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Two new coordination polymers employing 2,2′-bipyridine-3,3′,6,6′-tetracarboxylate as a ligand

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ABSTRACT

Two new coordination polymers employing 2,2′-bipyridine-3,3′,6,6′-tetracarboxylate (*bptc*) as a ligand are presented: $[Mn_2(H_2O)_5(bptc)]_n$ (**1**) and $[Cu_2(H_2O)_2(bptc)]_n\cdot 2nH_2O$ (**2**). **1** is a 2D coordination polymer stabilized by Mn–O coordination bonds, where magnetic interactions are transmitted within carboxylate-bridged chains. **2** forms polymeric double chains. **1** and **2** are characterized by X-ray diffraction studies, IR spectra, elemental analysis and TGA. Magnetic properties measurements show weak antiferromagnetic coupling of the metal ions in both compounds.

1. Introduction

In the design of new magnetic/luminescent materials the appropriate choice of the organic ligand is of crucial importance. It was shown that inclusion of such features as multiple carboxylic groups or pyridyl moieties extends the ligand coordination capabilities and promotes formation of 1D–3D motifs in the resulting metal complexes [1]. For instance, Massoud et al. [1f] characterized a series of $[Cu^{II}_2]$ complexes bridged by 2,5-pyrazine dicarboxylate, where the organic bridge does not promote magnetic superexchange interactions between the metal ions. Cui et al. [1h] introduced a series of polymeric transition metal complexes where pyridine-2,3,5,6-tetracarboxylic acid acts as a ligand and weak antiferromagnetic interactions between metal ions are revealed. In all cases the organic ligand is not fully deprotonated.

One of the designed ligands incorporating all these useful properties is 2,2′-bipyridine-3,3′,6,6′-tetracarboxylic acid (*bptcH₄*), first introduced by Pruchnik et al. [2]. The reported complexes of *bptcH₄* are scarce. They include iron(II) and cobalt(II) binuclear complexes, $[Fe_2(bptcH_2)_2(H_2O)_4]\cdot 4.74H_2O$ and $[Co_2(bptcH_2)_2(H_2O)_4]\cdot 4.5H_2O$ [2]. As part of our study on solvothermal syntheses of rhenium complexes we also showed a new system where a cleavage of a C–C bond in the organic ligand *bptcH₄* is observed [3]. As a result, a mononuclear rhenium(III) complex including concurrently the *bptc* ligand and its decomposition product in the central metal ion sphere was obtained [3]. Recently Ji et al. [4] introduced a series of 1D lanthanide coordination polymers, describing their solvothermal syntheses, structures, luminescence and magnetic properties. The coordination modes of the organic ligand in metal complexes reported so far are summarized in Scheme 1.

In this paper we extend the field of *bptcH₄* complexes chemistry, reporting on the synthesis, crystal structures and properties of new manganese(II)/copper(II) coordination polymers.

2. Experimental

2.1. Physical measurements

2.1.1. IR spectroscopy

IR spectra were recorded with Bruker VERTEX 70 FTIR spectrometer.

2.1.2. Elemental analyses

The elemental analyses were performed with the aid of the Elementar CHNS vario EL III device.

2.1.3. Thermogravimetric analyses

TGA measurements were carried out on SETARAM SetSys 16/18 TG-DTA device under nitrogen atmosphere with scanning rate at 10 K/min. for samples of **1** (11.204 mg) and **2** (10.270 mg).

2.1.4. X-ray diffraction studies and details of the structures refinement

X-ray diffraction: X-ray diffraction data for single crystals of **1** and **2** were collected on a STOE IPDSII diffractometer [7] with Mo Kα radiation at 100(2) K. Selected X-ray data are shown in Table S1 (ESI)).

