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Salts and solvents effect on the crystal structure of imidazolium dicarboxylate salt based coordination networks.

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ABSTRACT

The solvothermal synthesis of novel metal-organic networks from the 1,3-bis-(carboxymethyl)-imidazolium chloride ($[\text{H}_2\text{L}][\text{Cl}]$) and cobalt or nickel salts (acetate or nitrate) in different solvents (water or ethanol and water/ethanol or water/ethylene glycol mixture) has been explored leading to four isotypic compounds of general formula $[\text{M}(\text{L})(\text{H}_2\text{O})_4][\text{Cl}]\cdot\text{Solv}$ with $\text{M} = \text{Ni}$ or Co and $\text{Solv} = \text{H}_2\text{O}$ for **1** and **2**, respectively and $\text{M} = \text{Ni}$ or Co and $\text{Solv} = (\text{EG})_{0.5}$ for **3** and **4**, respectively and two other isostructural compounds, namely $[\text{Ni}(\text{L})(\text{ox})_{0.5}(\mu_2\text{-H}_2\text{O})_{0.5}]$ (**5**) and

$[\text{Co}(\text{L})(\text{ox})_{0.5}(\mu_2\text{-H}_2\text{O})_{0.5}]$ (**6**) where the *in situ* formation of oxalate (ox) was observed. The structural characterizations evidence a significant influence of the solvent as well as of the metal salt on the structure and crystallinity of the final compounds, the former leading to observation of different magnetic behaviors. A one-dimensional antiferromagnetic behavior is thus observed in compounds **5** and **6** containing oxalate ligand while compounds **1-4** exhibited typical behavior of quasi-isolated magnetic species.

INTRODUCTION

Metal-organic coordination networks have been the focus of considerable research in recent years evidenced by the increasing number of papers and crystalline structures published in the field. This interest in drafting new metal-organic networks stems from their chemical and structural versatility as well as their potential applications in many areas such as gas storage, catalysis, drug delivery, separations, sensing and more recently information storage.¹⁻⁷

Metal-organic coordination networks are in most cases obtained by reaction of metal salts with organic ligand bearing coordination functions (essentially carboxylate, sulfonate or pyridine functions) in solvothermal conditions. Next to this traditional way, the *in situ* modification of organic precursors into ligand (arising from decomposition, hydrolysis, oxidation or reduction, rearrangement or a combination of these different possibilities) during the synthesis of the metal-organic coordination networks has been developed.⁸⁻¹⁵ This approach is particularly interesting since it gives access to new compounds which cannot be obtained directly from the metal salt and the ligand.

Although these two synthetic approaches allow the formation of numerous functional compounds, they present often the main drawback of being unpredictable without a good knowledge of the chosen system. Indeed, different parameters such as solvent,^{16,17} nature of the metal ion and its counterion,^{18–22} reaction temperature or time,^{19,16,23} metal-ligand ratio,²² pH^{24–26} can have an effect on the nature of the final compound which renders difficult any prediction. Therefore, it is necessary to realize either mechanistic studies or screening of the reaction conditions in order to fully rationalize the assembling process governing the formation of the compounds.

Some authors and us have reported recently the synthesis and characterization of metal-organic coordination networks from the 1,3-bis-(carboxymethyl-)-imidazolium chloride ([H₂L][Cl]) and transition metal, lanthanide or actinide salts obtained in solvothermal conditions.^{24,27–39} We have chosen to extend this strategy to other transition metal salts in order to explore the influence of the synthesis parameters on the different types of structures adopted by this family of compounds and possibly tune the physical properties.

We report the synthesis of six new coordination networks obtained from reaction between [H₂L][Cl] and M(OAc)₂·4H₂O or M(NO₃)₂·6H₂O salts with M = Co²⁺ or Ni²⁺ using water/ethanol or water/ethylene glycol (EG) mixture. The structure of these networks obtained from single crystal X-ray diffraction evidenced an effect of the nature of the metal salt (nitrate *versus* acetate) as well as of the solvent on their crystal structure and their magnetic dimensionality. Indeed, when nitrate salts are used, *in situ* formation and incorporation of oxalate (ox) in the crystal structure is observed which is not the case with the acetate salts. In addition replacement of a water/ethanol mixture by a water/EG mixture in presence of acetate salts influences the stability of the structure due to a more extensive H-bond network.

EXPERIMENTAL SECTION

Materials and General Remarks. 1-trimethylsilylimidazole, methylchloroacetate were purchased from Alfa Aesar and $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ from Aldrich, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ from Fluka, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ from Acros and were used as received.

Elemental analyses for C, H, N were carried out at the Service de Microanalyses of the Institut de Chimie de Strasbourg. The SEM images were obtained with a JEOL 6700F scanning electron microscope (SEM) equipped with a field emission gun (FEG), operating at 3 kV in the SEI mode instrument. FT-IR spectra were collected on a Perkin Elmer Spectrum Two UATR-FTIR spectrometer. UV/Vis/NIR studies were performed on Perkin Elmer Lambda 950 spectrometer (spectra recorded in reflection mode using a 150 mm integrating sphere with a mean resolution of 2 nm and a sampling rate of $225 \text{ nm} \cdot \text{min}^{-1}$). TGA-TDA experiments were performed using a TA instrument SDT Q600 (heating rates of $5^\circ\text{C} \cdot \text{min}^{-1}$ under air stream). NMR spectra in solution were recorded using a Bruker AVANCE 300 (300 MHz) spectrometer. Magnetic measurements were performed using a Quantum Design SQUID-MPMS3 magnetometer. The static susceptibility measurements were performed in the 1.8-300 K temperature range with an applied field of 5 kOe. Magnetization measurements at different fields at a given temperature confirm the absence of ferromagnetic impurities. Data were corrected for the sample holder and diamagnetism was estimated from Pascal constants. The powder XRD patterns were collected with a Bruker D8 diffractometer ($\text{Cu K}\alpha_1 = 1.540598 \text{ \AA}$).

Synthesis

[LH2]/[Cl] was synthesized as previously described.⁴⁰

Synthesis of $[\text{Ni}(\text{L})(\text{H}_2\text{O})_4][\text{Cl}]\cdot\text{H}_2\text{O}$ (1). $[\text{LH}_2][\text{Cl}]$ (550 mg, 2.5 mmol) and $\text{Ni}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (622.1 mg, 2.5 mmol) were dissolved in a water-ethanol solution (6 mL, v/v: 1/1). The mixture was sealed in a Teflon-line stainless steel bomb (23 mL) and heated at 393 K for 72 h. After cooling to room temperature, the bomb was opened giving rise to a green solution. After evaporation of this solution, green crystals of **1** were obtained and washed with ethanol. These green crystals were isolated in ~50 % yield. Anal. Calcd. for $\text{C}_7\text{H}_{17}\text{N}_2\text{O}_9\text{Cl}_1\text{Ni}_1$: C, 22.87; H, 4.63; N, 7.62%. Found: C, 22.58; H 4.53; N 7.13%. IR/ cm^{-1} (ATR): 3351 (m), 3203 (m), 3143 (m), 3064 (m), 1569 (s), 1445 (m), 1396 (s), 1384 (s), 1311 (m), 1175 (m), 1112 (w), 1036 (w), 968 (m), 882 (m), 845 (m), 793 (s), 773 (s), 679 (s), 493 (s).

Synthesis of $[\text{Co}(\text{L})(\text{H}_2\text{O})_4][\text{Cl}]\cdot\text{H}_2\text{O}$ (2). $[\text{LH}_2][\text{Cl}]$ (550 mg, 2.5 mmol) and $\text{Co}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (622.7 mg, 2.5 mmol) were dissolved in a water-ethanol solution (6 mL, v/v: 1/1). The mixture was sealed in a Teflon-line stainless steel bomb (23 mL) and heated at 393 K for 72 h. After cooling to room temperature, the bomb was opened giving rise to a pink solution. After evaporation of this solution, pink crystals of **2** were obtained and washed with ethanol. These pink crystals were isolated in ~48 % yield. Anal. Calcd. for $\text{C}_7\text{H}_{17}\text{N}_2\text{O}_9\text{Cl}_1\text{Co}_1$: C, 22.86; H, 4.63; N, 7.62%. Found: C, 23.09; H, 4.53; N, 7.24%. IR/ cm^{-1} (ATR): 3352 (m), 3202 (m), 3146 (m), 3095 (m), 1566 (s), 1444 (m), 1392 (s), 1348 (w), 1310 (m), 1176 (m), 1100 (w), 1026 (w), 969 (m), 851 (m), 792 (s), 772 (s), 672 (s), 479 (s).

