Inorganica Chimica Acta 436 (2015) 214–219

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Hydrothermal synthesis and characterization of an Mn(II) coordination polymer with 3,3′-*bpdc*·H_2O as ligand

Małgorzata Hołyńska [b,*], Jerzy Kołodziejczak [a], Andrzej Kochel [a,*]

[a] *Department of Chemistry, Wrocław University, F. Joliot-Curie 14, 50 383 Wrocław, Poland*
[b] *Fachbereich Chemie and Wissenschaftliches Zentrum für Materialwissenschaften, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35043 Marburg, Germany*

ARTICLE INFO

Article history:
Received 25 May 2015
Received in revised form 31 July 2015
Accepted 1 August 2015
Available online 8 August 2015

Keywords:
Coordination polymer
Manganese(II)
Magnetic properties
Topological analysis

ABSTRACT

The new 2D coordination polymer with a new 3,3′-bipyridine-2,2′dicarboxylate monohydrate (3,3′-*bpdc*·H_2O) ligand is described: $[Mn(3,3'\text{-bpdc})]_n$. In the distorted octahedral coordination environment of the Mn^{2+} cations the 3,3′-*bptc* ligand is bonded through nitrogen/carboxylate oxygen atoms. The $[Mn(3,3'\text{-bpdc})]_n$ polymer is characterized by X-ray diffraction studies, IR spectra, elemental analysis, TGA, magnetic properties measurements and the Atoms-in-Molecules analysis of the electron density.

1. Introduction

Coordination polymers combine metal ions and organic ligands to form 1D, 2D or 3D networks [1]. The appropriate choice of the polydentate ligands allows for tuning of their magnetic and luminescence properties. Moreover, coordination polymers raise interest as potential ionoselective absorbents or catalytic, porous materials, also for non-linear optics [2]. In their synthesis the choice of solvent, reaction temperature and the reagents ratio influences the sort of the obtained product.

An interesting class of such compounds are derived from bipyridyl carboxylate ligands.

For instance, the complexes $[Cd(bpy\text{-}3,3'\text{-}dc)(bibp)(H_2O)_3]_n$ (1), $[Zn(bpy\text{-}3,3'\text{-}dc)(bibp)(H_2O)_{2.5}]_n$ (2), $[Cd_2(bpy\text{-}3,3'\text{-}dc)(ptd)_2(H_2O)_6](ClO_4)(H_2O)_5$ (3) and $[Zn_2(bpy\text{-}3,3'\text{-}dc)(ptd)_2(H_2O)_6](ClO_4)_2(H_2O)_6(CH_3CN)$ (4) were obtained in a reaction of 2,2′-bipyridine-3,3′-dicarboxylic acid (H_2*bpy*-3,3′-*dc*) and *bipb* or *ptd* with the Zn(II) or Cd(II) salts using different methods (*bipb* and *ptd* are 2,2′-bis(imidazol-1-ylmethyl)-biphenyl and 1,10-phenanthroline-5,6-dione, respectively) [3].

A new family of photoluminescent silver(I)–lanthanide(III) heterometallic organic frameworks with the general formula $[AgLn(bpdc)_2]$ (Ln = Eu, Tb, Sm, Dy, Y, Yb, Er, Ho; H_2*bpdc* = 2,2′-bipyridine-3,3′-dicarboxylic acid) were synthesized under hydrothermal conditions [1].

The complex $\{Mn[(R,S)\text{-}BDCD](H_2O)\}$ (BDCD = *rac*-(*R*,*S*)-2,2′-bipyridine-3,3′-dicarboxylic acid 1,1′-dioxide) was prepared by the treatment of the tetradentate (*R*,*S*)-H_2*BDCD* ligand with $Mn(OAc)_2{\cdot}2H_2O$ under the solvothermal reaction conditions [4].

In our previous work we introduced two new coordination polymers employing 2,2′-bipyridine-3,3′,6,6′-tetracarboxylate (bptc) as a ligand: the $[Mn_2(H_2O)_5(bptc)]_n$ and $[Cu_2(H_2O)_2(bptc)]_n{\cdot}2nH_2O$ complexes [5].

In this paper a new 3,3′-bipyridine-2,2′dicarboxylate monohydrate ligand and its polymeric complex with Mn^{2+} ions are reported, focusing on the synthesis, crystal structures and properties. Such coordination polymers containing paramagnetic metal ions raise interest as potential functional magnetic materials [6].

2. Experimental

2.1. General

In all syntheses double-distilled water was used as a solvent. The $MnCl_2{\cdot}2H_2O$ reagent was purchased and used as received. The ligand, 3,3′-bipyridine-2,2′ dicarboxylate acid monohydrate (3,3′-*bpdc*·H_2O), was synthesized as described below.

