

Semi-rigid imidazolium carboxylate controlled structural topologies in zwitterionic coordination networks



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ABSTRACT

The zwitterionic coordination networks $[\text{L}_2\text{Mn}(\text{H}_2\text{O})_2]_\infty$ (**1**), $[\text{L}_2\text{Co}(\text{H}_2\text{O})_2]_\infty$ (**2**), $[\text{L}_2\text{Ni}(\text{H}_2\text{O})_4]_\infty$ (**3**), $[\text{L}_2\text{Cu}]_\infty$ (**4**), $[\text{L}_2\text{Zn}(\text{H}_2\text{O})_2]_\infty$ (**5**) and $[\text{L}_3\text{Cd}(\text{Br})_2]_\infty$ (**6**) were synthesized from the reaction between the semi-rigid imidazolium carboxylate spacer LH_2^+Br^- and the corresponding metal nitrates in DMF/ H_2O at 130 °C. The solid state structures of **1–6** were confirmed by the single-crystal X-ray diffraction technique. The molecules **1**, **2** and **5** are isostructural one-dimensional coordination polymers. **3** was isolated as a monomer and the monomers are associated into a three dimensional fashion through O–H...O hydrogen bonds, while **4** was isolated as a 1D coordination polymer. Compound **6** was constructed as a two-dimensional coordination framework with a rare $[\text{Cd}_2(\mu_2\text{-Br})_2]$ core. The purity of **1–6** in the bulk was confirmed by the powder X-ray diffraction technique. Furthermore the electronic properties of **1–6** were studied using UV–Vis spectroscopy and the thermal stabilities of **1–6** were confirmed by TGA.

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1. Introduction

The construction of functionalized coordination polymers (FCPs) have been the subject of interest over the last few decades due to their fascinating architectures and versatile applications in different fields [1–7]. Suitable organic spacers, metal precursors and synthetic methodologies are essential criteria to design FCPs with different physical properties [8]. In addition, non-covalent interactions such as hydrogen bonds, $\pi\cdots\pi$, $\text{M}\cdots\pi$, $\text{C-H}\cdots\pi$ and anion $\cdots\pi$ interactions play a key role in FCPs to increase their dimensionality, supramolecular topology and porosity [9]. Therefore, the choice of organic spacer is extremely important to fine-tune the structural and desired functional properties of FCPs through the coordination mode or non-covalent interaction mode. Amongst these organic spacers, imidazolium carboxylic acids are of special interest as they have a $[\text{C-H}]^{\delta+}$ functional group (potential functional group for anion reorganization and post modification to generate N-heterocyclic carbene tethered catalytically active metal centers) along with excellent functional group tolerance at the N-positions [10–16]. However, the structurally characterized coordination polymers using imidazolium carboxylic acids are hampered due to the ionic nature of the organic spacer (often yielding an insoluble powder with metal salts).

Among the known imidazolium carboxylic acid ligands, *N,N'*-diacetic acid imidazolium halides $[\text{L}^1\text{H}_2^+\text{X}^-]$ and the zwitter ionic

(L^1H) ligands (Chart 1) are extensively studied systems for FCPs construction with transition metals (Zn and Co), main group metals (Ca, Sr, Ba, Cs, Pb and Bi) and rare earth metals (Er, Pr, La and Nd) [16b,17]. Notably, L^1 contains two flexible carboxylate wings, which allows the maximum degree of freedom. The Zn_8O cluster incorporated zinc coordination polymer $[\{(\text{Zn}_{0.25})_8(\text{O})\}\text{Zn}_6(\text{L}^2)_{12}(\text{H}_2\text{O})_{29}(\text{DMF})_{69}(\text{NO}_3)_2]_\infty$ was derived from the rigid carboxylate imidazolium ligand ($\text{L}^2\text{H}_2^+\text{X}^-$), where the carboxylate wings are in a fixed position [16c,18]. In addition, several coordination polymers derived from substituted ligands of $\text{L}^1\text{H}_2^+\text{X}^-$, $\text{L}^2\text{H}_2^+\text{X}^-$ and $\text{L}^3\text{H}_2^+\text{Cl}^-$ were reported (Chart 1) [19]. To the best of our knowledge, rigid and flexible biscarboxylate linked mono imidazolium salts have not been employed yet for the synthesis of coordination polymers [16d,e,19h–k]. Thus, we report the flexible and rigid carboxylate linked imidazolium salt (LH_2^+Br^-) (Chart 1) supported series of zwitterionic late transition metal(II) coordination polymers, $[\text{L}_2\text{Mn}(\text{H}_2\text{O})_2]_\infty$ (**1**), $[\text{L}_2\text{Co}(\text{H}_2\text{O})_2]_\infty$ (**2**), $[\text{L}_2\text{Ni}(\text{H}_2\text{O})_4]_\infty$ (**3**), $[\text{L}_2\text{Cu}]_\infty$ (**4**), $[\text{L}_2\text{Zn}(\text{H}_2\text{O})_2]_\infty$ (**5**) and $[\text{L}_3\text{Cd}(\text{Br})_2]_\infty$ (**6**). The compounds **1–6** have been characterized by FT-IR, TGA, SXRD, PXRD and UV–Vis spectroscopy.