Synthesis of $[\text{Ni}(\text{L})(\text{H}_2\text{O})_4][\text{Cl}]\cdot(\text{EG})_{0.5}$ (3). The procedure was similar to the preparation of **1**, except that the water-ethanol solution was replaced by a water/ethylene glycol solution (6 mL, v/v: 1/1). The green crystals were obtained in ~49 % yield. Anal. Calcd. for $\text{C}_8\text{H}_{18}\text{N}_2\text{O}_9\text{Cl}_1\text{Ni}_1$: C, 25.25; H, 4.73; N, 7.36%. Found: C, 24.63; H, 4.78; N, 7.28%. IR/ cm^{-1} (ATR): 3357 (w), 3215 (w), 3147 (w), 3114 (w), 3096 (w), 3075 (w), 2963 (w), 1612 (sh), 1574 (s), 1441 (m), 1394 (s),

1384 (s), 1350 (w), 1320 (w), 1309 (m), 1291 (w), 1264 (w), 1216 (w), 1182 (m), 1108 (w), 1021 (m), 966 (m), 952 (m), 886 (w), 852 (w), 793 (m), 778 (m), 711 (w), 680 (m), 574 (w), 552 (w), 489 (w).

Synthesis of $[Co(L)(H_2O)_4][Cl] \cdot (EG)_{0.5}$ (4**).** The procedure was similar to the preparation of **2**, except that the water-ethanol solution was replaced by a water/ethylene glycol solution (6 mL, v/v: 1/1). The pink crystals were obtained in ~49 % yield. Anal. Calcd. for $C_8H_{18}N_2O_9Cl_1Co_1$: C, 25.23; H, 4.73; N, 7.36%. Found: C, 25.35; H, 4.90; N, 7.41. IR/cm⁻¹ (ATR): 3354 (w), 3211 (w), 3145 (w), 3112 (w), 3101 (w), 3079 (w), 2958 (w), 1611 (sh), 1573 (s), 1437 (m), 1393 (s), 1382 (s), 1320 (w), 1307 (m), 1290 (w), 1265 (w), 1214 (w), 1180 (m), 1107 (w), 1021 (m), 974 (m), 966 (m), 862 (w), 793 (m), 777 (m), 703 (w), 675 (m), 563 (w), 482 (w).

Synthesis of $[Ni(L)(ox)_{0.5}(\mu_2-H_2O)_{0.5}]$ (5**).** $[LH_2][Cl]$ (550 mg, 2.5 mmol) and $Ni(NO_3)_2 \cdot 6H_2O$ (727.0 mg, 2.5 mmol) were dissolved in a 1:1 water-ethanol solution (6 mL). The mixture was sealed in a Teflon-line stainless steel bomb (23 mL) and heated at 393 K for 72 h. After cooling to room temperature, the bomb was opened and green crystals of **5** were filtered and washed with ethanol. The green crystals were isolated in ~20 % yield (based on Ni salt). Anal. Calcd. for $C_8H_8N_2O_{6.5}Ni_1$: C, 32.57; H, 2.71; N, 9.50%. Found: C, 31.83; H, 2.83; N, 9.20%. IR/cm⁻¹ (ATR): 3162 (w), 3105 (w), 2957 (w), 1667 (m), 1600 (s), 1581 (s), 1442 (m), 1395 (s), 1395 (s), 1350 (w), 1198 (w), 1164 (m), 1106 (w), 1046 (m), 977 (w), 911 (m), 804 (m), 768 (m), 740 (m), 677 (s), 633 (m), 619 (m), 584 (m), 465 (m), 430 (m).

Synthesis of $[Co(L)(ox)_{0.5}(\mu_2-H_2O)_{0.5}]$ (6**).** The procedure was similar to the preparation of **5**, except that $Ni(NO_3)_2 \cdot 6H_2O$ was replaced by $Co(NO_3)_2 \cdot 6H_2O$ (727.3 mg, 2.5 mmol). The pink crystals were isolated in ~21 % yield (based on Co salt). Anal. Calcd. for $C_8H_8N_2O_{6.5}Co_1$: C, 32.55; H, 2.71; N, 9.49%. Found: C, 31.63; H, 2.81; N, 9.18%. IR/cm⁻¹ (ATR): 3160 (w), 3101 (w), 2955

(w), 1666 (m), 1601 (s), 1583 (s), 1444 (m), 1393 (s), 1346 (w), 1315 (s), 1196 (w), 1163 (m), 1105 (w), 1035 (m), 977 (w), 907 (m), 801 (m), 767 (m), 737 (m), 673 (s), 633 (m), 618 (m), 582 (m), 488 (m), 445 (w), 416 (w).

Crystallographic Data Collection and Refinement. The diffraction intensities were collected with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). Data collection and cell refinement for the compounds **1** and **2** were carried out using ‘Bruker APEX-II Kappa CCD’ diffractometer at 100 K and room temperature, respectively. Data collection and cell refinement for the compounds **3**, **4**, **5** and **6** were carried out using a ‘Kappa Nonius CCD diffractometer’ at room temperature. Intensity data were corrected for Lorenz-polarization and absorption factors. The structures were solved by direct methods using SIR92,⁴¹ and refined against F^2 by full-matrix least-squares methods using SHELXL-2013 with anisotropic displacement parameters for all non-hydrogen atoms.^{42,43} All calculations were performed by using the Crystal Structure crystallographic software package WINGX.⁴⁴ The structures were drawn using Mercury.⁴⁵ All hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. The relevant crystallographic data are listed in Tables 1 and 2. The CCDC numbers are 1475566 for **1**, 1475565 for **2**, 1873829 for **3**, 1873828 for **4**, 1475568 for **5** and 1475567 for **6**.

Table 1. Crystallographic data for **1-4**.

Compound	1	2	3	4
Formula	C ₇ H ₁₅ Cl ₁ N ₂ Ni ₁ O ₉	C ₇ H ₁₅ Cl ₁ N ₂ Co ₁ O ₉	C ₈ H ₁₈ Cl ₁ N ₂ Ni ₁ O ₉	C ₈ H ₁₈ Cl ₁ N ₂ Co ₁ O ₉
M_r (g.mol ⁻¹)	365.39	365.59	380.40	380.62
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	5.0637(4)	5.154(2)	5.283(2)	5.319(3)
<i>b</i> (Å)	11.3937(7)	11.590(5)	11.710(7)	11.8033(16)
<i>c</i> (Å)	12.1332(10)	12.297(6)	12.217(7)	12.195(8)
α (°)	108.157(6)	108.645(14)	110.12(3)	110.47(2)
β (°)	98.020(7)	98.074(15)	98.85(4)	98.13(4)
γ (°)	90.839(6)	90.148(14)	90.18(5)	90.449(18)
<i>V</i> (Å ³)	657.40(9)	688.2(6)	699.9(7)	708.7(6)
<i>Z</i>	2	2	2	2
<i>T</i> (K)	100(2)	293(2)	293(2)	293(2)
D_{calc} (g.cm ⁻³)	1.855	1.783	1.805	1.784
F(000)	364	372	394	392
R _{int}	0.0864	0.0711	0.0375	0.0334
S	1.097	1.040	1.054	1.042
R1 [<i>I</i> >2σ(<i>I</i>)]	0.0778	0.0986	0.0415	0.0308
wR2 [all data]	0.2049	0.2772	0.0914	0.0667

Table 2. Crystallographic data for **5** and **6**.

Compound	5	6
Formula	C ₁₆ H ₁₆ Ni ₂ N ₄ O ₁₃	C ₁₆ H ₁₆ Co ₂ N ₄ O ₁₃
M _r (g.mol ⁻¹)	589.75	590.19
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pbcm</i>	<i>Pbcm</i>
<i>a</i> (Å)	7.6980(13)	7.7202(14)
<i>b</i> (Å)	15.575(2)	15.667(2)
<i>c</i> (Å)	16.478(4)	16.6691(19)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
<i>V</i> (Å ³)	1975.7(6)	2016.2(5)
<i>Z</i>	4	4
<i>T</i> (K)	293(2)	293(2)
<i>D</i> _{calc} (g.cm ⁻³)	1.983	1.944
F(000)	1200	1192
R _{int}	0.0674	0.0275
S	1.039	1.033
R1 [<i>I</i> > 2σ(<i>I</i>)]	0.0424	0.0276
wR2 [all data]	0.0960	0.0658

RESULTS AND DISCUSSION

Syntheses

Compounds **1** and **2** were obtained by reacting $[\text{H}_2\text{L}][\text{Cl}]$ and $\text{M}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ with $\text{M} = \text{Ni}, \text{Co}$ in a water/ethanol solution in a Teflon-line stainless steel autoclave at 393 K for 3 days. After cooling to room temperature, the solutions obtained were left to evaporate and a homogeneous phase made of single crystals was formed after few days. Compounds **3** and **4** were synthesized in a similar manner but replacing the water/ethanol solution by a water/ethyleneglycol solution. Substituting acetate salts $\text{M}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ by nitrate salts $\text{M}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in the water/ethanol solution led at the opening of the autoclaves to crystalline compounds **5** and **6**.

When these reactions were done in water only, acetate salts gave rise to compounds **1** and **2** while nitrate salts led, after evaporation of the solution, to amorphous gels whatever the metal involved. The use of ethanol with $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ or $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ led to compound **2** or to a mixture of non-identified powders, respectively. The use of ethanol with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ led to the formation of compound **5** and with $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to the formation of $[\text{Co}(\text{L})_2]^{29}$. All these synthetic conditions are summarized in Scheme 1.