2.2. Synthesis

2.2.1. 3,3′-Bipyridine-2,2′ dicarboxylic acid monohydrate (3,3′-bpdc·H_2O, **2**)

A 50 cm^3 round-bottom flask was equipped with a reflux condenser and filled with 30 cm^3 of water. 1 g (5.55 mmol) of

---

* Corresponding authors.
E-mail addresses: holynska@staff.uni-marburg.de (M. Hołyńska), andrzej.kochel@chem.uni.wroc.pl (A. Kochel).

http://dx.doi.org/10.1016/j.ica.2015.08.001

4,7-phenanthroline and 0.384 g (9.6 mmol) NaOH were added. The mixture was stirred for 5 min. Subsequently, 1.350 g (8.49 mmol) of $KMnO_4$ were added in small portions, rinsing the corresponding weighing vessel with additional 10 cm^3 of water. The mixture was heated in an oil bath and stirred at 95–97 °C for 8 h. The obtained solution was filtered from the MnO_2 side-product. Then active carbon was added and the suspension was heated at 95–97 °C for about 1 h. The mixture was filtered and left for cooling. The pH of the cool mixture was adjusted to 2–3 by addition of 3 M HCl dropwise. The obtained solution was left at room temperature for slow evaporation. After 2 days crystals in form of paralellepipeds suitable for X-ray diffraction studies were formed at 55% yield.

2.2.2. $[Mn(3,3'\text{-bpdc})]_n$ (**1**)

0.055 g (0.209 mmol) of 3,3′-*bpdc*·H_2O (**2**), 8 ml of water and $MnCl_2{\cdot}2H_2O$ (0.03 g, 0.185 mmol, **1**) were combined and sealed in a steel Teflon-lined Berghof100 autoclave. The mixture was heated at 130 °C for 5 days and subsequently slowly cooled down at 7 °C/h within 24 h. The resulting product comprised crystalline material with single crystals in form of pale yellow blocks at 30% yield (estimated with respect to the 3,3′-*bpdc*·H_2O reagent for the crystalline products directly crystallized from the reaction mixture).

2.3. Characterization

2.3.1. IR spectroscopy

IR spectra were recorded with Bruker VERTEX 70 FTIR spectrometer.

Complex **1** [Nujol, cm^{-1}]: 3590 w, 3405 w, 3206 w, ν_s (O–H), 3077 w, ν_s (O–H), 2216 vw, ν_s (C–H), 1685 w, ν_s (C=O), 1587 vs, 1529 m, 1467 s, δ (O–H), 1378 vs δ (O–H), 1303 m, ν_s (C–O), 1263 m, δ (CH_3), 1272 m, 1171 m, ν_s (C–O), 1090 w, 1087 w, 1002 m, ν_s (C–C), 1003 w, ν_s (C–C), 969 m, 896 w, 840 m, 792 vs δ (O–C=O), 772 vs, 678 s, π (C–H), π (COO), 556 s, π (C–H), π (COO), 551 s, 510 vs, 498 vs, δ (CH), 458 vs δ (CH), 437 vs, 458 vs, ν_s (Mn–N), 419 vs, ν_s (Mn–N), 398 s, ν_s (Mn–O), 376 s, ν_s (Mn–O), 248 w, 227 s, δ (O–Mn–O), 150 w, δ (O–Mn–O), 108 w, 101 w.

Ligand **2** [Nujol, cm^{-1}]: 3257 s, ν_s (OH), 3102 w, ν (CH), 2349 w, 2042 w, ν(OH), 1952 w, 1718 s, ν_{as} (COO), 1614 m, ν_s (COO) or ν_s (C=C), 1583 w, ν(C=C), 1570 w, ν_{as} (COO), 1534 s, 1460 m, ν (CC), 1416 ν, (CN) or δ (CH), 1439 w, ν (CN), 1377 s, δ (CH), 1304 m, δ (CH), 1276 m, ν (CO) or ν (CC), 1244 m, ν (CC) or δ (CH), 1206 w, ν (CC), 1162 w, δ (COH), 1148 m, ν_s (COO), 1118 m, δ (CH) or ν (CN), 1099 w, δ (CH) or ν (CN), 1064 w, ν (CC), ν (CN) or δ (CH), 1011 m, ν (CC) or δ (CH), 997 w, ν (CO), 940 w, ν (COO), 854 w, 839 m, ν (CN), 812 s, ν (CN), 742 m, ν (CN), 701 w, δ (COO), 688 m, 654 s, ρ (COO), 627 w, 584 w, δ (CH), 524 m, ν (CC), 445 w, δ (CNC) or δ (CH), 408 w, 356 w, 317 w, 288 w, 244 w, 217 w, 164 w, 138 w, 100 w, 89 w, 73 w, 57 w.

