Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Molecular Structure 796 (2006) 114–118

Journal of MOLECULAR STRUCTURE

www.elsevier.com/locate/molstruc

Delineating the principles controlling polymer formation and topology in zinc(II)- and cadmium(II)-dithiophosphate adducts of diimine-type ligands

Chian Sing Lai [a], Edward R.T. Tiekink [b,*]

[a] *Department of Chemistry, National University of Singapore, Singapore, Singapore 117543*
[b] *Department of Chemistry, The University of Texas at San Antonio, One UTSA Circle, San Antonio, TX 78249-0698, USA*

Received 25 January 2006; received in revised form 23 February 2006; accepted 4 March 2006
Available online 27 April 2006

Abstract

The crystal structure determination of polymeric $[Cd(S_2P(OCy)_2)_2(3\text{-}NC_5H_4C(H){=}NN{=}C(H)C_5H_4N\text{-}3)\cdot(CHCl_3)_2]_\infty$, where Cy is cyclohexyl and the bridging ligand is 3-pyridinealdazine, shows that the cadmium atom exists within a *trans*-N_2S_4 donor set and that the resultant polymer topology is of a step-ladder. It is argued that this is the expected structure for the compound as it concurs with the structure of the related iso-propyl derivative. Indeed, in most cases polymer topology in related cadmium dithiophosphate systems is controlled by the nature of the bridging diimine-type ligand. By contrast, in the analogous zinc dithiophosphate adducts, controlling polymer topology is possible by systematically varying the steric profile of the dithiophosphate-bound R groups, a phenomenon ascribed to the fact that in the zinc system, the zinc–ligand distances being shorter, bring all the components of the structure in close proximity and thereby exacerbates steric effects. An overview of our accomplishments in this area 'crystal engineering of coordination polymers' is presented herein.

Keywords: Cadmium; Zinc; Dithiophosphate; Dipyridyl-type ligands; Crystal and molecular structure; Polymer formation; Polymer topology

