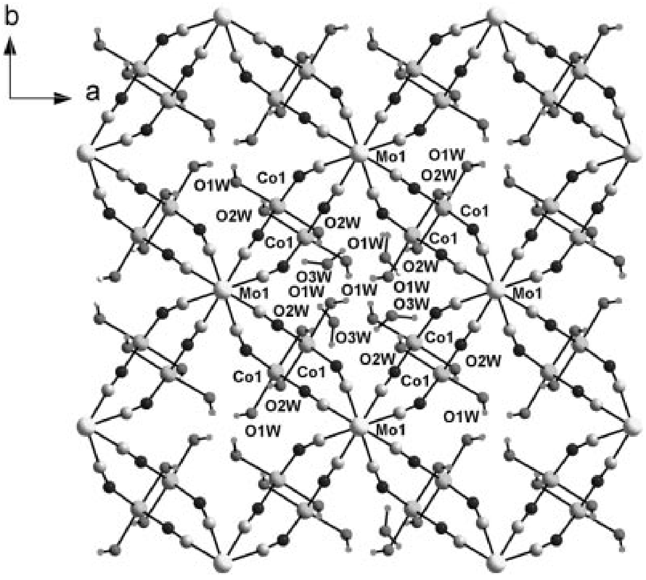

Figure 3. Global view of the crystal structure of **1** in the *ab* plane; the crystallised water molecules are only shown in one channel for clarity

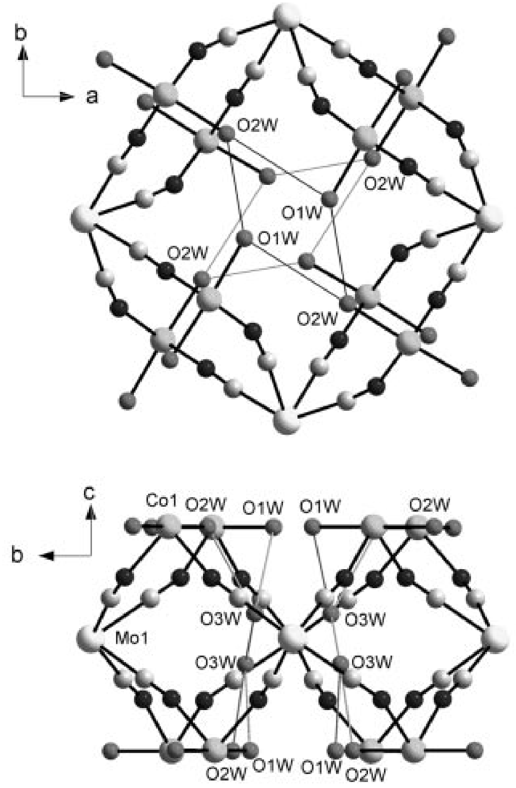

Figure 4. Top: fragment of the crystal structure of **1** along the *c* axis showing the cavity with a hydrogen bonding network coordinated between Co^{II}-coordinated water molecules; bottom: fragment of the crystal structure of **1** along the *b* axis showing the hydrogen bonding between the Co^{II}-coordinated and crystallised water molecules

As can be seen in Figure 4 (top), each of the four water molecules coordinated to the M^{II} ions situated in the *ab* plane are linked by means of hydrogen bonds forming a non-centrosymmetrical lozenge {O1WO2W}$_2$ in the centre of the channel [3.089(12) Å for O1···O2 and 3.554(13) Å for O2···O1] (dashed lozenge). Another identical lozenge (greg lozenge) is placed behind that of the first and turned by 90° in the *ab* plane. The two types of lozenges alternate along the *c* axis. Additionally, in each water lozenge at the centre of the cavity the O1 and O2 atoms are linked by hydrogen bonds to the O3 W atoms of the crystallised water molecule [2.894(9) Å for O2···O3 and 3.030(9) Å for O1···O3], resulting in columns of water molecules inserted in the channels delimited by the cavities along the *c* direction [Figure 4 (bottom)]. The cavity size may be estimated as 5.98 × 6.02 Å (or as the cavity volume of 133.4 Å^3), which leads to the possibility of intercalation of the appropriated molecules.

