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Synthesis, crystal structures, spectroscopic, thermal analysis, electrochemical and solution studies of two new mixed metal coordination polymers based on dipicolinic acid and 3,4-diaminopyridine

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Two new 2D heteronuclear coordination polymers with Ni(II), Zn(II) and Ca(II), namely $\{(dapH)_2[CaM_2(pydc)_4(H_2O)_2]\cdot 2H_2O\}_n$ (M = Ni (**1**) and M = Zn (**2**)) where [$pydcH_2$ = pyridine-2,6-dicarboxylic acid (dipicolinic acid), dap = 3,4-diaminopyridine] have been synthesized and characterized by elemental analysis, infrared spectroscopy, thermal (TG/DTG/DTA) analysis, electrochemical as well as X-ray single crystal diffraction. The compounds **1** and **2** display isostructural features and crystallized in the monoclinic $P2_1/n$ space group. Both of the compounds contain cationic and anionic fragments and two uncoordinated water molecules. In **1** and **2** $(pydc)^{2-}$ acts as tridentate ligands and connected to calcium ions through carboxylate bridging. Then each dipicolinate ligand bridges one calcium to a M(II) atom.

The equilibrium constants of the binary, ternary and quaternary complexes of ligands or proton transfer system with metal ions in an aqueous solution were investigated by a potentiometric pH titration method.

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1. Introduction

There is currently considerable interest in the design and construction of coordination polymers due to their potential applications in gas adsorption, magnetism, luminescence and catalysis technologies, unusual electrochemical, photophysical and porous properties [1–3].

As we know, construction of coordination polymers (CPs) is mainly dependent on the metal centers and organic ligands [4]. The coordination features of the organic ligand including the coordination mode and orientation of the donor groups also play an important role in controlling CPs' structures. Many reports demonstrate that the aromatic dicarboxylic acids acting as organic ligands have been extensively utilized in the preparation of coordination polymers [5–7]. Moreover, many other factors can affect the structures of the final products such as the type of the ligand, pH value [8], temperature [9], and the solvent system [10].

Herein we designed two new isostructural heterobimetallic coordination polymers (Ni cation, Zn cation and Ca cation) based on $pydcH_2$ in the presence of 3,4-diaminopyridine as counter cations. They were prepared with a traditional synthetic method. A general used strategy in building such heterometallic is that one kind of metal cations are assembled with ligands firstly, leaving one or more ligand sites open for subsequent bonding to the other types of metal cations [11]. Multifunctional ligands with many ligand sites are good for this process. Pyridine-2,6-dicarboxylic acid ($pydcH_2$) is such a ligands with variety of coordination fashions [12] through its one nitrogen atom and four carboxylate oxygen atoms, diverse subsistent groups on the pyridine ring are possible to form hydrogen bonds, which is helpful for self assembly. The $pydcH_2$ is therefore an excellent candidate for constructing heterometallic complex. However, the construction of designed and predictable heterometallic coordination frameworks with potential properties is still a formidable task because of the coordinative complexity of the heterometallic ions involved in the self-assembly process [13,14].

In this study we describe the synthesis, spectroscopic, elemental and thermal analysis, crystal structures, electrochemical and

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solution studies of the $pydcH_2$ complexes with 3,4-diaminopyridine (dap), {$(dapH)_2[CaM_2(pydc)_4(H_2O)_2]\cdot 2H_2O\}_n$, (M = Ni (**1**) and M = Zn (**2**).The two compounds consist of anionic metal complexes with protonated 2,3-diaminopyridine as counter cations. All of the components in **1** and **2** are tightly connected to each other *via* a complex arrangement of hydrogen bonds, electrostatic interactions, and $\pi\cdots\pi$ stacking.

2. Experimental

2.1. General methods and materials

All materials were purchased from Merck. Solvents used throughout the reactions were of high purity. IR spectroscopy was performed applying on a Perkin-Elmer Spectrum RXI FT-IR spectrophotometer in the 4000–400 cm^{-1} region using KBr pellet. Elemental analysis was performed with a Heraus CHN Pro apparatus. The X-ray data were obtained with a Bruker SMART ApexII Diffractometer. The TG-DTG and DTA curves of coordination polymers **1** and **2** were measured by the heating rate of 10 °C min^{-1} in the temperature range of 30–1000 °C under the N_2 atmosphere. Electrochemical experiments were performed *via* using an Autolab modular electrochemical system (Eco Chem. Utrecht, The Netherlands) equipped with PSTA 20 model and driven by GPES software (Eco Chem.). A conventional three-electrode cell was used with a saturated Ag|AgCl as reference electrode, a Pt wire as counter electrode and a modified carbon paste as working electrode. All experiments were carried out at ambient temperature of 20 ± 1 °C. A Metrohm pH-meter (model 691) was also applied for the pH measurements. A Model 794 Metrohm Basic Titrino was attached to an extension combined glass-calomel electrode mounted in an air-protected, sealed, thermostated jacketed cell maintained at 25.0 ± 0.1 °C by circulating water, from a constant-temperature bath Fisherbrand model FBH604, LAUDA, Germany, equipped with a stirrer and a 10.000-ml-capacity Metrohm piston burette. The pH meter-electrode system was calibrated to read –log [H^+].