The occurrence of oxalate ligand in the structure of **5** and **6** pushed us to try to introduce oxalic acid in the starting mixture. This approach was successfully used to obtain well crystallized lanthanide derivatives.^{46,47} We noticed however that if oxalic acid is introduced directly as starting reactant with acetate salts and $[\text{H}_2\text{L}][\text{Cl}]$ in the water/ethanol solution, nickel oxalate (JCPDS N° 01-073-2580) or cobalt oxalate (JCPDS N° 01-073-2579) crystalline powder is formed at the end of heating.

Scheme 1. Summary of the obtained compounds as a function of the solvents and the nature of the metal salts. The numbers in parentheses refer to the numbering of the compounds. * from reference 28.

Structural description of compounds 1, 2, 3 and 4. Compounds **1**, **2**, **3** and **4** are isotypes. Indeed, **1** and **2** differ only from **3** and **4** by the nature of the free solvent molecule, *i.e.* water vs ethyleneglycol. These compounds are also isotype with an already reported structure, namely **[Co(L)(H₂O)₄][Br]·H₂O**, in which chloride is substituted with bromide.³⁴ Thus, only the crystal structure of **3** is described here for clarity. **3** crystallizes in the *P*-1 (No. 2) triclinic space group. The asymmetric unit of compound **3** contains one Ni²⁺ ion, one ligand [L]⁺, one uncoordinated Cl[−]

anion and one uncoordinated ethyleneglycol (EG) on a special position, *i.e.* an inversion center (Figure 1). The Ni^{2+} ions in this compound adopts a slightly distorted octahedral environment (Table S1), two O atoms coming from the carboxylate functions of two different $[\text{L}]^-$ ligands (O1 and O3) and four O atoms from four different water molecules (O5, O6, O7 and O8). The Ni-O lengths are in good agreement with those observed in structurally related compounds (Tables S2).⁴⁸

Figure 1. Asymmetric unit in **3**.

The Ni^{2+} center is linked to the carboxylate functions of two different $[\text{L}]^-$ ligands giving rise to 1D polymeric chains running along the *b* direction. These 1D polymeric chain are repeated in an inverted way forming blocks of two chains. These blocks are separated by a layer of free chloride anions and free EG molecules (Figure 2). The cohesion of the crystal is due to extensive H-bonding throughout the structure.

Figure 2. Representation of the stacking along the a axis in **3** showing the 1D character of **3**.

It is worth noticing that the structure of compounds **1** and **2** is basically the same as that of **3** and **4**, by replacing EG by water molecules (Figure 3 and Table S1). Yet, the solvent molecules are much more disordered for water and rather high reliability factors values were obtained in **1** and **2**. This point is discussed below.

Figure 3. Representation of the stacking along the a axis in **1**.

Description of the structure of compounds 5 and 6. Compounds **5** and **6** are isostructural. The compounds form 1D networks crystallizing in the *Pbcm* (No. 57) orthorhombic space group. The asymmetric unit contains one M^{2+} ion, one $[L]^-$ ligand, one half oxalate ligand, which is formed *in situ*, and one half water molecule (Figure 4). The M^{2+} ions are coordinated by six oxygen atoms belonging to carboxylate functions of three different ligands $[L]^-$ (O1, O2 and O3), to half oxalate ligand (O6 and O7) and to one bridging water molecule (O5) leading to a distorted octahedral environment for the M^{2+} ions (Tables S1 and S3). The Ni-O and Co-O distances are in agreement with those reported in the literature (Table S2 and S4).^{34,48,49} The cohesion of the crystal is mainly due to weak H-bonds essentially between H atoms of $[L]^-$ ligands and the O atoms of oxalate groups.

Figure 4. View of the asymmetric unit in **5**.

In these compounds, the carboxylate functions of the fully deprotonated ligand L^- adopt two kinds of coordination mode, *i.e.* bridging bidentate between two metal centers and bidentate between one metal center and one hydrogen of the water molecule, and those of the oxalate ligands

are in a bis-bidentate bridging mode (Figure 5a). These different coordination modes give rise to ribbons formed of dimeric metallic units connected either by an oxalate ligand or by a bridging water molecule and a carboxylate function of a ligand L^- (Figure 5b).

Figure 5. View (a) of the different coordination modes and (b) stacking along *a* axis in **5**.

***In situ* formation of oxalate ligand and solvent effect.** Since no oxalate ligand was introduced into the starting reaction medium, the oxalate ligand incorporated in the structure of **5** and **6** is formed *in situ* during the reaction. This phenomenon is frequently encountered in solvothermal reactions. Four main mechanisms are proposed in literature to explain this phenomenon: i) the reductive coupling of carbon dioxide⁵⁰ ii) the oxidation of ethanol or oxidative coupling of methanol in presence of nitrate,⁵¹ iii) the decarboxylation of organic ligands followed by reductive coupling of the resulting carbon dioxide⁵² and iv) the oxidation-hydrolysis in a presence of a metal catalyst of the organic ligand leading to its decomposition.⁵³ In the present case, the formation of oxalate ligand is observed for the nitrate salts in the water/ethanol mixture regardless the nature of

the metal. For the nickel nitrate and for the cobalt nitrate, it occurs in ethanol and in water/EG mixture, respectively (Scheme 1). These observations indicating that the formation of oxalate ligand takes place in presence of an alcohol and nitrate anions with a possible effect of the metal salt seem to be in favor of mechanism **ii**. However, since the yield of the reaction in the case of oxalate formation is 2.5 times less than for the other reactions, a more complicated mechanism implying the decomposition of the imidazolium ligand such as decarboxylation or oxidation-hydrolysis can be envisaged. This decomposition probably leads to a slow release of oxalate ligand which reduces the coordination between the oxalate and the metal and promotes the formation of **5** and **6**. Such slow release effect is consistent with the fact that direct incorporation of oxalic acid in the starting reactants leads to metal oxalates.

The choice of the solvent has also a significant influence on the crystallinity of the compounds. Indeed, the high values of the reliability factors R1 and/or wR2 for **1** and **2** indicate disorder (*i.e.* R1 for $I > 2\sigma(I) = 0.0778$ and wR2 for all data = 0.2049 for **1** and R1 for $I > 2\sigma(I) = 0.0986$ and wR2 for all data = 0.2772 for **2**), as also observed in the reference brominated compound $[\text{Co}(\text{L})(\text{H}_2\text{O})_4][\text{Br}]\cdot\text{H}_2\text{O}$ (*i.e.* R1 for $I > 2\sigma(I) = 0.0867$ and wR2 for all data = 0.2251).³⁴ Such high values are not obtained in the refinement of the structures of **3** and **4** which exhibit very good R values (R1 = 4.1 – 3.0 %, and wR2 = 9.1 - 6.7 %). Hence, substitution of the uncoordinated water molecule in **1** and **2** by ethylene glycol molecule in **3** and **4** favor a better ordering of the structure. Our explanation is that this modification using a larger solvent molecule leads to a more extended H-bonding network in **3** and **4** which stabilizes the double layers formed by the imidazolium salt coordinated to the Co or Ni ions and increases the cohesion of the crystals. It leads also to a change of the crystal morphology, *i.e.* platelets for **1** and **2** vs thick block for **3** and **4** (Figure S5).

Powder X-Ray diffraction (PXRD) and Thermal Analysis. The experimental PXRD patterns of compounds **1-6** fit well with the one calculated from their single crystal structure confirming the phase purity of the compounds (Figures S1, S2, S3 and S4 in SI part). The SEM analysis in composition mode confirms also the homogeneity of the six compounds (Figure S5 in SI part). The infrared data and the observed weight losses for each compound are in good agreement with the structure and the formulae determined by diffraction on single crystal (see text and Figures S6 and S7 in SI part).

Magnetic Behavior. We investigated the magnetic behavior of the title compounds which involve different metal ions in different structure. The susceptibility of **1** and **3** increases slowly when the temperature decreases and follows a Curie-Weiss law above 50 K (Figure S9). Curie constants of 1.22 emu.K.mol⁻¹ and 1.32 emu.K.mol⁻¹ (in line with the expected value for isolated octahedral high spin Ni²⁺ ions, with $g = 2.2-2.3$)⁵⁴ and Weiss temperatures of -2.57 K and -3.31 K were deduced for **1** and **3** from the fit of the $\chi^{-1} = f(T)$ curve using the Curie-Weiss law. The χT product is nearly constant from room temperature down to 50 K at a value of 1.20 emu.K.mol⁻¹ for **1** and 1.32 emu.K.mol⁻¹ for **3**. Below 50 K, the $\chi T = f(T)$ curve decreases down to 0.65 emu.K.mol⁻¹ and 0.93 emu.K.mol⁻¹ at 1.8 K for **1** and **3**, respectively (Figure 6). This behavior corresponds to that of isolated Ni²⁺ ions showing a zero field splitting effect at low temperature.⁵⁵

For the cobalt analogues, the behavior is qualitatively the same. The Curie constant for **2** and **4** deduced from the curve $\chi^{-1} = f(T)$ above 150 K are in agreement with the values expected for octahedral high spin Co²⁺ ions.^{56,57} Negative Weiss temperatures (-16 K for **2** and -49 K for **4**) are also obtained from the fit of the susceptibility to the Curie-Weiss law. The χT product decreases continuously from 3.03 emu.K.mol⁻¹ at 300 K to 1.57 emu.K.mol⁻¹ at 1.8 K for **2** and from 3.41

emu.K.mol⁻¹ to 1.50 emu.K.mol⁻¹ for **4** (Figure 6). This behavior is typical of isolated $S = 3/2$, $L = 1$ octahedral Co²⁺ ions showing spin-orbit coupling effect with depopulation of the excited J levels towards the doublet ground state when decreasing the temperature.