Magnetic Properties of $[M(H_2O)_2]_2[Mo(CN)_8]\cdot 4H_2O$ [M = Co (1), Mn (2)]

The temperature dependence of the magnetic susceptibility (χ_M) for polycrystalline samples of **1** and **2** were recorded under an applied field of 1000 Oe. For compound **2**, χ_M can be fitted using the Curie−Weiss law [$\chi_M = C/(T$

$-\ \theta)]$ with $C = 8.58$ emu·K·mol^{-1} and $\theta = -1.4$ K, down to 1.8 K. The Curie constant (C) is in agreement with the expected value for two Mn^{2+} ions with $S = 5/2$ and $g = 1.98\pm0.05$. The negative sign of the Weiss constant obtained from the Curie−Weiss fitting, reveals the presence of weak antiferromagnetic interactions between the Mn^{II} ions through the diamagnetic NC−Mo^{IV}−CN bridges. The χ_MT value at room temperature for **1** is equal to 5.3 emu·K·mol^{-1}, which corresponds to the calculated spin value for two Co^{II} ions ($S = 3/2$, $g = 3.36$), since Mo^{IV} is diamagnetic. The decrease in χ_MT at low temperature may have two origins, spin−orbit coupling and antiferromagnetic interactions between the Co^{II} ions. Nonetheless, no theoretical model exists for the three-dimensional lattice, taking both factors into account.

Dehydration of 1 and 2 and Intercalation Reactions of $[M(H_2O)]_2[Mo(CN)_8]$ [M = Co (1), Mn (2)]

The thermogravimetric analysis (TGA) of **1** and **2** was performed under argon from room temperature up to 700 °C. The TGA curves exhibit four well-pronounced weight losses as the temperature was increased at a heating rate of 1 °C·min^{-1}, as shown in Figure 5 (top). The first and second weight-loss steps can be determined by inflection points at 88 and 131 °C, respectively; the third step contains two poorly pronounced inflexion points at 260 and 484 °C; the fourth step has an inflexion point at 575 °C.

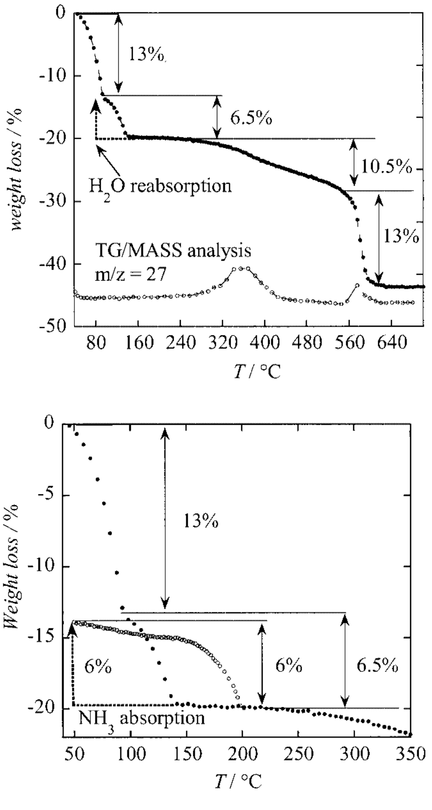

Figure 5. Top: TGA and TGA/MASS curves for $[Mn(H_2O)_2]_2[Mo(CN)_8]\cdot4H_2O$; heating rate 1 °C/min; bottom: TGA and ammonia absorption curves for $[Mn(H_2O)_2]_2[Mo(CN)_8]\cdot4H_2O$