2.3.2. Elemental analyses

CHN elemental: **1**: (Calc./obs. for $C_{12}H_6MnN_2O_4$): C 48.55 (47.6), H 2.03 (1.87), N 9.42 (9.01); **2** (Calc./obs. for $C_{12}H_{10}N_2O_5$): C 54.96 (53.89), H 3.84 (3.09), N 10.68 (9.31)%.

2.3.3. MS spectrum

For **1** (see Sup. Figs. S6 and S7): *m*/*z* positive: 245.15, 267.05 $[M+Na]^+$, 288.95 $[M+2Na]^+$, *m*/*z* negative: 243.30, 225.25, 166.30.

2.3.4. NMR spectrum

For **1** (see Sup. Figs. S1–S3): ^1H NMR 500 Hz [D_2O, ppm, δ]: 8.13 dd 1H J = 5.7 Hz, 8.45 d 1H J = 8 Hz, 8.77 d 1H J = 5.7 Hz.

^{13}C NMR [125 MHz, D_2O, 300 K, ppm]: 127.82, 136.02, 141.22, 144.45, 147.17, 162.91.

2.3.5. 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 the samples of **1** (1.550 mg) and **2** (11.992 mg).

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

X-ray diffraction data for single crystals of **1** and **2** were collected on an Xcalibur RUBY diffractometer and KM4-CCD [7], respectively, with MoKα radiation at 100(2) K. Selected X-ray data are shown in Table S1 (ESI). CCDC reference numbers for **1** and **2**: CCDC 1059393 and 1059392 (Supplementary data available from CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK on request).

Details of the structures refinement: All structures were solved by direct methods in SHELXS2014 and refined by full-matrix method in SHELXL2014 [8]. Water/hydroxyl H atoms positions were first refined with DFIX restraints setting the O–H/N–H bond lengths at 0.84 and 0.86 Å, respectively, with $U_{eq} = 1.5\ U_{eq}$(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 $U_{eq} = 1.2\ U_{eq}$(parent C atom). In the ligand **2** the carboxylate H atoms were found to be disordered and were refined fixing the occupancy factors at 0.5 (the occupancies were initially refined until convergence and values close to 0.5 were achieved). The H atom bonded to N1 is given a full occupancy for charge balance. The second pyridine ring N, N2, is not protonated. Molecular graphics was prepared with the *DIAMOND 3.2* software [9].

On the final difference Fourier map the highest maximum of 0.72 e/$Å^3$ is situated at 0.06 Å from Mn1 in **1**; of 0.27 e/$Å^3$ is situated at 0.78 A from C6 (in the middle of the C6–C14 bond to carboxylate group in the 3,3′-*bpdc*·H_2O ligand) in **2**.

2.3.7. Studies of the magnetic property

Magnetic susceptibility data were measured on a Quantum Design MPMS-XL5 SQUID magnetometer over the 300–1.8 K temperature range. Magnetic data were corrected for diamagnetic contributions which were estimated from the Pascal's constants [10].

2.3.8. Mass spectrometry

Mass spectrometry experiments were performed on Shimadzu System LCMS–MS-8030 equipped with an ESI source. The instrument was operated in the positive and negative mode. The sample for MS experiments (~0.05 mg) were dissolved in 1 ml water. The spectra were recorded in the *m*/*z* range from 10 to 300. The obtained mass spectra were analyzed using the LabSolutions software (LabSolutions, ver. 5.75, copyright 2008–2015, Shimadzu-Corporation).

2.3.9. Topological analysis

Calculations were performed using the Density Functional Theory (DFT) framework. The hybrid M06 exchange–correlation functional [11] was selected. The Mn metal was described by the effective core potential CEP-31G with the associated basis set [12] while the remaining atoms were assigned a Pople-type double-zeta basis set with polarization functions 6-31G(d,p) [13].

The initial coordinates were taken from the X-ray diffraction data, and a full coordination sphere around one of the manganese atoms was constructed, giving one mer of the polymeric structure (assumed high-spin). In order to retain the arrangement found in the crystal structure, the geometry optimization was carried out with freezing the coordinates of the carbon atoms of the non-coordinating carboxylic groups (facing away from the metal). The remaining degrees of freedom were free to optimize. A final check *via* harmonic frequency generation found no imaginary frequencies. Then, wave function was exported for further analysis.