Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

troscopic techniques along with crystallography.

Note Structural study of few *p*-phenylenediacetate complexes of Mn^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+}

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ARTICLE INFO

ABSTRACT

Article history: Received 24 April 2009 Received in revised form 2 June 2009 Accepted 3 June 2009 Available online 9 June 2009

Keywords: Dicarboxylic acid Coordination polymer Nitrogen donor ligand Crystal structure

1. Introduction

The formation of polymeric metal carboxylate complexes is guided by various factors [1-3] and the dimensionality of such coordination polymers can be changed by substituents on the ligand and/or by solvents [4]. The structural features of metal carboxylate coordination polymers originate from different types of geometries constructed around a metal center by coordinated carboxylate ligand/s [5]. Structurally rigid dicarboxylate, for example, terephthalate anion leads to interesting metallo-organic framework [6], whereas flexible carboxylates, such as malonate anion is useful in making polymers with different dimensions [7-10]. There is good numbers of studies on coordination complexes of p-phenylenediacetate [11] and most of the study is directed towards making porous materials through solvothermal process. In this study, a series of carboxylate complexes are prepared by reactions carried out at ambient condition with different metal ions in the presence and absence of nitrogen containing ligands. The reactions through which these complexes are prepared are presented in Scheme 1. We discuss the structures of each of these complexes.

2. Experimental

2.1. Synthesis of coordination polymer I and complexes II and III

To a well stirred solution of 1,4-phenylenediacetic acid (0.2 g, 1 mmol) in methanol (7 ml) a solution of manganese (+2) acetate

(0.245 g, 1 mmol) in methanol (3 ml) was added. The reaction mixture was stirred for 5 min, a white precipitate was obtained. The white solid was filtered and the residue was re-dissolved in milli-Q water (10 ml). The aqueous solution on slow evaporation gave crystalline product I. The complex II or III were prepared from I by reacting with corresponding nitrogen donor ligand. For their synthesis an aqueous solution of I was prepared as described above and to this solution a solution of 1,10-phenanthroline (0.180 g, 1 mmol) or 2,2'-bipyridine (0.158 g, 1 mmol) in milli-Q water (10 ml) were added to make a homogeneous solution. The solution on slow evaporation gave the corresponding complex II or III as per the nitrogen donor ligand.

2.2. Synthesis of coordination polymers IV, V and VI

Different metal carboxylate complexes are prepared by reactions of manganese (+2) acetate, copper (+2)

acetate, zinc (+2) acetate and cadmium (+2) acetate with p-phenylenediacetic acid under ambient condi-

tion with or without a nitrogen donor ligands and each of them are characterized by conventional spec-

To a solution of 1,4-phenylenediacetic acid (0.2 g, 1 mmol) in methanol (7 ml) a solution of the corresponding hydrated metal (+2) acetate (1 mmol) was added. The reaction mixture on stirring for 5 min gave precipitate (green in the case of copper, white in the case of zinc or cadmium). The precipitate was filtered and it was dissolved in pyridine/methanol (1:5 v/v, 5 ml). A homogeneous solution was obtained in each case. The solution was allowed to evaporate slowly for 4–5 days at room temperature, which yielded the desired coordination polymer **IV–VI** in pure crystalline form.

2.3. Spectral properties of the complexes

Coordination polymer **I** : *Yield*: 93%. IR (KBr, cm⁻¹) 3625(s), 3092 (bw), 2926(w), 1552(s), 1405(s), 1283(w), 1203(m), 1164(m), 930(w), 797(m), 720(s), 622(m). Elemental *Anal.* Calc. for





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^{0020-1693/\$ -} see front matter \odot 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2009.06.002



Scheme 1.

 $C_{10}H_{12}O_6Mn: C, 42.38; H, 4.24. Found: C, 42.44; H, 4.23%. Magnetic moment (RT) 4.3BM.$ *Complex***II**: Yield: 68%. IR (KBr, cm⁻¹) 3307 (bw), 3126(bw), 1557(s), 1426(s), 1385(s), 1305(w), 1176(m), 1141(m), 848(s), 772(m), 726(s), 715(w). Elemental*Anal.* $Calc. for <math>C_{20}H_{24}N_2O_8Mn: C, 50.49, H, 5.05.$ Found: C, 50.47; H, 5.10%. Magnetic moment (RT) 5.78BM. *Complex* **III**: Yield: 67%. It is identified by comparing its spectroscopic data and crystal structure with