The first and second weight-loss steps of 13.0 and 6.5%, respectively, are consistent with the loss of the four crystallized and the two coordinated water molecules, leading to $[Co(H_2O)]_2[Mo(CN)_8]$ (**1a**) and $[Mn(H_2O)]_2[Mo(CN)_8]$ (**2a**). After heating at 150 °C, the compounds retain their crystallinity and appear to be isomorphous with their corresponding hydrated phases based on X-ray powder diffraction pattern. The coordination number decreases upon dehydration as evidenced in the case of the cobalt derivative, which undergoes a colour change from orange-yellow, with $\lambda = 410$ nm, to green, with $\lambda = 590$ nm, according to the UV/Vis spectra. The M^{2+} ions are in an octahedral environment in **1** and **2** with two water molecules (O1 and O2) occupying two coordination sites in the *trans* positions (Figure 1). The heating of these compounds, up to 150 °C, leads to the loss of one of these coordinated water molecules and to five-coordinate metal ions. It should be outlined that this unusual change of the coordination number from six to five has already been observed for metal phosphonates $Co(O_3PCH_3)\cdot H_2O$.[16] The magnetic moment of the dehydrated cobalt compound **1** decreased from 5.3 emu·K·mol^{-1} to 4.7 emu·K·mol^{-1}, which indicated a decrease in coordination number, as previously reported by Cunningham.[16c] However, it is difficult to indicate which water molecule (O1W or O2W) is leaving. It should also be noted that the infrared C−N stretch (2154 cm^{-1}) for both dehydrated phases are reversibly shifted toward higher frequencies from those of the hydrated phases (2144 cm^{-1}) showing a reversible change in the symmetry of $[M^{II}(H_2O)]_2[Mo(CN)_8]$ fragments upon heating.

The third weight-loss step of 10.5% could be attributed to the simultaneous loss of the last two coordinated water molecules (6.4%) and one CN^- group (4.6%). The TGA/MASS analysis of the gas evolved during this weight loss step indicates the presence of the water (ionic current $m/z = 18$ for H_2O^+) and the cyanide (ionic current $m/z = 27$ for HCN^+) (Figure 5). Such losses of cyano ligands upon heating around 350 °C has also been observed for the precursor $K_4[Mo(CN)_8]\cdot2H_2O$[17a] and for octacyanometallates of alkaline metals.[17b] The X-ray powder pattern for the title compounds heated to 500 °C indicated decomposition of the original structures.

The generation of an open metal coordination site on the M^{II} ions implies that the dehydration reaction should be reversible. After heating of samples **1** and **2** up to 150 °C under argon, the exposure of the dehydrated powders to air moisture at 25 °C leads to intercalation/coordination of two water molecules [Figure 5 (top)]. As a result, the X-ray powder pattern of the rehydrated sample was restored and the colour of the cobalt-containing compound recovered its original orange-yellow colour.

In a similar approach, the behaviour towards an intercalation/coordination of ammonia and amines was studied. The intercalation of NH_3 gas was observed at room temperature for samples **1** and **2** that had originally been outgassed at 150 °C. As shown in Figure 5 (bottom), it is possible to approximate the amount of NH_3 molecules that have intercalated. The mass gain (6.0%) is in good agreement with the calculated value (5.9%) for $[M(H_2O)(NH_3)]_2[Mo(CN)_8]$. Further evidence for the formation of $[Co(H_2O)(NH_3)]_2[Mo(CN)_8]$ and $[Mn(H_2O)(NH_3)]_2[Mo(CN)_8]$ was obtained from thermogravimetric, elemental and FTIR analyses. As shown in Figure 5 (bottom), the loss of NH_3 (inflexion point at 181 °C) occurs at 50 °C higher than the temperature of water loss in the hydrated compounds (inflexion point at 131 °C). The weight loss between 30 and 200 °C constitutes 6% of the total mass and the theoretical value calculated by assuming the formula $[M(H_2O)(NH_3)]_2[Mo(CN)_8]$ is 5.9%. In addition, the elemental analysis shows good agreement between the calculated and experimental values. IR data provide strong evidence that the NH_3 molecule occupies the empty coordination site created upon dehydration. The IR spectra of both compounds $[Co(H_2O)(NH_3)]_2[Mo(CN)_8]$ and $[Mn(H_2O)(NH_3)]_2[Mo(CN)_8]$ show the antisymmetric and symmetric NH_3 stretching in the 3400−3000 cm^{-1} region; NH_3 deformation is observed in the 1612 cm^{-1} region with symmetric deformation taking place at 1401 and 1221 cm^{-1}. Finally, rocking vibrations occur at 950−595 cm^{-1}.[18]

A remarkable feature of the amine intercalation reactions of $[M(H_2O)]_2[Mo(CN)_8]$ is their selectivity with respect to shape and size. Experiments in which $[M(H_2O)]_2[Mo(CN)_8]$ (M^{II} = Mn, Co) were subjected to methyl-, ethyl-, and dodecylamines for prolonged reaction times showed the formation of intercalation compounds with all primary amines except dodecylamine. The formation of compounds having a general formula $[M(H_2O)(amine)]_2[Mo(CN)_8]$ have been observed. The intercalation reactions were surveyed by thermogravimetric analyses and the final compounds were characterised by IR spectra. In addition, in the case of bulkier amines such as pyridine no intercalation reaction was observed. This selectivity with respect to shape and size may be accounted for by considering the structural environment of the water molecule in $[M(H_2O)_2]_2[Mo(CN)_8]$, which is assumed to occupy the amino coordination site. Its cavity size (71.1 Å^3) can obviously limit the accessibility to the open coordination site.