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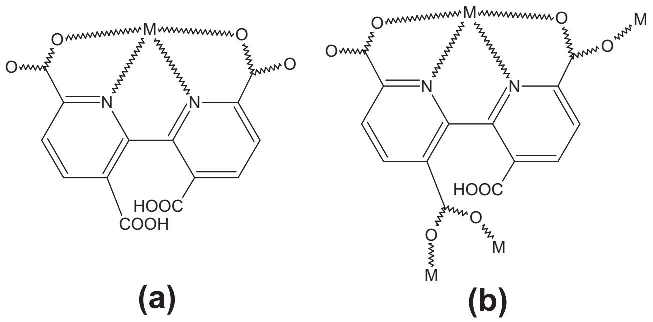


Scheme 1. Coordination modes of the deprotonated 2,2′-bipyridine-3,3′,6,6′-tetracarboxylic acid acting as a ligand in the reported metal complexes: (a) [Fe_2], [Co_2] [2], [Re^{III}] [3]; (b) polymeric [Ln] [4].

Details of the structures refinement: All structures were solved by direct methods in SHELXS and refined by full-matrix method in SHELXL [9]. Water/hydroxyl H atoms positions were first refined with DFIX restraints setting the O–H bond lengths at 0.840(2) Å and with $U_{eq} = 1.5U_{eq}$(parent atom). Subsequently these H atoms parameters were constrained. Aromatic C-bonded H atoms were generated in their calculated positions and a riding model was used with $U_{eq} = 1.2U_{eq}$(parent C atom).

On the final difference Fourier map the highest maximum: of 0.25 e/Å^3 is situated at 0.65 Å from C61 (in the middle of the C61–C71 bond) in **1**; of 0.38 e/Å^3 is situated at 0.77 Å from C1 (in the middle of the C–C bond joining pyridyl rings in the *bptc* ligand) in **2**.

2.1.5. Studies of the magnetic properties

Magnetic properties: Magnetic susceptibility data were measured on a Quantum Design MPMS-XL5 SQUID magnetometer over the 1.8–300 K range. Magnetic data were corrected for diamagnetic contributions, which were estimated from the Pascal's constants [8a,b] and for temperature independent paramagnetism estimated at 60 × 10^{-6} emu/mol for the Cu^{2+} ion [8c].

2.2. Synthesis

Double-distilled water was used. $MnCl_2{\cdot}4H_2O$ and $Cu(BF_4)_2{\cdot}H_2O$ were purchased and used as received. The ligand *bptcH₄* was synthesized in accordance with the literature method [2].

2.2.1. Compound 1

0.033 g (0.1 mmol) of *bptcH₄*, 2 ml of water and $MnCl_2$ (0.04 g, 0.2 mmol) were combined and sealed in a steel Teflon-lined autoclave. The mixture was heated at 120 °C for 5 days and subsequently slowly cooled down within 24 h. The resulting product comprised crystalline material in form of colorless blocks (**1**) isolated at 19% yield (estimated with respect to the *bptcH₄* reagent for the crystalline products directly crystallized from the reaction mixture).

IR/FIR bands [cm^{-1}] (relative intensity) [5–6]: **1**: 3481 (w), 3393 (w), 3207 (w, ν_s O–H), 3023 (w, ν_s O–H), 2225 (vw, ν_s C–H), 1644 (w, ν_s C=O), 1556 (vs), 1461 (m), 1400 (s, δ O–H), 1370 (vs δ O–H), 1281 (m, ν_s C–O), 1263 (m, δ CH_3), 1232 (m), 1200 (m, ν_s C–O), 1147 (w), 1134 (w), 1084 (m, ν_s C–C), 1002 (w, ν_s C–C), 886 (m), 850 (w), 824 (m), 775 (vs, δ (O–C=O)), 727 (vs), 652 (s, π C–H, π COO), 635 (s, π C–H, π COO), 613 (s), 585 (vs) /556 (vs, δ CH), 534 (vs, δ CH), 505 (vs), 456 (vs, ν_s Mn–N), 419 (vs, ν_s Mn–N), 392 (s, ν_s Mn–O), 324 (s, ν_s Mn–O), 248 (w), 185 (s, δ O–Mn–O), 156 (w, δ O–Mn–O), 105 (w).