In contrast, the magnetic behavior of the two compounds exhibiting a ribbon structure, **5** and **6**, is characteristic of extended magnetic coupling. The Curie constants (1.22 emu.K.mol⁻¹ and 3.21 emu.K.mol⁻¹ for **5** and **6** respectively) are in keeping with octahedral high spin Ni²⁺ ions and octahedral high spin Co²⁺ ions, respectively. The Weiss temperatures (-32 K and -43 K for **5** and **6** respectively) are significantly lower than those deduced for compounds **1-4** which suggests the presence of significant antiferromagnetic coupling between neighboring magnetic centers. Indeed, the susceptibility of the two compounds, **5** and **6**, increases progressively with cooling up to a maximum of 0.012 emu.K.mol⁻¹ at 40.22 K and of 0.055 emu.K.mol⁻¹ at 18.20 K respectively (Figure S9). This maximum is followed first by a rapid decrease of the susceptibility and then by a slight increase at very low temperature. The χT product decreases continuously from 1.11 emu.K.mol⁻¹ at 300 K to almost 0.02 emu.K.mol⁻¹ at 1.8 K for **5** and from 3.23 emu.K.mol⁻¹ at 300 K to almost 0.03 emu.K.mol⁻¹ at 1.8 K for **6** (Figure 6). The decrease is much steeper than observed for compounds **1-4** containing quasi-isolated metal centers and is characteristic of weak antiferromagnetic interactions. The increase of χ at low temperature can be ascribed to a Curie-tail behaviour, classical in antiferromagnetically coupled species, and corresponds to defects (non-coupled ions) and/or to side effects (crystal edges). The effect of antiferromagnetic interactions superimposes with that of spin orbit coupling for the cobalt compound and zero field splitting for nickel compound.

Figure 6. Temperature dependence of magnetic susceptibility in the forms of χT vs T under an applied field of 5000 G between 1.8 and 300 K for the compounds **1** (orange), **2** (purple), **3** (pink), **4** (blue), **5** (green) and **6** (red). The black lines represent the best fits of the data (see text).

Regarding the magnetization versus field curves (Figure S9 in SI part), the magnetization saturates at $2.2 \mu_B$, $2.2 \mu_B$, $2.7 \mu_B$ and $2.3 \mu_B$ for **1** and **2**, **3** and **4**, respectively. These values agree well with isolated $S = 1$ Ni^{2+} in **1** and **3** and $S = 3/2$ Co^{2+} ions in **2** and **4**. Conversely, the magnetizations are much lower in the case of the ribbon structures, without saturation in the case of **5** and even more in the case of **6**. These features support the occurrence of antiferromagnetic couplings in these compounds.

The low temperature behavior of the isolated Ni(II) complexes **1** and **3** can be ascribed to the effect of zero field splitting. The data were fit using the single ion spin Hamiltonian $\mathbf{H} = g_{\text{iso}}\beta\mathbf{H}\mathbf{S} + D[\mathbf{S}_z^2 - \mathbf{S}(\mathbf{S}+1))/3]$, where g is the Landé factor and D is the axial zero-field splitting parameter (see expression E1 in SI). The fit leads to $g_{\text{iso}} = 2.14(1)$ and $|D| = 6.9(3) \text{ cm}^{-1}$ for **1** and $g_{\text{iso}} = 2.31(5)$ and $|D| = 3.8(1)$ and for **3**, in good agreement with values reported in the literature.⁵⁸

The behavior of the isolated Co(II) complexes **2** and **4** can be related to the effect of spin-orbit coupling and Zeeman interactions. Considering isolated Co(II) complexes in a strictly octahedral environment, the magnetic susceptibility as a function of the temperature can be deduced from the following equations⁵⁹:

$$\chi = \frac{N\beta^2}{kT} * \frac{F1}{F2} + \text{TIP}$$

With

$$F1 = \frac{7\lambda}{5kT} * (3 - \alpha)^2 + \frac{12(2+\alpha)^2}{25\alpha} + \left[\frac{2\lambda}{45kT} (11 - 2\alpha)^2 + \frac{176(2+\alpha)^2}{675\alpha} \right] \exp\left(\frac{-5\alpha\lambda}{2kT}\right) + \left[\frac{\lambda}{9kT} (5 + \alpha)^2 - \frac{2(2+\alpha)^2}{27\alpha} \right] \exp\left(\frac{-4\alpha\lambda}{kT}\right)$$

$$F2 = \frac{\lambda}{kT} * \left[3 + 2 \exp\left(\frac{-5\alpha\lambda}{2kT}\right) + \exp\left(\frac{-4\alpha\lambda}{kT}\right) \right]$$

$$\alpha = \kappa * A$$

where A is a constant related with the ligand field. The value of A = 1.4 was determined from UV-visible spectroscopy (see UV-Visible part in SI). κ is a parameter taking into account the orbital reduction, λ is the spin-orbit coupling constant, N the Avogadro number, k the Boltzmann constant and β is the Bohr magneton. TIP corresponds to Temperature Independent Paramagnetism. The data was fit using these equations leading to $\lambda = -67.9(1) \text{ cm}^{-1}$ with $\kappa = 0.64 \text{ cm}^{-1}$ and $\text{TIP} = 0.0025 \text{ cm}^3 \cdot \text{mol}^{-1}$ for **2** and $\lambda = -87.5(1) \text{ cm}^{-1}$ with $\kappa = 0.60 \text{ cm}^{-1}$ and $\text{TIP} = 0.0033 \text{ cm}^3 \cdot \text{mol}^{-1}$ for **4**. The λ and κ values are slightly lower than those reported in the literature for Co^{2+} systems, probably relying to a slight distortion of the coordination sphere from a perfect octahedron.^{57,60}

In order to determine the strength of the magnetic interactions in the nickel compound **5**, a numerical model taking into account two different exchange coupling interactions $J1$ and $J2$ was used (see E1 in SI part). The two exchange coupling interactions correspond to the two exchange pathways along the chains, *i.e.* through the oxalate or through the aquo/bis carboxylate bridges. A

good fit of the magnetic data above 16 K was obtained with the software SPIN v.2.3.5 considering the spin topology described in Scheme 2, leading to $g = 2.24$, $J1 = -5.3 \text{ cm}^{-1}$ and $J2 = -23.0 \text{ cm}^{-1}$.⁶¹ Actually, it is rather difficult to determine which of $J1$ or $J2$ corresponds to interaction through aquo or oxalato bridges even if a higher interaction can be expected for the shorter Ni-Ni distance (*i.e.* through aquo bridge here).

Scheme 2. Representation of the different interactions in **5**. The imidazolium ligand has been cut for clarity.

In order to estimate the strength of the antiferromagnetic interaction in the cobalt compound **6**, the numerical approach taking into account spin-orbit coupling in infinite chains was not handable. Thus, a phenomenological approach was used, using an equation composed of the sum of two exponentials:⁶²

$$\chi T = A * \exp\left(\frac{-E1}{kT}\right) + B * \exp\left(\frac{-E2}{kT}\right)$$

This expression is well suited to describe the spin-orbit coupling together with exchange coupling (both characterized by a split between discrete levels). In this expression, $A+B$ corresponds to the Curie constant, E_1 , E_2 to the activation energies assigned to the spin-orbit coupling and to the mean J exchange interaction within the chains. A very good agreement of the

experimental data was obtained as shown in Figure 6. The refined value of the Curie constant is consistent with that obtained from the fit to the Curie Weiss law: $A = 1.4$ and $B = 2.2$, providing $C = A+B = 3.6 \text{ emu.K.mol}^{-1}$. The value found for the effect of spin-orbit coupling and site distortion is $E1 = -56.2 \text{ cm}^{-1}$ and is consistent with Co(II) in distorted site.^{62,63} Exchange interaction of $-J = 2 * E2 = -19.4 \text{ cm}^{-1}$ can be estimated and is of the same order of magnitude as the mean J value of -15.7 cm^{-1} determined for **5**.