reported structure [7]. *Coordination polymer* **IV**: Yield: 69%. IR (KBr, cm⁻¹) 3409(bs), 2925 (w), 1578 (s), 1562(s), 1450(m), 1384(s), 1217(m), 1159(w), 1071(w), 763(w), 698(m). Elemental *Anal.* Calc. for $C_{20}H_{22}N_2O_6Cu$: C, 53.34; H, 4.89. Found: C, 53.52; H, 5.01%. Magnetic moment (RT) 1.70BM. *Coordination polymer* **V** : *Yield*: 80%. IR (KBr, cm⁻¹) 3067(bw), 2966(w), 1599(s), 1557(s), 1414(m), 1392(s), 1305(m), 1222(w), 1142(m), 1070(w), 817(w), 770(s), 701(s), 663(m). Elemental *Anal.* Calc. for $C_{15}H_{15}NO_5Zn$: C, 50.75; H, 4.23. Found: C, 50.81; H, 4.31%. *Coordination polymer* **V**: Yield: 88%. IR (KBr, cm⁻¹) 3400(bs), 3039 (bw), 2950(w), 1595(s), 1573(s), 1444(m), 1397(s), 1215(w), 1151(w), 753(m), 751(m), 699(s). Elemental *Anal.* Calc. for $C_{20}H_{24}N_2O_7Cd$: C, 46.44; H, 4.64. Found: C, 46.45; H, 4.62%.

3. Results and discussion

The reaction of *p*-phenylenediacetic acid with manganese (+2) acetate tetrahydrate under ambient condition leads to a coordination polymer I as shown in Scheme 1. The coordination polymer has six coordinated environments around the manganese centers. Each of the carboxylate group bridges two manganese centers and each manganese ion is anchored by four carboxylate groups



Fig. 1. (a) Repeated units in the structure of coordination polymer derived from manganese (+2) with *p*-phenylenediacetate (**I**), (b) coordination geometry around manganese ion, (c) the packing pattern of the coordination polymer. Bond distances (Å): Mn1–O1, 2.15(9); Mn1–O3, 2.19(9); Mn1–O2, 2.21(1). Bond angles (°): O1–Mn1–O3, 85.5(4); O1–Mn1–O3', 94.5(4); O1–Mn1–O2, 92.0(4); O1–Mn1–O2', 88.0(4); O3–Mn1–O2, 88.5(5); O3–Mn1–O2', 91.5(5); O3–Mn1–O2, 91.5(5).



Fig. 2. Structure of manganese (+2) *p*-phenylenediacetate complex with 4,4'-bipyridine ligand (II).

of four independent dicarboxylate anions. The manganese centers are also associated with two water ligands. The manganese polymer has a two dimensional network structure. This is in contrast to the manganese dicarboxylate coordination polymer having pyridine as ancillary ligand that has one dimensional aqua-bridged dinuclear manganese cores [12]. Grid-like structures containing dinuclear manganese cores are also reported in literature [13]. These suggest that the different types of structures are possible for manganese dicarboxylate coordination polymers from different dicarboxylates depending on the ancillary ligand (see Fig. 1).

Metal dicarboxylate coordination polymers with nitrogen containing bidentate chelate ligands are reported in literature; such ligands also have advantages to control the dimensionality of coordination polymers [14-17]. Thus, a few complexes as well as coordination polymes of metal *p*-phenylenediacetate that has 2,2'-bipyridine and 1,10-phenanthroline as ancillary ligand are prepared for structural study. The reaction of manganese (+2) acetate tetrahydrate with *p*-phenylenediacetic acid in the presence of ancillary ligands such as 2,2'-bipyridine or 1,10-phenanthroline leads to the formation of mononuclear (II) (Fig. 2) and dinuclear complex (III) as illustrated in Scheme 1. The dinuclear complex **III** was reported in the literature [11] and it was earlier prepared through a solvothermal process, however we obtained this complex under ambient condition. Each of these complexes has six coordination environments. In these complexes the two carboxylate groups of the ligands are anti to each other across the phenylene ring. These complexes have very low solubility in common solvents making it difficult to perform spectroscopic study in solution.