Conclusion

In summary, two new coordination polymers $[M(H_2O)_2]_2[Mo(CN)_8]·4H_2O$ (M = Co^{II} and Mn^{II}) have been prepared and crystallised. These compounds form three-dimensional networks containing channels occupied by coordinated and crystallised water molecules. The title compounds can easily be dehydrated to yield $[M(H_2O)]_2[Mo(CN)_8]$ compounds. The dehydration is reversible and both derivatives readily reabsorb moisture from the atmosphere. Furthermore, the dehydration reaction leaves an empty coordination site on the bivalent metal ion, which has been exploited by reaction with ammonia and primary amines upon exposure to a flow of respective gases in order to form intercalation compounds. Since the interaction of inserted molecules with the dehydrated compounds takes place mainly through coordination to the M^{II} ions, the porosity should not be regarded as a prerequisite for reversible absorption.[24] Studies concerning intercalation reactions of coordination polymers presenting ferromagnetic ordering, and the influence of this on the magnetic properties, are currently in progress.

Experimental Section

Syntheses: Unless otherwise noted, all manipulations were performed at ambient temperature using reagents and solvents as received. The precursor $K_4[Mo(CN)_8]·2H_2O$ was prepared as already described.[15,16]

$[M^{II}(H_2O)_2]_2[Mo(CN)_8]·4H_2O$ [M^{II} = Co (1) or Mn (2)]: $[M^{II}(H_2O)_6](NO_3)_2·4H_2O$ (2.0 mmol) (M^{II} = Mn or Co) in water (30 mL) was added to a solution of $K_4[Mo(CN)_8]·2H_2O$ (1.0 mmol) in water (30 mL, natural pH), which immediately led to a precipitation of orange-yellow (**1**) or yellow (**2**) products. The solids were washed three times with water and then and dried in air with ethanol. Yield: 0.45 g, 82%. **1**: $C_8H_{16}Co_2MoN_8O_8$: calcd. C 16.96, H 2.82, Co 20.82, Mo 16.94, N 19.78; found C 17.26, H 3.54, Co 20.41, Mo 17.23, N 20.36. IR (KBr): $\tilde{\nu}$ = 3404(sh), 2144, 1616, 537, 431 cm^{-1}. **2**: $C_8H_{16}Mn_2MoN_8O_8$: calcd. C 17.20, H 2.87, Mn 19.68, Mo 17.19, N 20.07; found C 17.63, H 3.85, Mn 20.16, Mo 17.27, N 19.87. IR (KBr): $\tilde{\nu}$ = 3404(sh), 2145, 1616, 537, 431 cm^{-1}. The crystals, suitable for X-ray analysis, were obtained by slow diffusion in an H-shaped tube with two 10^{-4} M aqueous solutions containing $K_4[Mo(CN)_8]·H_2O$ and $[M(H_2O)_6](NO_3)_2$, respectively. After two months, yellow (M = Mn^{II}) and orange-red (M = Co^{II}) crystalline plates were obtained. The crystals were insoluble in most common solvents and stable in air. The composition of the crystalline compound was also established by single-crystal X-ray diffraction at 160 K.