2.2. Synthesis of {$(dapH)_2[CaNi_2(pydc)_4(H_2O)_2]\cdot 2H_2O\}_n$ (**1**)

A mixture of $Ni(NO_3)_2\cdot 6H_2O$ (145 mg, 0.5 mmol), pyridine-2,6-dicarboxylic acid (176 mg, 1 mmol) and 3,4-diaminopyridine (109 mg, 1 mmol) in water (30 ml), which was adjusted to pH = 6.0 with $Ca(OH)_2$ aqueous solution, was stirred and heated very slightly (80 °C) for 1 h, in a 1:2:2 molar ratio. After a week, Green crystals were obtained by slow evaporation of the solvent at room temperature. *Anal.* Calc. for $C_{38}H_{40}CaN_{10}O_{22}Ni_2$: C, 39.78; H, 3.49; N, 12.21. Found: C, 39.82; H, 3.52; N, 12.26%. **IR** (KBr disc, v/cm^{-1}): 3335(b), 3207(s), 2820(b) 1633(s), 1573(s, sh), 1515(s, sh), 1429(s), 1384(S), 1282(s), 1237(m), 1166(s), 1080(s), 1039(s), 919(s), 825(s), 769(s), 733(s), 680(s), 530(w), 443(m).

2.3. Synthesis of {$(dapH)_2[CaZn_2(pydc)_4(H_2O)_2]\cdot 2H_2O\}_n$ (**2**)

This compound was prepared in a similar manner as described for 1, Just here we replaced the salt with $Zn(NO_3)_2\cdot 4H_2O$ (120 mg, 0.5 mmol). After 2 weeks, rhombic, yellow crystals of 2 were obtained by slow evaporation of the solvent at room temperature. *Anal.* Calc. for $C_{38}H_{40}CaN_{10}O_{22}Zn_2$: C, 39.32; H, 3.45; N, 12.07. Found: C, 39.36; H, 3.48; N, 12.08%. IR (KBr disc, v/cm^{-1}): 3343(b), 3102(b), 2824(b) 1639(s), 1589(s, sh), 1573(s, sh), 1516(s), 1433(S), 1383(s), 1282(s), 1170(s), 1081(s), 1037(s), 910(s), 823(s), 769(s), 730(s), 690(s), 540(s), 436(s).

2.4. Crystal structure determination and refinement

X-ray data were collected at room temperature with a Bruker APEX II CCD area-detector diffractometer using Mo Kα radiation (λ = 0.71073 A). Data collection, cell refinement, data reduction and absorption correction were performed using multiscan methods with Bruker software [15]. The structures were solved by direct methods using SIR2004 [16]. The non hydrogen atoms were refined anisotropically by the full matrix least squares method on F^2 using SHELXL [16]. All the hydrogen (H) atoms were placed at the calculated positions and constrained to ride on their parent atoms. Details concerning collection and analysis are reported in Table 1.

2.5. Solution studies procedure

The jacketed cell containing test solution was equipped with a magnetic stirrer and a tightly fitting cap, through which the electrode system and 10-ml capacity Metrohm piston burette were inserted and sealed with clamps and O-rings. The atmospheric CO_2 was excluded from the titration cell with a purging steam of purified nitrogen gas.

The concentration of pydc and dap was 2.5×10^{-3} M, for the potentiometric *p*H titrations of pydc, dap and pydc–dap in the absence and presence of 1.25×10^{-3} metal ions including $Ni^{2+}$and Zn^{2+} as the first or Ca^{2+} as the second metal ion. A standard carbonate-free NaOH solution (0.10316 M) was used in titrations of dap and pydc–dap in the absence and presence of metal ions. The ionic strength was adjusted to 0.1 M with $NaNO_3$. Before an experimental point (pH) was measured, sufficient time was allowed to establish the equilibrium protonation constants of the ligands.

The HYPERQUAD program (2008 version) was used for computation of protonation constants in equilibrium state [17]. Distribution diagrams were drawn using the Hyss2009 program as a new version of a software program that had previously been used in the reports [18]. The value of the autoprotolysis constant for the aqueous system, Kw = [H^+] [OH^-], was chosen according to literature [19].

Thermal analyses (TG–DTG–DTA) including the thermogravimetery (TG), derivative thermogravimetery (DTG) and differential thermal analysis (DTA) were carried out using a PerkinElmer simultaneous thermal analyzer (STA Pyris Diamond Model) with the heating rate of 10 °C/min in N_2 atmosphere.

Table 1
Crystallographic data and structural refinement summary for **1**and **2**.

Compound	1	2
Empirical formula	$C_{38}H_{40}CaN_{10}Ni_2O_{22}$	$C_{38}H_{40}CaN_{10}O_{22}Zn_2$
Formula weight	1146.30	1159.62
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	12.5801(3)	12.6890(2)
b (Å)	14.2925(4)	14.4179(3)
c (Å)	13.8442(4)	13.6435(3)
β (°)	114.0020(10)	114.2580(10)
Z	2	2
V ($Å^3$)	2273.96(11)	2275.67(8)
D_{calc} (Mg m^{-3})	1.674	1.692
F(000)	1180	1188
Reflections	78818	29377
Collected/unique	R_{int} = 0.0199	R_{int} = 0.0160
Goodness-of-fit on F^2 (GOF)	0.985	1.028
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0247, wR_2 = 0.0696	R_1 = 0.0263, wR_2 = 0.0718
R indices (all data)	R_1 = 0.0302, wR_2 = 0.0750	R_1 = 0.0339, wR_2 = 0.0768

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