

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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

A metal-organic coordination polymer based on 1,2-bis(diphenylphosphino)ethane dioxide: Synthesis, crystal structure and fluorescence of $[ZnI_2{Ph_2P(O)-CH_2CH_2-P(O)Ph_2}]_n$

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ARTICLE INFO

Article history: Received 26 December 2008 Accepted 31 March 2009 Available online 7 April 2009

Keywords: Coordination polymer Crystal structure Zinc(II) 1,2-Bis(diphenylphosphino)ethane dioxide

The coordination chemistry of phosphine oxides $R_3P(O)$ with transition metals [1–6], lanthanides [7–9] and actinides [10–12] has been extensively studied in the past decades. In particular, phosphine oxides have been used in solvent extraction and separation processes of the oxophilic lanthanide metal ions. The dimeric bis(phosphine oxides), e.g. Ph₂P(O)(CH₂)₂P(O)Ph₂, have three different coordination modes: the most common chelating bidentate fashion (η^2 -O, O'), the bridging mode between two metal centers $(\mu_2$ -O, O') [13], and the monodentate one $(\eta^1$ -O) [14]. Therefore, complexes of such ligands can exhibit richer structural topologies than the mono phosphine oxides. Actually, there are some examples of metal complexes with different structures based on these bis(phosphine oxide) ligands, such as coordination polymers [15-18], macrocyclic compounds [19] and cage molecules [20]. The use of zinc ion to assemble with bis-phosphine oxide ligands is of interest because zinc atom with the d^{10} electron configuration can produce a diversity of complexes that may find potential applications in photoluminescent and second-order nonlinear optical (NLO) materials [21,22]. However, these areas have been relatively less explored [13]. Herein we report the synthesis, crystal structure and fluorescence properties of a zinc coordination polymer constructed with 1,2-bis(diphenylphosphino)ethane dioxide, dppeO₂, $[ZnI_2{Ph_2P(O)-CH_2CH_2-P(O)Ph_2}]_n$ (1).

The ligand dppe [23] and its oxidized derivative $dppeO_2$ [16] were synthesized according to the reported methods. The zinc

ABSTRACT

A zinc coordination polymer, $[Znl_{2}{Ph_{2}P(O)-CH_{2}CH_{2}-P(O)Ph_{2}]_{n}$ (1), has been prepared, which features a one-dimensional concavo-convex chain with alternative Znl_{2} and 1,2-bis(diphenylphosphino)ethane dioxide (dppeO₂) moieties. The dppeO₂ ligand adopts the bridging coordination mode between two zinc atoms.

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complex **1** was obtained as a colorless material by slow diffusion of ZnI_2 in aqueous ethanolic solution with dppeO₂ in dichloromethane at room temperature (Scheme 1) [24]. It can also be prepared by reaction of ZnI_2 with dppe followed by oxidation in air or by H₂O₂. The polymer **1** is slightly soluble in DMSO and is insoluble in other common organic solvents such as diethyl ether, tetrahydrofuran and ethanol.

Single crystal X-ray analysis [25] revealed that compound 1 consists of one-dimensional concavo-convex chains with alternative ZnI₂ and dppeO₂ units along the *c*-direction (Fig. 1a). The zinc(II) center is coordinated by two oxygen atoms of two dppeO₂ ligands and two iodine atoms in a slightly distorted tetrahedral geometry with bond angles ranging from 106.94(6)° to 118.55(2)°. There are two halves of dppeO₂ ligand, one zinc atom and two iodine atoms in the asymmetric unit, with the remaining parts being generated by a crystallographic inversion center at the mid-point of the C-C bond of the ethylene group. The ligand dppeO₂ is coordinated in the bridging bidentate fashion, which is similar to that in the dinuclear zinc complex anion [Cl₃ZnO:(Ph)₂PCH₂CH₂P(Ph)₂:OZnCl₃]²⁻ [13]. Such linear coordination polymers of transition metals bridged by bis(phosphine oxide) are relatively rare in the literature, and only a few complexes of bis(phosphine oxide) have previously been reported to form polymeric structure, e.g. $[CuCl_2(dppeO_2)]_n$ [15], and $[CoCl_2(dppeO_2)]_n$ [26]. The chains are further packed parallel to each other in the bc plane (Fig. 1b).