CONCLUSIONS

Six novel metal-organic networks have been reported involving the 1,3-bis-(carboxymethyl)-imidazolium ligand. In particular, the three compounds **1**, **3** and **5** constitute the first reported examples of structures based on this imidazolium dicarboxylate ligand and Ni^{2+} ions. The structural characterizations reveal a significant influence of the solvent as well as of the metal salt on the structure and crystallinity of the final compounds. The former has an effect on the cohesion of the crystals while the latter has an effect on dimensionality of the structures which induces different magnetic properties. The fact the replacing water by ethylene glycol increases the cohesion of the structure without change of the metal framework is quite noticeable. Accordingly to the structural finding, the magnetic behaviour is either characteristic of isolated species in the structures without oxalate ligand or antiferromagnetic 1D chains in the structures including the oxalate ligand.

ASSOCIATED CONTENT

Supporting Information. SI contains the tables S1-S4 for selected bonds and angles in compounds **1-6**, the PXRD patterns, Le Bail refinements, the SEM images in composition, the

infrared analysis, the thermal analysis, the UV-Visible-NIR analysis and the magnetic data and expression E1 for the compounds **1-6**.

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REFERENCES

- (1) Xu, W.; Thapa, K. B.; Ju, Q.; Fang, Z.; Huang, W. Heterogeneous Catalysts Based on Mesoporous Metal–Organic Frameworks. *Coord. Chem. Rev.* **2018**, *373*, 199–232.
- (2) Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; Couvreur, P.; Férey, G.; Morris, R. E.; Serre, C. Metal–Organic Frameworks in Biomedicine. *Chem. Rev.* **2012**, *112* (2), 1232–1268.
- (3) Férey, G.; Serre, C.; Devic, T.; Maurin, G.; Jobic, H.; Llewellyn, P. L.; De Weireld, G.; Vimont, A.; Daturi, M.; Chang, J.-S. Why Hybrid Porous Solids Capture Greenhouse Gases? *Chem. Soc. Rev.* **2011**, *40* (2), 550–562.
- (4) Janiak, C.; Vieth, J. K. MOFs, MILs and More: Concepts, Properties and Applications for Porous Coordination Networks (PCNs). *New J. Chem.* **2010**, *34* (11), 2366–2388.
- (5) Férey, G. Hybrid Porous Solids: Past, Present, Future. *Chem. Soc. Rev.* **2008**, *37* (1), 191–214.
- (6) Dincă, M.; Long, J. R. Hydrogen Storage in Microporous Metal–Organic Frameworks with Exposed Metal Sites. *Angew. Chem. Int. Ed.* **2008**, *47* (36), 6766–6779.
- (7) Horcajada, P.; Serre, C.; Vallet-Regí, M.; Sebban, M.; Taulelle, F.; Férey, G. Metal–Organic Frameworks as Efficient Materials for Drug Delivery. *Angew. Chem. Int. Ed.* **2006**, *45* (36), 5974–5978.

- (8) Zhang, X.-M. Hydro(Solvo)Thermal in Situ Ligand Syntheses. *Coord. Chem. Rev.* **2005**, 249 (11–12), 1201–1219.
- (9) Gong, K.; Zhao, X.; Xiao, T.; Zhao, C.; Han, Z.; Yu, H.; Zhai, X. A Novel LaMo Double-Metal Polymer from Hydrothermal Reaction Involving in Situ Formation of Oxalate Ligand. *J. Mol. Struct.* **2014**, 1068, 270–274.
- (10) Cepeda, J.; Balda, R.; Beobide, G.; Castillo, O.; Fernández, J.; Luque, A.; Pérez-Yáñez, S.; Román, P. Synthetic Control to Achieve Lanthanide(III)/Pyrimidine-4,6-Dicarboxylate Compounds by Preventing Oxalate Formation: Structural, Magnetic, and Luminescent Properties. *Inorg. Chem.* **2012**, 51 (14), 7875–7888.
- (11) Cepeda, J.; Balda, R.; Beobide, G.; Castillo, O.; Fernández, J.; Luque, A.; Pérez-Yáñez, S.; Román, P.; Vallejo-Sánchez, D. Lanthanide(III)/Pyrimidine-4,6-Dicarboxylate/Oxalate Extended Frameworks: A Detailed Study Based on the Lanthanide Contraction and Temperature Effects. *Inorg. Chem.* **2011**, 50 (17), 8437–8451.
- (12) Deng, Z.-P.; Kang, W.; Huo, L.-H.; Zhao, H.; Gao, S. Rare-Earth Organic Frameworks Involving Three Types of Architecture Tuned by the Lanthanide Contraction Effect: Hydrothermal Syntheses, Structures and Luminescence. *Dalton Trans.* **2010**, 39 (27), 6276–6284.
- (13) Xiao, H.-P.; Zhu, L.-G. In Situ Facile Nitration in Hydrothermal Reaction Generating Novel Metal-Organic Coordination Polymer. *Inorg. Chem. Commun.* **2006**, 9 (11), 1125–1128.
- (14) Tong, M.-L.; Li, L.-J.; Mochizuki, K.; Chang, H.-C.; Chen, X.-M.; Li, Y.; Kitagawa, S. A Novel Three-Dimensional Coordination Polymer Constructed with Mixed-Valence Dimeric Copper(I,II) Units. *Chem. Commun.* **2003**, 0 (3), 428–429.

- (15) Zhang, X.-M.; Tong, M.-L.; Chen, X.-M. Hydroxylation of N-Heterocycle Ligands Observed in Two Unusual Mixed-Valence CuI/CuII Complexes. *Angew. Chem. Int. Ed.* **2002**, *41* (6), 1029–1031.
- (16) Luo, L.; Chen, K.; Liu, Q.; Lu, Y.; Okamura, T.; Lv, G.-C.; Zhao, Y.; Sun, W.-Y. Zinc(II) and Cadmium(II) Complexes with 1,3,5-Benzenetricarboxylate and Imidazole-Containing Ligands: Structural Variation via Reaction Temperature and Solvent. *Cryst. Growth Des.* **2013**, *13* (6), 2312–2321.
- (17) Yi, F.-Y.; Sun, Z.-M. Solvent-Controlled Syntheses, Structure, and Magnetic Properties of Trinuclear Mn(II)-Based Metal–Organic Frameworks. *Cryst. Growth Des.* **2012**, *12* (11), 5693–5700.
- (18) Li, H.-Y.; Xu, J.; Li, L.-K.; Du, X.-S.; Li, F.-A.; Xu, H.; Zang, S.-Q. Photochromic Properties of a Series of Zinc(II)–Viologen Complexes with Structural Regulation by Anions. *Cryst. Growth Des.* **2017**, *17* (12), 6311–6319.
- (19) Wan, J.; Cai, S.-L.; Zhang, K.; Li, C.-J.; Feng, Y.; Fan, J.; Zheng, S.-R.; Zhang, W.-G. Anion- and Temperature-Dependent Assembly, Crystal Structures and Luminescence Properties of Six New Cd(II) Coordination Polymers Based on 2,3,5,6-Tetrakis(2-Pyridyl)Pyrazine. *CrystEngComm* **2016**, *18* (27), 5164–5176.
- (20) Hu, J.; Liao, C.; Chen, S.; Jin, P.; Zhao, J.; Zhao, H. Anion-Triggered Structural Diversity of Binuclear-Based Ag(I) Coordination Architectures and Rich Luminescence Properties. *Inorg. Chem. Commun.* **2014**, *43*, 126–130.

- (21) Li, D.-P.; Zhou, X.-H.; Liang, X.-Q.; Li, C.-H.; Chen, C.; Liu, J.; You, X.-Z. Novel Structural Diversity of Triazolate-Based Coordination Polymers Generated Solvothermally with Anions. *Cryst. Growth Des.* **2010**, *10* (5), 2136–2145.
- (22) Xu, G.-C.; Hua, Q.; Okamura, T.; Bai, Z.-S.; Ding, Y.-J.; Huang, Y.-Q.; Liu, G.-X.; Sun, W.-Y.; Ueyama, N. Cadmium(II) Coordination Polymers with Flexible Tetradentate Ligand 1,2,4,5-Tetrakis(Imidazol-1-ylmethyl)Benzene: Anion Effect and Reversible Anion Exchange Property. *CrystEngComm* **2009**, *11* (2), 261–270.
- (23) Zhang, Z.-H.; Okamura, T.; Hasegawa, Y.; Kawaguchi, H.; Kong, L.-Y.; Sun, W.-Y.; Ueyama, N. Syntheses, Structures, and Luminescent and Magnetic Properties of Novel Three-Dimensional Lanthanide Complexes with 1,3,5-Benzenetriacetate. *Inorg. Chem.* **2005**, *44* (18), 6219–6227.
- (24) Martin, N.; Falaise, C.; Volkringer, C.; Henry, N.; Farger, P.; Falk, C.; Delahaye, E.; Rabu, P.; Loiseau, T. Hydrothermal Crystallization of Uranyl Coordination Polymers Involving and Imidazolium Dicarboxylate Ligand: Effect of PH on the Nuclearity of Uranyl-Centred Sub-Units. *Inorg. Chem.* **2016**, *55* (17), 8697–8705.
- (25) Wu, Q.; Cao, M. J.; Wei, B.; Bai, Y.; Tian, H.; Wang, J.; Liu, Q.; Li, Q. Y.; Yang, G. W. PH Dependent Synthesis of Structurally Diverse Praseodymium(III) Coordination Polymers Based on Isomeric Ligands. *Inorg. Chem. Commun.* **2015**, *62*, 111–114.
- (26) Volkringer, C.; Loiseau, T.; Guillou, N.; Férey, G.; Haouas, M.; Taulelle, F.; Elkaim, E.; Stock, N. High-Throughput Aided Synthesis of the Porous Metal–Organic Framework-Type Aluminum Pyromellitate, MIL-121, with Extra Carboxylic Acid Functionalization. *Inorg. Chem.* **2010**, *49* (21), 9852–9862.