CHN elemental: **1**: *Anal.* Calc. for $C_{14}H_{14}Mn_2N_2O_{13}$: C, 31.84; H, 2.67; N, 5.30. Found: C, 32.20; H, 2.34 N, 5.11%.

2.2.2. Compound 2

0.033 g (0.1 mmol) of *bptcH₄*, 2 ml of water and $Cu(BF_4)_2$ (0.048 g, 0.2 mmol) were combined and sealed in a steel Teflon-lined autoclave. The mixture was heated at 120 °C for 5 days and subsequently slowly cooled down within 24 h. The resulting product comprised crystalline material in form of pale blue plates (**2**) isolated at 10% yield (estimated with respect to the *bptcH₄* reagent for the crystalline products directly crystallized from the reaction mixture).

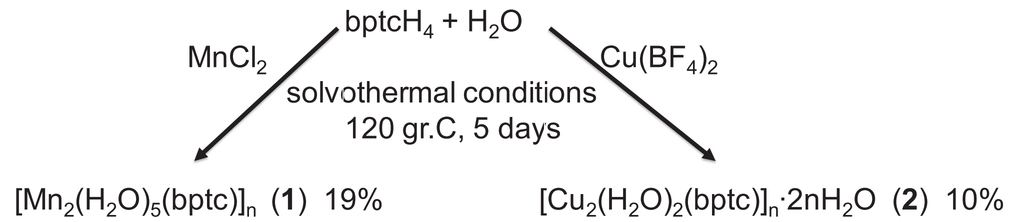
IR/FIR bands [cm^{-1}] (relative intensity) [5–6]: **2**: 3503 (m), 2962 (vs, ν_s O–H), 2857 (vs), 1929 (s), 1720 (s, ν_s C=O), 1693 (s, ν_s C=O), 1618 (m), 1467 (s, δ O–H), 1380 (vw, δ O–H), 1276 (m, ν_o C–O), 1232 (m, ν_o C–O), 1182 (m, ν_s C–O), 1096 (m), 992 (m, δ O–H), 914 (s, δ O–H), 858 (m), 828 (w), 735 (w, δ (O–C=O)), 621 (m, π C–H, π COO) /556 (s, δ CH), 535 (w, δ CH), 484 (m, ν_s Cu–N), 412 (m, ν_{as} Cu–N), 380 (m, ν_s Cu–O), 297 (w, ν_s Cu–O), 210 (w, δ Cu–O), 205 (s), 165 (s, δ Cu–O), 146 (w), 131 (w), 122 (w), 118 (vw).

CHN elemental: **2**: *Anal.* Calc. for $C_{14}H_{12}Cu_2N_2O_{12}$: C, 31.89; H, 2.29; N, 5.31. Found: C, 32.0; H, 2.34; N, 5.66%.

3. Results and discussion

3.1. Syntheses

1 and **2** are obtained in solvothermal syntheses from the following systems:



Ji et al. [4] also applied solvothermal conditions to obtain a series of lanthanide complexes with *bptcH₄* acting as a ligand. In the case of **1** use of other manganese(II) starting products, such as acetate, did not yield crystalline products.

3.2. Crystal structures

1 is manganese(II) complex, whereas **2** is a copper(II) complex, obtained in form of a monohydrate (Fig. 1, Scheme 1). In **1** two independent Mn^{2+} ions are present. Heptacoordinate Mn1 coordination sphere includes four atoms from a chelating *bptc* ligand: two pyridyl N atoms and two carboxyl O11, O22 atoms (Fig. 1). Two water ligands (O1W, O2W) and one carboxyl O21 atom complete the Mn1 ion coordination environment. Mn1–O_{water} bond lengths are 2.179(2)/2.302(2), Mn1–N bond lengths are 2.284(2)/2.343(2) and Mn1–$O_{carboxyl}$ bond lengths are at 2.201(2)–2.305(2) Å range, respectively (Table S2). The second independent Mn^{2+} ion (Mn2) includes three water ligands (O3W, O4W, O5W) in its coordination sphere, along with three carboxyl