The Zn–O distances in **1** (1.958(2) and 1.964(2) Å) are slightly shorter than that in the $[Cl_3ZnO:(Ph)_2PCH_2CH_2P(Ph)_2:OZnCl_3]^{2-}$

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^{1387-7003/\$ -} see front matter @ 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.inoche.2009.03.019



Scheme 1.

anion (2.009 Å) [13], while the P=O distances (1.494(2) and 1.506(9)Å) fall in the normal range for complexes with similar bis(phosphine oxide) ligands, e.g. $[CuCl_2(dppeO_2)]_n$ (P=O: 1.497(2) Å) [15], and $[Cl_3ZnO:(Ph)_2PCH_2CH_2P(Ph)_2:OZnCl_3]^{2-}$ (P=O: 1.520 Å) [13]. The average $P-C(sp^3)$ and $P-C(sp^2)$ distances of 1.804 and 1.792 Å, respectively, in compound 1 compare well to those in $[CuCl_2(dppeO_2)]_n$ (1.809 and 1.797 Å, respectively) [15], but is obviously shorter than that of the non-oxidized bis(tertiaryphosphine) compounds such as $[Hg(CN)_2 \{P(C_6H_5)_2 CH_2\}_2]_n$ (P-C: 1.825(2) Å) [27] or [Cu(dppe)(NO₃)(CH₃CN)]_n (P-C: 1.840(3) Å) [28], indicating that the oxidation of the P atom can influence the P–C bond lengths. Interestingly, the Zn(1)-O(1)-P(1) bond angle in compound 1 (148.8(2)°) is significantly larger than the corresponding P(2)-O(2)-Zn(1) angle $(132.4(1)^{\circ})$, which exactly parallels the behavior previously noted for Co-O-P angles in the two halves of the linear polymer [CoCl₂{O:(Ph)₂PCH₂CH₂-

P(Ph)₂:O}]_{*n*} (147.8(4)° and 138.7(4)°, respectively) [26] and the cyclic dimer [CoCl₂{O:(Ph)₂PCH₂CH₂P(Ph)₂:O}]₂ (148.0(2)° and 138.9(2)°, respectively) [19]. This has been attributed to the orientation of the phenyl rings relative to the Znl₂ units [26]. The bridging dppeO₂ ligands preserve their *anti*-conformation of the oxygen donor atoms, while in the chelating mode they should adopt the *syn* conformation. The corresponding dihedral angle between $O=P-C\cdots C-P=O$ planes is 0° (due to the crystallographically imposed symmetry) for the antiparallel (anti) alignments of the P=O groups in complex **1**.

IR spectrum of **1** shows a distinct absorption at 1148 cm⁻¹ due to the P=O stretching, which is particularly affected by the coordination, as the frequency is significantly red-shifted with respect to the free ligand ($\nu_{P=O} = 1180 \text{ cm}^{-1}$) [29]. This agrees fairly well with the coordination of the phosphoryl oxygen atom to zinc, and has also been observed previously for other coordinated phosphine oxides [29–31].

The fluorescence properties of the ligand and complex **1** have been studied. Free dppeO₂ molecule in the solid state displayed an emission band centered at about 375 nm when excited at 294 nm, while compound **1** showed an emission at 374 nm and two weak, broad emission peaks at around 477 nm and 510 nm, respectively, upon excitation at 332 nm (Fig. 2). The peak at 374 nm can be assigned to the intraligand fluorescent emission. Since no emission bands for the dppeO₂ ligand were observed in the region 450–550 nm, the longer wavelength fluorescence bands of **1** may be ascribed to the ligand-to-metal charge transfer (LMCT) between Zn(II) centers and dppeO₂ upon formation of the coordination polymer [32,33].