Dehydration of $[M^{II}(H_2O)_2]_2[Mo(CN)_8]·4H_2O$ [M^{II} = Co (1) or Mn (2)] and Intercalation of Ammonia and Amines into the Resulting Product: Both manganese- and cobalt-containing compounds were dehydrated by heating under argon at 150 °C for 1 h. Dehydrated samples **1a** and **2a** were stored in a drybox prior to use. **1a** (after heating at 150 °C): $C_8H_4Co_2MoN_8O_2$: calcd. C 20.98, Co 25.73, Mo 20.95, N 24.47; found C 20.51, Co 25.47, Mo 20.67, N 24.64. IR (KBr): $\tilde{\nu}$ = 3604, 3411, 3224, 2145, 1616, 537, 431 cm^{-1}. **2a** (after heating at 150 °C): $C_8H_4Mn_2MoN_8O_2$: calcd. C 21.35, Mn 24.42, Mo 21.32, N 24.90; found C 21.45, Mn 24.89, Mo 21.01, N 24.47. IR (KBr): $\tilde{\nu}$ = 3606, 3417, 3190, 2145, 1616, 537, 431 cm^{-1}. The intercalation of ammonia and primary amines was carried out by exposing the dehydrated compounds to a flow of ammonia or corresponding amine gases at 150 °C. For the dehydrated cobalt-containing compound **1**, the reaction appeared to be complete in 5 min, as evidenced by a colour change from green (dehydrated) to orange-yellow and by mass-gain measurements determined by thermogravimetry analysis [Figure 5 (insert)]. To ensure complete reaction, the compounds dehydrated at 150 °C were usually exposed to ammonia or amine gas for 30 min. Longer exposure to the flow of ammonia or amine gas did not produce different results. In the case of dodecylamine (b.p. 247 °C), **1a** or **2a** was added to the dodecylamine and the mixture was stirred for 30 min. The solid was filtered, washed three times with cyclohexane and dried under vacuum. $[Co(H_2O)(NH_3)]_2[Mo(CN)_8]$: $C_8H_{10}Co_2MoN_{10}O_2$: calcd. C 19.53, Co 23.95, Mo 19.50, N 28.47; found C 19.70, Co 23.41, Mo 19.36, N 28.63. IR (KBr): $\tilde{\nu}$ = 3607, 3371, 3283, 3199, 2138, 1615, 1400, 1220, 1096, 1021, 807, 593, 461 cm^{-1}.

Table 1. Crystal data and structure refinement for **1** and **2**

Empirical formula	$C_2H_4N_2O_2Co_{0.5}Mo_{0.25}$ (**1**)	$CH_2NOMo_{0.13}Mn_{0.25}$ (**2**)
Formula mass	141.5	75.6
Temperature [K]	160(2)	160(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	tetragonal	tetragonal
Space group	$I4/m$ (87)	$I4/mcm$ (140)
Unit cell dimensions [Å]	$a = b =$11.748(2) $c =$ 13.022(3)	$a = b=$ 11.679(2) $c =$ 13.276(3)
Volume [Å^3]	1797.2(6)	1810.83(60)
Z	16	32
Calculated density [Mg/m^3]	2.092	1.988
Absorption coefficient [mm^{-1}]	2.568	2.109
F(000)	1120	1040
2θ range for data collection [°]	3.3−51.86	3.3−48.75
Reflections collected/unique	2794/866 [R(int) = 0.0620]	6999/412 [R(int) = 0.0263]
Completeness to 2θ	25.93°, 94.1%	24.36°, 96.3%
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
Data/restraints/parameters	866/0/83	412/0/39
Absorption correction:	semiempirical (DIFABS)[18]	semiempirical (DIFABS)[18]
$T_{\min} - T_{\max}$	0.238−0.699	0.460−0.824
Goodness-of-fit on F^2	1.148	1.270
Weight [$P = (F_o^2 + 2F_c^2)/3$]	$1/[\sigma^2(F_o^2) + (0.0628P)^2 + 19.361P]$	$1/[\sigma^2(F_o^2) + (0.0292P)^2 + 21.012P]$
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0530$, $wR2 = 0.1355$	$R1 = 0.0325$, $wR2 = 0.0869$
R indices (all data)	$R1 = 0.0589$, $wR2 = 0.1391$	$R1 = 0.0325$, $wR2 = 0.0869$
Largest diff. peak/hole [e·Å^{-3}]	0.830/−0.861	0.513/−0.632