- (27) Farger, P.; Leuvrey, C.; Gallart, M.; Gilliot, P.; Rogez, G.; Rocha, J.; Ananias, D.; Rabu, P.; Delahaye, E. Magnetic and Luminescent Coordination Networks Based on Imidazolium Salts and Lanthanides for Sensitive Ratiometric Thermometry. *Beilstein J. Nanotechnol.* **2018**, *9* (1), 2775–2787.
- (28) Farger, P.; Leuvrey, C.; Gallart, M.; Gilliot, P.; Rogez, G.; Rabu, P.; Delahaye, E. Elaboration of Luminescent and Magnetic Hybrid Networks Based on Lanthanide Ions and Imidazolium Dicarboxylate Salts: Influence of the Synthesis Conditions. *Magnetochemistry* **2017**, *3*, 1–20.
- (29) Farger, P.; Guillot, R.; Leroux, F.; Parizel, N.; Gallart, M.; Gilliot, P.; Rogez, G.; Delahaye, E.; Rabu, P. Imidazolium Dicarboxylate Based Metal–Organic Frameworks Obtained by Solvo-Ionothermal Reaction. *Eur. J. Inorg. Chem.* **2015**, *2015* (32), 5342–5350.
- (30) Abrahams, B. F.; Maynard-Casely, H. E.; Robson, R.; White, K. F. Copper(II) Coordination Polymers of Imdc- (H_2imdc^+ = the 1,3-Bis(Carboxymethyl)Imidazolium Cation): Unusual Sheet Interpenetration and an Unexpected Single Crystal-to-Single Crystal Transformation. *CrystEngComm* **2013**, *15* (45), 9729–9737.
- (31) Chai, X.-C.; Sun, Y.-Q.; Lei, R.; Chen, Y.-P.; Zhang, S.; Cao, Y.-N.; Zhang, H.-H. A Series of Lanthanide Frameworks with a Flexible Ligand, N,N'-Diacetic Acid Imidazolium, in Different Coordination Modes. *Cryst. Growth Des.* **2010**, *10* (2), 658–668.
- (32) Han, L.; Zhang, S.; Wang, Y.; Yan, X.; Lu, X. A Strategy for Synthesis of Ionic Metal–Organic Frameworks. *Inorg. Chem.* **2009**, *48* (3), 786–788.

- (33) Wang, X.-W.; Han, L.; Cai, T.-J.; Zheng, Y.-Q.; Chen, J.-Z.; Deng, Q. A Novel Chiral Doubly Folded Interpenetrating 3D Metal–Organic Framework Based on the Flexible Zwitterionic Ligand. *Cryst. Growth Des.* **2007**, 7 (6), 1027–1030.
- (34) Fei, Z.; Ang, W. H.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J. Ionic Solid-State Dimers and Polymers Derived from Imidazolium Dicarboxylic Acids. *Chem. – Eur. J.* **2006**, 12 (15), 4014–4020.
- (35) Fei, Z.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J. Metal–Organic Frameworks Derived from Imidazolium Dicarboxylates and Group I and II Salts. *Inorg. Chem.* **2006**, 45 (16), 6331–6337.
- (36) Zhang, X.-F.; Gao, S.; Huo, L.-H.; Zhao, H. A Two-Dimensional Cobalt(II) Coordination Polymer: Poly[Chloro(μ -Imidazole-1,3-Diylldiacetato-K₄O:O':O'':O''')Cobalt(II)]. *Acta Crystallogr. Sect. E* **2006**, 62 (12), m3359–m3361.
- (37) Zhang, X.-F.; Gao, S.; Huo, L.-H.; Zhao, H. Poly[[Chloromanganese(II)]-[Mu]4-Imidazole-1,3-Diylldiacetato]. *Acta Crystallogr. Sect. E* **2006**, 62 (12), m3365–m3367.
- (38) Zhang, X.-F.; Gao, S.; Huo, L.-H.; Ng, S. W. Poly[Bis([Mu]2-1H-Imidazolyl-1,3-Diylldiacetato-[Kappa]4O,O':O''',O''''')Cadmium(II)]. *Acta Crystallogr. Sect. E* **2006**, 62 (11), m2910–m2912.
- (39) Fei, Z.; Geldbach, T. J.; Zhao, D.; Scopelliti, R.; Dyson, P. J. A Nearly Planar Water Sheet Sandwiched between Strontium–Imidazolium Carboxylate Coordination Polymers. *Inorg. Chem.* **2005**, 44 (15), 5200–5202.

- (40) Fei, Z.; Zhao, D.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J. Brønsted Acidic Ionic Liquids and Their Zwitterions: Synthesis, Characterization and PKa Determination. *Chem. – Eur. J.* **2004**, *10* (19), 4886–4893.
- (41) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. SIR92 - a Program for Automatic Solution of Crystal Structures by Direct Methods. *J. Appl. Crystallogr.* **1994**, *27* (3), 435.
- (42) Sheldrick, G. A Short History of SHELX. *Acta Crystallogr. Sect. A* **2008**, *64* (1), 112–122.
- (43) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; University of Göttingen, Göttingen, Germany, 1997.
- (44) Farrugia, L. WinGX Suite for Small-Molecule Single-Crystal Crystallography. *J. Appl. Crystallogr.* **1999**, *32* (4), 837–838.
- (45) Edgington, P. R.; McCabe, P.; Macrae, C. F.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; Van De Streek, J. Mercury: Visualization and Analysis of Crystal Structures. *J. Appl. Crystallogr.* **2006**, *39* (3), 453–457.
- (46) Feng, X.; Zhao, J.; Liu, B.; Wang, L.; Ng, S.; Zhang, G.; Wang, J.; Shi, X.; Liu, Y. A Series of Lanthanide–Organic Frameworks Based on 2-Propyl-1H-Imidazole-4,5-Dicarboxylate and Oxalate: Syntheses, Structures, Luminescence, and Magnetic Properties. *Cryst. Growth Des.* **2010**, *10* (3), 1399–1408.
- (47) Wang, X.-J.; Cen, Z.-M.; Ni, Q.-L.; Jiang, X.-F.; Lian, H.-C.; Gui, L.-C.; Zuo, H.-H.; Wang, Z.-Y. Synthesis Structures, and Properties of Functional 2-D Lanthanide Coordination Polymers $[\text{Ln}_2(\text{Dpa})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]_n$ (Dpa = 2,2'-(2-Methylbenzimidazolium-1,3-

Diyl)Diacetate, $C_2O_4^{2-}$ = Oxalate, Ln = Nd, Eu, Gd, Tb). *Cryst. Growth Des.* **2010**, *10* (7), 2960–2968.

(48) Yang, Z.; Wang, C.; Cao, X.; Wang, C.; Li, G. Synthesis, Crystal Structures, and Thermal Properties of Two Ni(II) Supramolecules Constructed from Imidazole Dicarboxylates. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2011**, *41* (8), 1039–1045. <https://doi.org/10.1080/15533174.2011.591341>.

(49) Midollini, S.; Orlandini, A.; Rosa, P.; Sorace, L. Structure and Magnetism of a New Hydrogen-Bonded Layered Cobalt(II) Network, Constructed by the Unprecedented Carboxylate–Phosphinate Ligand $[O_2(C_6H_5)PCH_2CO_2]^{2-}$. *Inorg. Chem.* **2005**, *44* (6), 2060–2066.

(50) Min, D.; Lee, S. W. Terbium-Oxalate-Pyridinedicarboxylate Coordination Polymers Suggesting the Reductive Coupling of Carbon Dioxide (CO_2) to Oxalate ($C_2O_4^{2-}$): $[Tb_2(3,5-PDC)_2(H_2O)_4(C_2O_4)] \cdot 2H_2O$ and $[Tb(2,4-PDC)(H_2O)(C_2O_4)_{0.5}]$ (PDC = Pyridinedicarboxylate). *Inorg. Chem. Commun.* **2002**, *5* (11), 978–983.

(51) Evans, O. R.; Lin, W. Synthesis of Zinc Oxalate Coordination Polymers via Unprecedented Oxidative Coupling of Methanol to Oxalic Acid. *Cryst. Growth Des.* **2001**, *1* (1), 9–11.

(52) Han, Z.-B.; Cheng, X.-N.; Li, X.-F.; Chen, X.-M. Hydrothermal Syntheses and Structural Studies of Lanthanide Coordination Polymers Involving In-Situ Decarboxylation and Their Luminescence Properties. *Z. Für Anorg. Allg. Chem.* **2005**, *631* (5), 937–942.