Fig. 1. (a) The one-dimensional chain of **1**; (b) Packing diagram of **1** showing the parallel chains in the *bc* plane. Selected bond lengths (Å) and bond angles (°): Zn1–O1 1.958(2), Zn1–O2 1.964(2), C26–C26a 1.534(5), O1–P1 1.494(2), O2–P2 1.506(9), Zn1–I1 2.582(4), Zn1–I2 2.556(4), C7–P1 1.805(3), C26–P2 1.804(3), O1–Zn1–O2 100.6(9), O1–Zn1–I2 108.9(7), O2–Zn1–I2 109.8(6), O1–Zn1–I1 110.3(7), O2–Zn1–I1 106.9(6), I2–Zn1–I1 118.5(6), P1–O1–Zn1 148.8(5), P2–O2–Zn1 132.4(2), O1–P1–C7 112.9(3), O2–P2–C26 111.9(2). Symmetry transformation used to generate equivalent atoms: -x + 1, -y + 2, -z + 1.



Fig. 2. Solid-state emission spectra of the ligand \mbox{dppeO}_2 and compound 1 at room temperature.

In conclusion, we report a novel metal-organic coordination polymer of Zn(II) with the bis(phosphine oxide) ligand dppeO₂. The compound features a 1D concavo-convex chain where the dppeO₂ ligand coordinates in the bridging bidentate fashion. The solid-state fluorescence of the polymer has been investigated, which showed a ligand-based emission along with two weak bands of the LMCT process.

Acknowledgement

This work was supported by the "Bairen Jihua" program of Chinese Academy of Sciences.

Appendix A. Supplementary material

CCDC 725492 contains 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.inoche.2009.03.019.

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- [24] Coordination polymer 1 was synthesized by layering an aqueous ethanolic solution (5 ml) of Znl₂ (23.9 mg, 0.075 mmol) over a solution of ligand dppeO₂ (30 mg, 0.075 mmol) in 5 ml dichloromethane. After a couple of days, X-ray quality single crystals of 1 were obtained (35 mg, 62.2%). M.p. > 300 °C. Anal. calc. for C₂₆H₂₄I₂O₂P₂Zn: C, 41.66; H, 3.23, found: C, 42.02, H, 3.10. FT-IR (KBr, cm⁻¹): 3052 w, 2901 w, 1482 m, 1434 s, 1399 m, 1311 w, 1275 w, 1180 m, 1159 m, 1148 s, 1114 m, 1099 s, 1069 m, 997 m, 880 m, 727 s, 690 s, 513 s, 474 s.
- [25] Crystal data for 1: $C_{26}H_{24}I_2O_2P_2Zn$ (749.56), Crystal system: triclinic, Space group $P\bar{1}$, $a = 8.9254(5)^\circ$, $b = 11.7200(8)^\circ$, $c = 15.182(1)^\circ$, $\alpha = 69.243(3)^\circ$, $\beta = 88.554(3)^\circ$, $\gamma = 73.663(3)^\circ$, V = 1420.2(2)Å³, Z = 2, $D_{calc} = 1.753$ g cm⁻³, $F(0 \ 0 \ 0) = 724$, $\mu = 3.171$ mm⁻¹, T = 293(2) K, 8753 reflections collected, 6065 independent ($R_{int} = 0.0116$), $R_1 = 0.0255$, $wR_2 = 0.0706$ [$I > 2\sigma(I)$]. Diffraction data were collected on a Bruker SMART APEX II diffractometer with graphitemonochromated Mo K α radiation ($\lambda = 0.71073$ Å). An empirical absorption correction using SADABS [34] was applied for the data. The structures were solved by direct methods using the SHELXS-97 program [35]. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares on P^2 by the use of the program SHELXL-97 [35], and hydrogen atoms were included in idealized positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached.
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