$[Mn(H_2O)(NH_3)]_2[Mo(CN)_8]$: $C_8H_{10}Mn_2MoN_{10}O_2$: calcd. C 19.85, Mn 22.70, Mo 19.82, N 28.94; found C 19.55, Mn 22.97, Mo 19.06, N 28.20. IR (KBr): ṽ = 3609, 3380, 3290, 3099, 2146, 1611, 1400, 1220, 1038, 600, 468, 436 cm^{-1}. $[Co(H_2O)(CH_3NH_2)]_2[Mo(CN)_8]$: $C_{10}H_{14}Co_2MoN_{10}O_2$: calcd. C 23.09, Co 22.66, Mo 18.45, N 26.93; found C 24.20, Co 22.41, Mo 18.36, N 26.69. IR (KBr): ṽ = 3600, 3325, 3268, 3182, 2725, 2695, 2114, 1611, 1402, 1220, 1036, 595, 461, 436 cm^{-1}. $[Mn(H_2O)(CH_3NH_2)]_2[Mo(CN)_8]$: $C_{10}H_{14}Mn_2MoN_{10}O_2$: calcd. C 23.44, Mn 21.46, Mo 18.74, N 27.36; found C 23.67, Mn 21.97, Mo 18.06, N 27.20. IR (KBr): ṽ = 3609, 3380, 3290, 3099, 2146, 1611, 1400, 1220, 1038, 600, 468, 436 cm^{-1}. $[Co(H_2O)(C_2H_5NH_2)]_2[Mo(CN)_8]$: $C_{12}H_{18}Co_2MoN_{10}O_2$: calcd. C 26.29, Co 21.50, Mo 17.50, N 25.55; found C 24.80, Co 21.41, Mo 17.36, N 25.50. IR (KBr): ṽ = 3372, 3268, 3182, 2974, 2137, 1682, 1608, 1502, 1470, 1384, 1215, 1035, 840, 582, 461, 436 cm^{-1}. $[Mn(H_2O)(C_2H_5NH_2)]_2[Mo(CN)_8]$: $C_{12}H_{18}Mn_2MoN_{10}O_2$: calcd. C 26.68, Mn 20.34, Mo 17.76, N 25.93; found C 26.73, Mn 20.97, Mo 17.06, N 25.20. IR (KBr): ṽ = 3370, 3270, 3185, 2974, 2137, 1682, 1608, 1502, 1470, 1384, 1215, 1035, 846, 580, 465, 430 cm^{-1}.

X-ray Crystallography and Structure Solution: For **1** and **2**, data were collected at a low temperature (T = 160 K) with a Stoe Imaging Plate Diffraction System (IPDS), equipped with an Oxford Cryosystems Cryostream Cooler Device and using a graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Final unit cell parameters were obtained by means of a least-squares refinement of a set of 8000 well-measured reflections, and a crystal decay was monitored during data collection by measuring 200 reflections per image, no significant fluctuations of intensities were observed (Table 1). Structures were solved by means of Direct Methods using the program SIR92,[19] and subsequent difference Fourier maps, models were refined by least-squares procedures on F^2 by using SHELXL-97[20] integrated in the package WINGX version 1.64.[21] For complex **1** hydrogen atoms connected to the H_2O molecules were located on a difference Fourier map and isotropically refined. For compound **2**, owing to the symmetry operators on which H_2O molecules were located, hydrogen atoms were statistically disordered and consequently could not be located. For compounds **1** and **2** a semiempirical correction absorption was applied[22] and all non-hydrogen atoms were anisotropically refined; in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. CCDC-194778 and -194779 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Physical Measurements: Infrared spectra were recorded using KBr disks or Nujol mulls between NaCl plates with a Nicolet Model 510P spectrophotometer. UV/Vis spectra were recorded with a Cary-17D spectrometer. Thermogravimetry (TG) analyses were performed using a Netzsch STA 409 instrument under argon, from 30 to 700 °C, at a heating rate of 1 °C·min^{-1}; volatiles were determined using a Balzers QMG 421 quadruple Mass Spectrometer coupled with ATG equipment. Magnetic susceptibility data were collected with a Quantum Design MPMS-XL SQUID magnetometer. The compounds were measured on finely grounded polycrystalline samples between 1.8 and 320 K at 1000 G. The data were corrected for the sample holder and the diamagnetism contributions calculated from Pascal's constants.[23] Powder X-ray data were recorded with a Bruker D5000 diffractometer using a Bragg−Brentano geometry; a Cu target and a back monochromator were used ($K_{\alpha1} + K_{\alpha2}$); 2θ range 5−88°; 2θ steps 0.02°.

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