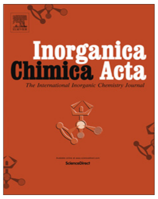
Inorganica Chimica Acta 423 (2014) 46–51

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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



Syntheses, crystal structures and luminescent properties of three complexes with mercapto-thiadiazole ligand involving in situ ligand synthesis

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A R T I C L E   I N F O

Article history:
Received 24 April 2014
Received in revised form 30 June 2014
Accepted 19 July 2014
Available online 29 July 2014

Keywords:
Mercapto-thiadiazole
In situ reaction
Crystal structures
Luminescent properties

A B S T R A C T

Three coordination complexes, namely, $[Co(ddc)_3]$ (**1**), $[Zn(4\text{-}ptt)_2{\cdot}H_2O]_n$ (**2**) and $[Pb(4\text{-}ptt)_2]_n$ (**3**), (Hddc = *N*,*N*-dimethyldithiocarbamic acid; 4-Hptt = 5-(4-pyridyl)-1,3,4-thiadiazole-2-thione) have been successfully synthesized under the same reaction conditions but tuned by different metal salts. Notably, in situ ligand reaction exists in the formation of complex **1**, in which the ligand 4-Hptt reacted with DMF to generate the ligand Hddc. The X-ray single diffraction analysis reveals that **2** features a 2D layer structure, constructed from Zn(II) ions and 4-Hptt ligand. Complex **3** exhibits a 1D chain with 4-Hptt bridged four-coordinated Pb(II). Complexes **1**–**3** were characterized by elemental analyses, IR. The possible mechanism of the formation of Hddc for complex **1** has been discussed, and in addition, solid-state luminescent properties of polymers **2**, **3** and ligand (4-Hptt) have also been investigated.

1. Introduction

Recently, the research on coordination compounds is an abundant field, which is reflected by increased number of research in magnetism, molecular recognition, selective gas adsorption and gas storage, catalysis, luminescence, etc [1–8]. Although there are numerous research achievements in this field, many challenges remain, and one of them is to rationally design and prepare appropriate multidentate ligands that play a key role in determining the architecture of the ultimate products [9,10]. For many decades, compounds with N/S-donor, especially thiadiazole derivatives, which possess a wide variety of biological activity, have been extensively researched in the fields of pesticides and medicines [11,12]. However, these compounds with N/S-donor like mercapto-thiadiazole and its derivates are relatively few used as ligands in coordination chemistry [13]. Therefore, it deserves further attention for the sake of more versatile structures and properties in the future.

On the other hand, organic ligands usually are synthesized by the conventional methods, but some ligands, which are inaccessible or not easily achieved via routine synthetic methods, are obtained through hydro(solvo)thermal in situ reactions [14–16]. Until now, several types of in situ ligand reactions have appeared under hydro(solvo)thermal conditions, which include alkylation, hydroxylation, carbon–carbon bond formation, hydrolysis, triazole and tetrazole formation, etc [14,17–19]. These in situ ligand reactions have attracted much attention because they are effective ways to generate unexpected structures and more intriguing network topologies [20,21]. To our best knowledge, the study on in situ ligand transformation about mercapto-thiadiazole and its derivates has not been reported. Therefore, we have taken an interest in the possibility of in situ ligand transformation about mercapto-thiadiazole and its derivates.

In this paper, we used 5-(4-pyridyl)-1,3,4-thiadiazole-2-thione (4-Hptt) (Scheme 1) as a ligand to assemble with different metal ions. As a consequence, one mononuclear structure $[Co(ddc)_3]$ (**1**) (Hddc = *N*,*N*-dimethyldithiocarbamic acid) was synthesized successfully under solvothermal condition, in which the Hddc ligand was obtained from the reaction of 4-Hptt and DMF. The possible reaction mechanism is discussed in detail. And two new zinc(II) and lead(II) coordination polymers were also synthesized successfully under solvothermal conditions without in situ synthesis of Hddc, namely, a grid layer 2D framework $[Zn(4\text{-}ptt)_2{\cdot}H_2O]_n$ (**2**), 1D chain structure $[Pb(4\text{-}ptt)_2]_n$ (**3**). In this study, 4-Hptt can adopt various coordination modes to show flexible coordination geometries with metal centers (as shown in Scheme 2). In addition, solid-state photoluminescent properties of polymers **2**, **3** and ligand (4-Hptt) have also been described in detail.

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http://dx.doi.org/10.1016/j.ica.2014.07.041
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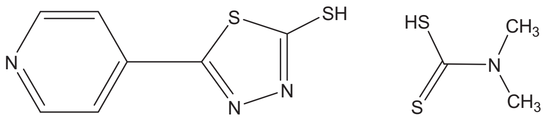


Scheme 1. Ligands 4-Hptt and Hddc used in this study.

2. Experimental

2.1. General methods

The 4-Hptt was prepared according to the literature method [22]. Other chemical, reagents, and solvents were purchased from commercial sources and used without further purification. Elemental analyses (C, H, and N) were carried out on a FLASH EA 1112 elemental analyzer. The IR data were recorded from KBr disks in the range of 400–4000 cm^{-1} on a Bruker Tensor 27 spectrophotometer. The fluorescence spectra for the solid samples were measured at room temperature on a Hitachi 850 fluorescence spectrophotometer.