2. Experimental

2.1. Materials and methods

The solvents were purchased from commercial sources and purified according to standard procedures [20]. Unless otherwise stated, the chemicals were purchased from commercial sources.

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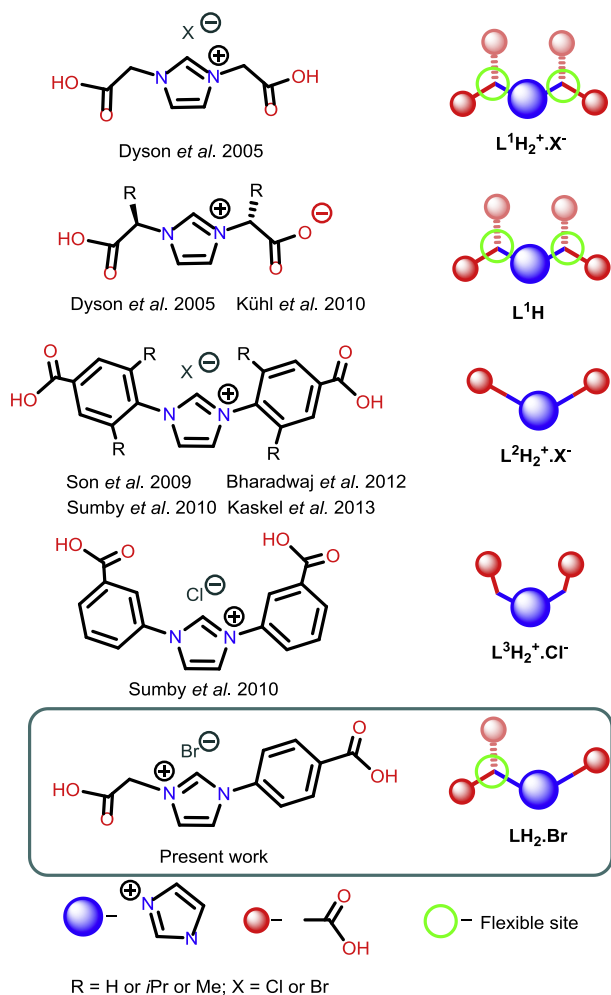


Chart 1. Schematic illustrations of $L^1H_2^+X^-$ ($X = Br$ or Cl), L^1H , $L^2H_2^+X^-$, $L^3H_2^+Cl^-$ and LH_2Br^- organic spacers [16b,17b,19].¹

LH_2Br^- was prepared as reported [21]. FT-IR measurement (neat) was carried out on a Bruker Alpha-P Fourier transform spectrometer. The UV–Vis spectra were measured on a T90+ UV–Visible spectrophotometer. Thermogravimetric analysis (TGA) was performed using a TA-SDT Q600, Tzeropress. Powder X-ray diffraction (PXRD) studies were carried out on a PANalytical X'pert Pro powder X-ray diffractometer operated at an acceleration voltage of 40 kV and an applied current of 30 mA. Elemental analyses were performed by the Euro Vector EA-300 elemental analyzer.

2.2. Synthesis of 1–6

2.2.1. $[L_2Mn(H_2O)_2]_\infty$ (**1**)

LH_2Br^- (0.1 g, 0.306 mmol) and $Mn(NO_3)_2 \cdot 4H_2O$ (0.039 g, 0.155 mmol) were taken in a Schlenk tube and 1:1 DMF and water (3 mL) were added. The reaction mixture was heated at 130 °C for 12 h then slowly brought to room temperature to obtain colorless crystals. The crystals were washed with MeOH and dried under vacuum. Yield: 76% (based on $Mn(NO_3)_2 \cdot 4H_2O$). *Anal. Calc.* for $C_{24}H_{22}N_4O_{10}Mn$ (581.40): C, 49.58; H, 3.81; N, 9.45. Found: C, 49.7; H, 3.7; N, 9.4%. FT-IR (neat) $\bar{\nu}$ (cm^{-1}): 3111 (w), 1609 (s), 1545 (s), 1383 (s), 1324 (m), 1217 (m), 1128 (w), 1070 (m).

¹ The coordination chemistry of 1-(carboxymethyl)-1,3-benzimidazol-3-ium-3-acetate is excluded in the current discussion [19k–n,d].

2.2.2. $[L_2Co(H_2O)_2]_\infty$ (**2**)

Compound **2** was synthesized using a similar method as for **1**, but with $Co(NO_3)_2 \cdot 6H_2O$ (0.045 g, 0.155 mmol) instead of $Mn(NO_3)_2 \cdot 4H_2O$. Yield: 81% (based on $Co(NO_3)_2 \cdot 6H_2O$). *Anal. Calc.* for $C_{24}H_{22}N_4O_{10}Co$ (585.40): C, 49.24; H, 3.79; N, 9.57. Found: C, 49.3; H, 3.8; N, 9.5%. FT-IR (neat) $\bar{\nu}$ (cm^{-1}): 3108 (w), 1608 (s), 1577 (w), 1544 (s), 1381 (s), 1325 (m), 1216 (m), 1129 (w), 1069 (m), 954 (m).