- (53) Li, X.; Cao, R.; Sun, D.; Shi, Q.; Bi, W.; Hong, M. A Novel Sm–Co Polymeric Complex Formed via Metal-Mediated Oxidation–Hydrolysis of Orotic Acid in a Hydrothermal Reaction. *Inorg. Chem. Commun.* **2003**, 6 (7), 815–818.
- (54) Kahn, O. *Molecular Magnetism*; Wiley-VCH, 1993.
- (55) Boča, R. *Theoretical Foundations of Molecular Magnetism*; Elsevier Science, 1999.
- (56) Carlin, R. L. *Magnetochemistry*; Springer Berlin Heidelberg, 1986.
- (57) Mabbs, F. E.; Machin, D. J. *Magnetism and Transition Metal Complexes*; Chapman and Hall, 1973.
- (58) Ebralidze, I. I.; Leitus, G.; Shimon, L. J. W.; Neumann, R. Structural and Magnetic Behavior of Mono- and Dinuclear Nickel (II) Complexes of N,N'-Bis-(3,5-Dipiperidin-1-Yl-[2,4,6]Triazin-1-Yl)-Pyridin-2-Ylmethyl-Ethane-1,2-Diamine. *Inorganica Chim. Acta* **2009**, 362 (13), 4760–4766.
- (59) Lloret, F.; Julve, M.; Cano, J.; Ruiz-García, R.; Pardo, E. Magnetic Properties of Six-Coordinated High-Spin Cobalt(II) Complexes: Theoretical Background and Its Application. *Inorganica Chim. Acta* **2008**, 361 (12), 3432–3445.
- (60) Figgis, B. N.; Hitchman, M. A. *Ligand Field Theory and Its Applications*; Wiley-Blackwell: New York, NY, 2000.
- (61) Monfort, M.; Resino, I.; Ribas, J.; Solans, X.; Font-Bardia, M.; Rabu, P.; Drillon, M. Synthesis, Structure, and Magnetic Properties of Two New Ferromagnetic/Antiferromagnetic One-Dimensional Nickel(II) Complexes. Magnetostructural Correlations. *Inorg. Chem.* **2000**, 39 (12), 2572–2576.

(62) Rueff, J.-M.; Masciocchi, N.; Rabu, P.; Sironi, A.; Skoulios, A. Synthesis, Structure and Magnetism of Homologous Series of Polycrystalline Cobalt Alkane Mono- and Dicarboxylate Soaps. *Chem. – Eur. J.* **2002**, 8 (8), 1813–1820.

(63) Huang, F.-P.; Tian, J.-L.; Gu, W.; Liu, X.; Yan, S.-P.; Liao, D.-Z.; Cheng, P. Co(II) Coordination Polymers: Positional Isomeric Effect, Structural and Magnetic Diversification. *Cryst. Growth Des.* **2010**, 10 (3), 1145–1154

Table of contents

The synthesis and characterization of six novel metal organic networks based on octahedral Co^{2+} and Ni^{2+} ions and imidazolium salt is reported. Metal salt effect as well as solvent effect on the crystalline structures of these networks are reported and related to the magnetic properties of these compounds.

SI PART.

Influence of metal salts and solvents on the crystal structure of coordination networks made from imidazolium dicarboxylate salt.

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X ray diffraction

Table S1. Selected angles for the compounds **1**, **3**, **5**.

1		3		5	
O2-Ni1-O5	92.7(3)	O1-Ni1-O8	91.54(11)	O2-Ni1-O7	92.14(9)
O5-Ni1-O6	88.8(3)	O8-Ni1-O5	90.67(11)	O7-Ni1-O6	82.60(9)
O6-Ni1-O7	91.3(3)	O5-Ni1-O6	91.88(10)	O6-Ni1-O5	93.56(8)
O7-Ni1-O2	87.2(3)	O6-Ni1-O1	86.13(10)	O5-Ni1-O2	91.65(8)
O2-Ni1-O4	87.2(2)	O1-Ni1-O3	92.10(9)	O2-Ni1-O1	95.71(10)
O8-Ni1-O4	177.7(3)	O3-Ni1-O7	175.71(9)	O1-Ni1-O3	170.06(10)

Table S2. Selected bonds for the compounds **1**, **3**, **5**.

1		3		5	
Ni1-O5	2.043(7)	Ni1-O1	2.072(2)	Ni1-O1	2.041(2)
Ni1-O4	2.057(7)	Ni1-O3	2.086(2)	Ni1-O2	2.017(2)
Ni1-O2	2.059(7)	Ni1-O5	2.094(2)	Ni1-O3	2.093(2)
Ni1-O7	2.065(5)	Ni1-O6	2.066(3)	Ni1-O5	2.0743(18)
Ni1-O6	2.081(7)	Ni1-O7	2.095(2)	Ni1-O6	2.059(2)
Ni1-O8	2.084(7)	Ni1-O8	2.041(3)	Ni1-O7	2.048(2)
Ni-O _{av}	2.065	Ni-O _{av}	2.076	Ni-O _{av}	2.055

Table S3. Selected angles for the compounds **2**, **4**, **6**.

2		4		6	
O2-Co1-O4	91.9(3)	O1-Co1-O5	91.53(8)	O1-Co1-O2	93.14(5)
O4-Co1-O6	91.3(3)	O5-Co1-O7	91.58(8)	O2-Co1-O3	92.20(5)
O6-Co1-O8	86.3(2)	O7-Co1-O6	92.74(8)	O3-Co1-O7	93.46(6)
O8-Co1-O2	90.4(3)	O6-Co1-O1	84.58(7)	O7-Co1-O1	81.14(5)
O2-Co1-O7	85.9(3)	O1-Co1-O3	95.22(7)	O1-Co1-O6	86.82(7)
O7-Co1-O5	177.6(3)	O3-Co1-O8	174.17(6)	O6-Co1-O4	169.26(6)

Table S4. Selected bonds for the compounds **2**, **4**, **6**.

2		4		6	
Co1-O5	2.053(8)	Co1-O1	2.1022(16)	Co1-O1	2.0855(17)
Co1-O2	2.080(6)	Co1-O3	2.1258(15)	Co1-O2	2.1326(12)
Co1-O4	2.083(7)	Co1-O5	2.054(2)	Co1-O3	2.0469(14)
Co1-O7	2.098(7)	Co1-O6	2.099(2)	Co1-O4	2.1270(15)
Co1-O6	2.128(7)	Co1-O7	2.1310(17)	Co1-O6	2.0808(15)
Co1-O8	2.127(6)	Co1-O8	2.1416(17)	Co1-O7	2.0849(13)
Co-O _{av}	2.095	Co-O _{av}	2.109	Co-O _{av}	2.093

Figure S1. Comparison of the experimental powder X-ray diffraction pattern **(a)** for **1** (orange line) and **(b)** for **2** (purple line) with the calculated pattern from single crystals X-ray data (black line). The brown vertical lines indicate the position of the calculated diffraction lines.

Figure S2. Comparison of the experimental powder X-ray diffraction pattern (a) for **3** (pink line) and (b) for **4** (blue line) with the calculated pattern from single crystals X-ray data (black line). The brown vertical lines indicate the position of the calculated diffraction lines.

Figure S3. Comparison of the experimental powder X-ray diffraction pattern (a) for **5** (green line) and (b) for **6** (red line) with the calculated pattern from single crystals X-ray data (black line). The brown vertical lines indicate the position of the calculated diffraction lines.

Figure S4. Observed (red), Le Bail calculated (black) and difference (blue) XRPD patterns for compounds (a) 1, (b) 2, (c) 3, (d) 4, (e) 5 and (f) 6. The vertical bars indicate the Bragg positions.

SEM analysis

Figure S5. Representative SEM images in composition of the compounds (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5** and (f) **6**.

Infrared analysis

The infrared spectra of the six compounds are shown in Figure S6. The infrared spectrum of the imidazolium salt under its saline form [**LK**] is given for comparison.

The infrared spectra of **1** and **2** are very similar. They show a large band around 3400 cm^{-1} coming from hydrogen-bond involving water molecules. The vibration bands from the aromatic C-H are visible at 3144 and 3090 cm^{-1} while those coming from the aliphatic C-H are visible at 3067 , 3006 and 2960 cm^{-1} . Moreover, two bands are observed at 1566 cm^{-1} and at 1384 cm^{-1} assigned to the asymmetric (ν_{asym}) and symmetric (ν_{sym}) vibration of the carboxylate function, respectively. The

difference $\Delta\nu$ ($\Delta\nu = \nu_{\text{asym}} - \nu_{\text{sym}}$) equal to 182 cm^{-1} is lower than the $\Delta\nu$ value of **[LK]** ($\Delta\nu = 236\text{ cm}^{-1}$). These spectral features indicate that the carboxylate functions are in a bidentate coordination mode between one Co^{2+} and one H atom of the water molecule which is in good agreement with the crystal structure.