2.2. Syntheses

2.2.1. Synthesis of $[Co(ddc)_3]$ (**1**)

A mixture of $CoCl_2 \cdot 6H_2O$ (7.1 mg, 0.03 mmol), 4-Hptt (11.7 mg, 0.06 mmol), H_2O (5 mL) and DMF (1 mL) was sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 130 °C for 4 days, and then slowly cooled to room temperature. Pale yellow crystals of complex **1** were separated suitably for X-ray diffraction (Yield: 40%). *Anal.* Calc. for $C_{36}H_{72}Co_4N_{12}S_{24}$: C, 25.76; H, 4.32; N, 10.01. Found: C, 25.61; H, 4.47; N, 10.14%. IR (KBr, cm^{-1}): 3238.19(s), 2923.71(w), 2852.34(w), 1650.86(w), 1436.32(m), 1401.77(m), 1144.30(s), 1097.40(s), 982.25(w), 739.59(m), 628.34(s), 459.95(w).

2.2.2. Synthesis of $[Zn(4\text{-ptt})_2 \cdot H_2O]_n$ (**2**)

Complex **2** was prepared in a similar method as for **1** but using $Zn(NO_3)_2 \cdot 6H_2O$ (9.0 mg, 0.03 mmol) in place of $CoCl_2 \cdot 6H_2O$. Yellow crystals of complex **2** were separated suitably for X-ray diffraction (Yield: 45%). *Anal.* Calc. for $C_{56}H_{40}N_{24}O_4S_{16}Zn_4$: C, 35.63; H, 2.14; N, 17.81. Found: C, 35.47; H, 2.25; N, 17.69%. IR (KBr, cm^{-1}): 3443.36(s), 1862.18(w), 1613.88(s), 1602.26(s), 1558.12(w), 1507.94(w), 1474.51(w), 1416.99(m), 1330.38(m), 1292.81(s), 1257.66(s), 1216.50(w), 1107.60(w), 1057.35(m), 1014.71(w), 826.13(s), 723.38(s), 645.57(s).

2.2.3. Synthesis of $[Pb(4\text{-ptt})_2]_n$ (**3**)

The same synthetic method as that for **1** was used except that $CoCl_2 \cdot 6H_2O$ was replaced by $Pb(NO_3)_2$ (9.9 mg, 0.03 mmol). Yellow crystals of complex **3** were separated suitably for X-ray diffraction (Yield: 50%). *Anal.* Calc. for $C_7H_4N_3S_2Pb_{0.5}$: C, 35.97; H, 1.72; N, 17.97. Found: C, 35.79; H, 1.86; N, 17.81%. IR (KBr, cm^{-1}): 3446.18 (s), 1593.70(s), 1551.96(w), 1442.88(w), 1408.10(m), 1308.63(s), 1207.68(w), 1099.08(m), 1070.95(m), 1082.30(s), 1042.38(s), 993.41(w), 818.68(s), 761.53(m), 701.73(m), 638.81(m), 581.44(m).

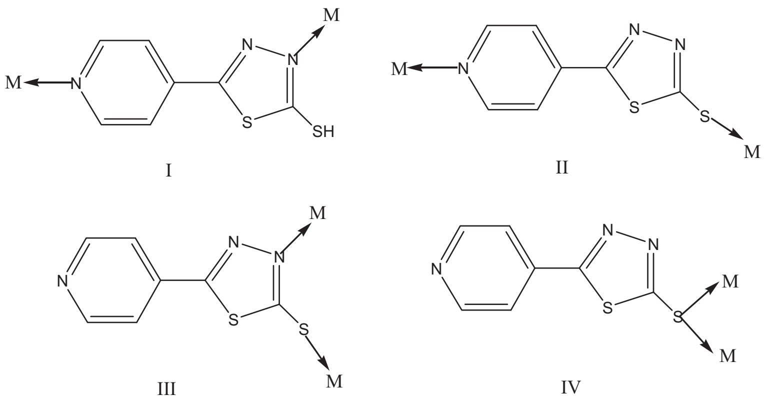
2.3. X-ray crystallographic determinations for the complexes

The data of complexes **1**, **3** were collected by using a Rigaku Saturn 724 CCD diffractomer with graphite monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å), whereas for **2**, single-crystal X-ray data were collected on a Rigaku D/max-3B diffractometer with graphite monochromatic Cu Kα radiation ($\lambda = 1.5406$ Å). Single crystals were selected and mounted on a glass fiber. The data were collected at a temperature of 291(3) K and corrected for Lorentz-polarization effects. The structures were solved by direct methods and refined with a full-matrix least-squares technique based on F^2 with the SHELXL-97 crystallographic software package [23]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical restrains. Crystallographic crystal data and structure processing parameters for complexes **1**–**3** are summarized in detail in Table 1. Selected bond lengths and bond angles are listed in Table S1.

3. Results and discussions

3.1. Synthesis

The 4-Hptt (4-Hptt = 5-(4-pyridyl)-1,3,4-thiadiazole-2-thione) was used as the original organic ligand to assemble with different metal ions at 130 °C for 4 days in H_2O/DMF mixed-solvent systems. It's worth noting that the ligand Hddc (Hddc = *N*,*N*-dimethyldithiocarbamic acid) was unexpectedly obtained in complex **1**, in which the ligand 4-Hptt was converted into Hddc and transition metal Co(II) was oxidized to Co(III) ion. However, the Hddc could not be obtained in the presence of metal ions zinc(II) and lead(II). The study reflected that the transition metal Co(II) plays a unique catalytic role in the in situ transformation of 4-Hptt, then Co(II) is oxidized to Co(III) ion in the presence of the Hddc ligand, forming the complex **1** [24]. The possibly schematic mechanism for the formation of Hddc is illustrated in Scheme 3.



Scheme 2. Coordination modes of 4-Hptt in complexes **2–3**.