2.2.3. $[L_2Ni(H_2O)_4]_\infty$ (**3**)

Compound **3** was synthesized using a similar method as for **1**, but with $Ni(NO_3)_2 \cdot 6H_2O$ (0.045 g, 0.155 mmol) instead of $Mn(NO_3)_2 \cdot 4H_2O$. Yield: 85% (based on $Ni(NO_3)_2 \cdot 6H_2O$). *Anal. Calc.* for $C_{24}H_{26}N_4O_{12}Ni$ (621.20): C, 46.40; H, 4.22; N, 9.02. Found: C, 46.3; H, 4.3; N, 9.2%. FT-IR (neat) $\bar{\nu}$ (cm^{-1}): 3036 (w), 2910 (w), 1605 (s), 1530 (w), 1433 (w), 1385 (s), 1306 (m), 1228 (m), 1130 (w), 1075 (m).

2.2.4. $[L_2Cu]_\infty$ (**4**)

Compound **4** was synthesized using a similar method as for **1**, but with $Cu(NO_3)_2 \cdot 3H_2O$ (0.037 g, 0.153 mmol) instead of $Mn(NO_3)_2 \cdot 4H_2O$. Yield: 79% (based on $Cu(NO_3)_2 \cdot 3H_2O$). *Anal. Calc.* for $C_{24}H_{18}N_4O_8Cu$ (553.98): C, 52.03; H, 3.28; N, 10.11. Found: C, 51.9; H, 3.4; N, 10.1%. FT-IR (neat) $\bar{\nu}$ (cm^{-1}): 3068 (w), 2991 (w), 2946 (w), 1630 (w), 1610 (s), 1579 (w), 1548 (s), 1511 (w), 1367 (s), 1315 (m), 1231 (m), 1140 (m), 1072 (m), 1042 (w).

2.2.5. $[L_2Zn(H_2O)_2]_\infty$ (**5**)

Compound **5** was synthesized using a similar method as for **1**, but with $Zn(NO_3)_2 \cdot 6H_2O$ (0.046 g, 0.154 mmol) instead of $Mn(NO_3)_2 \cdot 4H_2O$. Yield: 88% (based on $Zn(NO_3)_2 \cdot 6H_2O$). *Anal. Calc.* for $C_{24}H_{22}N_4O_{10}Zn$ (591.86): C, 48.71; H, 3.75; N, 9.47. Found: C, 48.8; H, 3.8; N, 9.4%. FT-IR (neat) $\bar{\nu}$ (cm^{-1}): 3108 (w), 1609 (s), 1577 (w), 1544 (s), 1381 (s), 1326 (m), 1301 (w), 1218 (m), 1130 (w), 1070 (m), 974 (m).

2.2.6. $[L_3Cd_2(Br)_2]_\infty$ (**6**)

Compound **6** was synthesized using a similar method as for **1**, but with $Cd(NO_3)_2 \cdot 4H_2O$ (0.095 g, 0.308 mmol) instead of $Mn(NO_3)_2 \cdot 4H_2O$. Yield: 82% (based on $Cd(NO_3)_2 \cdot 4H_2O$). *Anal. Calc.* for $C_{12}H_9N_2O_4CdBr$ (437.52): C, 32.94; H, 2.07; N, 6.40. Found: C, 32.8; H, 2.2; N, 6.4%. FT-IR (neat) $\bar{\nu}$ (cm^{-1}): 3119 (w), 3098 (m), 2940 (w), 1621 (s), 1609 (s), 1577 (w), 1532 (s), 1392 (s), 1363 (w), 1332 (w), 1310 (w), 1295 (m), 1270 (w), 1214 (m), 1186 (w), 1129 (w), 1106 (w), 1067 (m), 1035 (w), 1013 (m), 954 (w).

2.3. Crystallography

The crystal structures of **1–6** were measured on an Oxford Xcalibur 2 diffractometer with a standard 4-circle kappa-goniometer, Eos detector (Active area 92 mm diagonal) and two X-ray sources, one of which is a Supernova Cu source (wavelength 1.5418 Å) with focusing mirrors. A suitable crystal was selected and mounted on a Gemini E goniometer. Data were collected at 150 or 298 K using an Oxford Cryojet Low-Temperature device. The structures of **1–6** were solved with the olex2.solve structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Gauss–Newton minimization [22]. Absorption corrections were performed on the basis of multi-scans. Non-hydrogen atoms were anisotropically refined. H atoms were included in the refinement in calculated positions riding on their carrier atoms. No restraint has been made for any of the compounds. The function minimized was $[\sum w(F_o^2 - F_c^2)^2]$ ($w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$), where $P = (\max(F_o^2, 0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The functions R_1 and wR_2 were $(\sum ||F_o| - |F_c||) / \sum |F_o|$ and $[\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^4)]^{1/2}$, respectively.

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