The infrared spectra of compounds **3-4** are rather similar to those of **1** in the range between 1700 cm^{-1} and 400 cm^{-1} . Some differences can be observed between 2900 cm^{-1} and 3700 cm^{-1} since free water molecules are replaced by ethylene glycol molecules.

The infrared spectra of **5** and **6** are identical. They show a large band around 3370 cm^{-1} from the water molecule. The bands located at 3163 and 3100 cm^{-1} correspond to the aromatic C-H while those at 3008 , 2985 and 2955 cm^{-1} to the aliphatic C-H vibrations. The band at 1666 cm^{-1} is attributed to the bending vibration of the water molecule. Three asymmetric vibration bands coming from the C=O bonds can be observed at 1632 , 1603 and 1583 cm^{-1} , the latter coming from the oxalate ligand while the two formers are ascribed to the carboxylate functions of the imidazolium ligand. The symmetric vibration band of the C-O moieties is located at 1394 cm^{-1} . Based on the two different positions of the asymmetric vibration bands of the carboxylate functions, it is possible to determine two values of $\Delta\nu$ indicating various mode of coordination of the carboxylate functions. The first one is equal to 209 cm^{-1} and corresponds to a bridging bidentate coordination mode between two metals while the second, equal to 189 cm^{-1} , corresponds to a monodentate coordination mode between one Co^{2+} and one H coming from the water molecule. All features in the FTIR powder spectra are consistent with the single crystal structure.

Figure S6. Infrared spectra of the compounds **[LK]** (black line), **1** (orange line), **2** (purple line), **3** (blue line), **4** (pink line), **5** (green line) and **6** (red line).

Thermal analysis

The thermal stability of the six compounds has been studied by thermal analysis (Figure S7). The experiments were performed under air with a heating rate of 5° C/min.

Figure S7. TGA (plain line) and TDA (dotted line) curves of the compounds **(a)** **1** (orange line) and **2** (purple line), **(b)** **3** (green line) and **4** (red line), **(c)** **5** (pink line) and **6** (blue line).

For the compound **1**, the first endothermic weight loss between 20° C and 195° C corresponds to the departure of the uncoordinated and the four coordinated water molecules (obsd. 25.23 %, calcd. 24.51 %). The two successive weight losses between 195° C and 600° C, associated with exothermic peaks, correspond to the decomposition of the organic part, the removal of the free chloride anion and to the formation of nickel oxide NiO as identified by powder X-ray diffraction (obsd. 54.53 %, calcd. 55.14 %).

The TGA of **2** is nearly the same except that the departure of uncoordinated and coordinated water molecules occurs in two distinct steps. Thus, the first endothermic weight loss between 20° C and 60° C is ascribed to the departure of the uncoordinated water molecule (obsd. 5.00 %, calcd. 4.90 %) while the second between 60° C and 190° C is ascribed to the departure of the four coordinated

water molecules (obsd. 19.41 %, calcd. 19.60 %). The two last exothermic weight losses at higher temperature correspond to the decomposition of the organic part, the removal of the free chloride anion and to the formation of cobalt oxide Co_3O_4 as identified by powder X-ray diffraction of the residue (obsd. 54.42 %, calcd. 53.67 %).

For the compound **3** and **4**, the first endothermic peak between 20° C and 190° C are ascribed to the departure of the four water molecules (obsd. 19.10 %, calcd. 18.94 % for **3** and obsd. 19.10 %, calcd 18.92 % for **4**). Then, the two successive exothermic weight losses between 190° C and 600° C are associated to the removal of the ethyleneglycol, the decomposition of the organic ligand and the formation of NiO or Co_3O_4 as identified by powder X-ray diffraction of the residue (obsd. 60.33 %, calcd. 61.68 % for **3** and obsd. 57.81%, calcd 60.25 % for **4**).

The TGA curves of **5** and **6** are simpler since there is only one exothermic weight loss between 200° C and 400° C associated with the elimination of the bridging water molecule, the organic part (i. e. the oxalate ligand and the [L]⁻ ligand) and the concomitant formation of cobalt oxide Co_3O_4 or nickel oxide NiO, respectively, as identified by powder X-ray diffraction of the residue (obsd. 73.18 %, calcd. 73.87 % for **5** and obsd. 74.95 %, calcd. 75.28 % for **6**).

All these data underline the homogeneity of the different compounds.

UV-Visible-NIR spectroscopy

The six compounds have been characterized by UV-Visible-NIR spectroscopy in the solid state. The compounds **1**, **3** and **5** show the characteristic transitions of Ni^{2+} ions in octahedral environment (see Figure S8a and Table S5). The compounds **2**, **4** and **6** show the characteristic transitions of Co^{2+} ions in octahedral environment in a high spin configuration (see Figure S8b and Table S6).

Figure S8. Solid state UV-Visible-NIR spectra of the compounds (a) **1** (orange line), **3** (pink line), **5** (green line) and (b) **2** (purple line), **4** (blue line) and **6** (red line).

Table S5. Bands assignment and crystal field parameters¹ for **1**, **2** and **3**.

	λ_1	λ_2	λ_3	Dq	B	Dq/B	β
	(nm)	(nm)	(nm)	(cm ⁻¹)	(cm ⁻¹)		
[Ni(L)(H ₂ O) ₄][Cl].H ₂ O (1)	396	664	1148	871	883	0.99	0.82
[Ni(L)(H ₂ O) ₄][Cl].(EG) _{0.5} (3)	397	664	1178	849	922	0.92	0.85
[Ni(L)(ox) _{0.5} (μ ₂ -H ₂ O) _{0.5}] (5)	396	662	1144	874	908	0.96	0.84

N.B.: λ_1 , λ_2 , λ_3 corresponds to the transitions ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ of octahedral Ni²⁺, respectively.^{2,3}

Table S6. Bands assignment and crystal field parameters¹ for **2**, **4** and **6**.

	λ_1	λ_2	λ_3	Dq	B	Dq/B	β	c	A
	(nm)	(nm)	(nm)	(cm ⁻¹) 1)	(cm ⁻¹) 1)				
[Co(L)(H ₂ O) ₄][Cl].H ₂ O (2)	515	625	1257	907	838	1.08	0.75	0.19	1.4
[Co(L)(H ₂ O) ₄][Cl].(EG) _{0.5} (4)	498	624	1255	911	883	1.03	0.79	0.19	1.4
[Co(L)(ox) _{0.5} (μ ₂ -H ₂ O) _{0.5}] (6)	520	-	1246	913	821	1.11	0.73		1.4

N.B.: $\lambda_1, \lambda_2, \lambda_3$ corresponds to the transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ of octahedral Co^{2+} , respectively.^{2,4}

Using the transitions observed corresponding to octahedral Co^{2+} species, it was possible to determine the constant A with the following expression:⁵

$$A = \frac{3/2 - c^2}{1 + c}$$

$$\text{where } c = 0.75 + 1.875 \frac{B}{Dq} - 1.25 \left[1 + 1.8 \frac{B}{Dq} + \left(\frac{B}{Dq} \right)^2 \right]^{1/2}$$

Magnetic data

Figure S9. Temperature variation of the magnetic susceptibility at an applied field of 5000 G between 1.8 and 300 K for the compounds **1** (orange) and **2** (purple), **3** (pink) and **4** (blue), **5** (green), **6** (red).

Figure S10. Magnetization versus field curve at 1.8 K for the compounds **1** (orange) and **2** (purple), **3** (pink) and **4** (blue), **5** (green), **6** (red).

Expression E1

$$\widehat{H} = \sum_1^{\infty} (J_1 \hat{S}_i \hat{S}_{i+1} + J_2 \hat{S}_{i+1} \hat{S}_{i+2}) - g\mu_B \sum_1^{\infty} \hat{S}_i H$$

Where the first term corresponds to the exchange Hamiltonian and the second to the Zeeman interaction.

References

- (1) Dou, Y. Equations for Calculating Dq and B. *J. Chem. Educ.* **1990**, 67 (2), 134. <https://doi.org/10.1021/ed067p134>.
- (2) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier, 1984.
- (3) Demessence, A.; Mesbah, A.; François, M.; Rogez, G.; Rabu, P. Structure and Magnetic Properties of a New 1D Nickel(II) Hydroxythiophenedicarboxylate. *Eur. J. Inorg. Chem.* **2009**, 2009 (25), 3713–3720. <https://doi.org/10.1002/ejic.200900329>.
- (4) Delahaye, E.; Moulin, R.; Aouadi, M.; Trannoy, V.; Beaunier, P.; Fornasieri, G.; Bleuzen, A. Co²⁺@Mesoporous Silica Monoliths: Tailor-Made Nanoreactors for Confined Soft Chemistry. *Chem. – Eur. J.* **2015**, 21 (47), 16906–16916. <https://doi.org/10.1002/chem.201501918>.
- (5) Lloret, F.; Julve, M.; Cano, J.; Ruiz-García, R.; Pardo, E. Magnetic Properties of Six-Coordinated High-Spin Cobalt(II) Complexes: Theoretical Background and Its Application. *Inorganica Chim. Acta* **2008**, 361 (12), 3432–3445. <https://doi.org/10.1016/j.ica.2008.03.114>.