While formation of these complexes the nitrogen donor ligands competes with the carboxylate for coordination to the metal ion and upon coordination they block some of the coordination sites to prevent coordination polymerization. Bis-chelated mononuclear complex of manganese with 1,10-phenanthroline having carboxylate anion are reported in literature [18]. The nickel (2+) meditated ring opening reactions of pyromellitic dianhydride in the presence of 2,2'-bipyridine leads to mononuclear cationic complex of nickel (+2) [16] that has structural similarity to complex **II**. Coordination polymer of *p*-phenylene diacetate of manganese [19] and nickel [20] containing 1,10-phenanthroline are reported in literature. From these available data on formation of coordination polymer as well low nuclearity metal complexes of manganese in the absence or presence of nitrogen containing chelates, it may be said that it is the reaction condition along with coordination effect



Fig. 3. (a) Structure of *p*-phenylenediacetate copper (+2) coordination polymer (IV). (b) The coordination environment around copper (+2) ion. Selected bond distances (Å): Cu1–O1, 1.96(2), Cu1–N1, 2.00(2), Cu1–O3 2.83. Bond angles (°): O1–Cu1–O1, 180.0; O1–Cu1–N1, 92.6(9); O1–Cu1–N1, 87.4(9); O1–Cu1–N1, 87.4(9); O1–Cu1–N1, 92.6(9); N1–Cu1–N1, 180.0.



Fig. 4. (a) Structure of *p*-phenylenediacetate zinc (+2) complex (**V**), (b) coordination environment around zinc (selected bond distances (Å): Zn1–O4, 1.96(1); Zn1–O1, 1.97(1); Zn1–O3, 1.98(1); Zn1–N1, 2.05(1); selected bond angles (°): O4–Zn1–O1, 98.2(5); O4–Zn1–O3, 123.0(5); O1–Zn1–O3, 105.8(5); O4–Zn1–N1, 100.2(5); O1–Zn1–N1, 128.1(5); O3–Zn1–N1, 103.7(5).



Fig. 5. (a) Repeated units in the structure of *p*-phenylenediacetate cadmium (+2) complex (**VI**). (b) The coordination environment around cadmium (bond distances (Å): Cd1–O3, 2.26(3); Cd1–O2, 2.35(1); Cd1–N1, 2.38(2); Cd1–O1, 2.56(1); bond angles (°): O3–Cd1–O2, 137.6(4); O2–Cd1–O2, 84.7(9); O3–Cd1–N1, 84.4(5); O2–Cd1–N1, 87.5(6); O2–Cd1–N1, 100.8(7), N1–Cd1–N1, 168.8(9); O3–Cd1–O1, 86.3(4); O2–Cd1–O1, 52.5(6); O2–Cd1–O1', 134.7(6); N1–Cd1–O1, 92.4(6); N1–Cd1–O1, 86.9(6)).

which decides the dimensionality of the polymerization process in these manganese dicarboxylate complexes. Thermogravimetric analysis of the three manganese complexes **I–III** shows that they lose water molecules around 80 °C in all the cases.

An one dimensional coordination polymer **IV** of copper(II) (Fig. 3a) can be prepared from simple reaction of copper(II) acetate with *p*-phenylenediacaetic acid followed by crystallization from pyridine water mixed solvent. It has two pyridine ligands and two aqua ligands. Two carboxylate ligands act as bridges the copper ions. The polymer has octahedral geometry around the copper ions (Fig. 3b). In this coordination polymer the pyridine ligands are *trans* to each other and the aqua ligands are also *trans* to each other. The Cu1–O3 bond (2.83 Å) is much longer than the Cu1–O1 bond (2.00 Å). This is obvious for copper (+2) which shows Jahn–Teller distortion.

Similarly, the corresponding zinc (2+) p-phenylenediacetate coordination polymer having pyridine has a distorted tetrahedral geometry around the zinc (Fig. 4a and b). In the coordination polymer the zinc-nitrogen bond is slightly longer than zinc-oxygen bonds and it has a chain like structure (Fig. 4a). Similarly, the cadmium complex of *p*-phenylenediacetate and pyridine ligand is also a one dimensional coordination polymer with all the cadmium ions having two pyridine and one agua ligand anchored to them. The polymer forms a zig-zag chain like structure in which each cadmium ions have seven coordination number (Fig. 5). The carboxylate groups are chelating in this polymer (Fig. 5a). The seven coordination number for cadmium is common in coordination chemistry [21]. While using pyridine as ancillary ligand we obtained a coordination polymer; whereas cadmium p-phenylenediacetate with 4-aminopyridine has uncoordinated amino group [22] leading to supramolecular assembly.

The geometrical features of the dicarboxylic acids in these complexes are of interest from the orientation of the carboxylic acids across the rings. *Syn* or *anti* arrangements of the carboxylate groups across the phenylene rings are associated in these metal complexes. There is a competition between coordination of dicarboxylates with aromatic nitrogen containing ligands. The dicarboxylate complexes derived from *p*-phenylenediacetate having pyridine ligand favors one dimensional coordination polymer irrespective of coordination number of the central metal atom.

Appendix A. Supplementary data

CCDC 714474, 714475, 714476, 714477, 716805 and 716806 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.06.002.

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