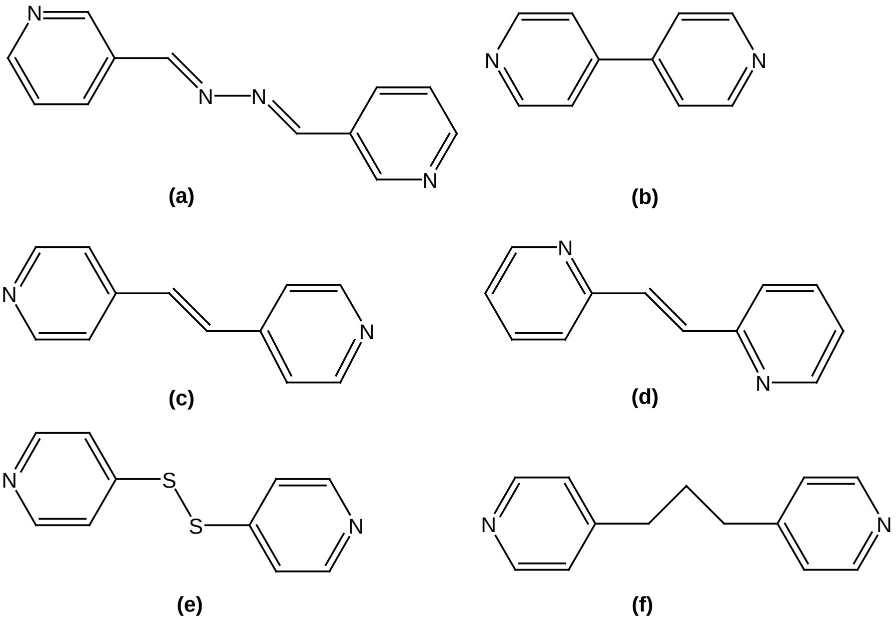
1. Introduction

There are now a relatively large number of zinc(II)- and cadmium(II)-dithiophosphate adducts with potentially bridging dipyridyl-type ligands in the literature [1–9]. The formation, e.g. monomeric, dimeric and polymeric, and topology, when polymers are formed, of these adducts are varied, e.g. straight chain, zig-zag, step-ladder, etc. Up to recently, there has been no concerted nor systematic study directed towards ascertaining the principles of (i) polymer formation, and (ii) once formed, polymer topology in these and related 1,1-dithiolate systems. Here, we report the X-ray crystal structure determination of a new polymeric structure for a cadmium(II) dithiophosphate adduct, isolated as its di-chloroform solvate, with the 3-pyridinealdazine ligand, namely that of $[Cd(S_2P(OCy)_2)_2(3\text{-}NC_5H_4C(H){=}NN{=}C(H)C_5H_4N\text{-}3)\cdot(CHCl_3)_2]_\infty$, where Cy is cyclohexyl and see Scheme 1(a) for the chemical structure 3-pyridinealdazine. This structure adopts, as expected, a step-ladder chain motif as reported very recently for the iso-propyl (i-Pr) derivative [9]; this species was unsolvated. It is claimed that the structure is as expected, or even as predicted, as the combined steric requirements of the dithiophosphate-bound organic substituents and the bridging ligand, allow for the adoption of this configuration. This assertion arises as a principle dictating control of supramolecular aggregation has emerged from our systematic studies of main group element systems that relates to the influence exerted by ligand- and metal-bound substituents [10–13]. Put simply, when smaller substituents are present, supramolecular association is allowed and polymer motifs are formed. By contrast, more sterically demanding substituents preclude supramolecular aggregation and may lead to the isolation of mono- or di-nuclear aggregates instead [3,8]. Further, in favourable circumstances, the steric effects alluded to above can indeed direct polymer topology [3,10]. Gratifyingly, this principle of steric control of supramolecular aggregation is not restricted to the aforementioned zinc(II)- and cadmium(II)-dithiophosphate adducts, but has been invoked with great success to rationalise crystalline architectures of binary zinc-triad 1,1-dithiolates [14] (e.g. xanthates, (^-S_2COR) dithiocarbamates ($^-S_2CNR_2$) and dithiophosphates), organotin

---

* Corresponding author. Tel.: +1 210 458 5774; fax: +1 210 458 7428.
E-mail address: edward.tiekink@utsa.edu (E.R.T. Tiekink).

0022-2860/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2006.03.036



Scheme 1.

carboxylates [15,16], antimony(III) dithiocarbamates [17], and more recently, organometallic phosphorus-group 1,1-dithiolates [18]. In addition, and related to the present study, our recent work has focussed upon determining the principles of polymer formation and, when formed, polymer topology of zinc(II) and cadmium(II) dithiophosphate adducts of dipyridyl-type ligands (Scheme 1) [3–5,8,9]. An extension of this study is reported herein, with the crystal structure determination of a new species, $[Cd(S_2P(OCy)_2)_2(3\text{-}NC_5H_4C(H){=}C(H)C_5H_4N\text{-}3)]_\infty$, and an evaluation of the progress made, thus far, with the rationalising of the observed aggregation patterns in these systems.

2. Experimental

2.1. Synthesis

The adduct, $[Cd(S_2P(OCy)_2)_2(3\text{-}NC_5H_4C(H){=}NN{=}C(H)C_5H_4N\text{-}3)\cdot(CHCl_3)_2]_\infty$, was prepared using a literature method [9]. Thus, the $Cd(S_2P(OCy)_2)_2$ compound was prepared in high yield from the in situ reaction of $Cd(SO_4)\cdot H_2O$ (Aldrich) and the ammonium dithiophosphate (Cheminova) in aqueous solution. The adduct was obtained from refluxing (2 h) the parent cadmium compound (0.2 g) with a 1:1 stoichiometric amount of the 3-pyridinealdazine ligand (Aldrich) in $CHCl_3$ solution. After reaction, the solvent was removed in vacuo and the residue recrystallised by slow evaporation from chloroform/acetonitrile (3/1) solution of the compound to yield crystals suitable for the X-ray study. The compound was isolated as its di-chloroform solvate (Figs. 1 and 2).

2.2. Crystallography

Intensity data were measured at 223 K on a Bruker SMART CCD employing Mo Kα radiation so that $\theta_{max} = 30.0°$. The structure was solved by heavy-atom methods [19] and refinement (anisotropic displacement parameters, hydrogen atoms in the riding model approximation and a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (0.066P)^2 + 0.292P]$ for $P = (F_o^2 + 2F_c^2)/3$) was on F^2 [20]. Data manipulation was with teXsan [21] and the crystallographic diagram, Fig. 3, was drawn using ORTEP-II [22] at the 50% probability level; all remaining diagrams were drawn with DIAMOND [23] with arbitrary spheres. The residual electron density peak of 1.01 e Å^{-3} was located 0.88 Å from the cadmium atom. The refinement converged to final R [for 6025 reflections with $I > 2\sigma(I)$] = 0.046 and $wR = 0.119$ (all 7148 data). *Crystal data.* $C_{38}H_{56}CdCl_6N_4O_4P_2S_4$, $M = 1148.15$, triclinic, space group $P{-}1$, $a = 9.3811(6)$, $b = 11.8334(7)$, $c = 13.0174(8)$ Å, $\alpha = 113.721(1)$, $\beta = 105.738(1)$, $\gamma = 93.088(1)°$, $V = 1251.41(13)$ Å^3, $Z = 1$, $D_c = 1.524$ g/cm^3, $\mu = 1.029$ mm^{-1}, $F(000) = 588$.

CCDC 292950 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

3. Results

The coordination geometry for the cadmium atom in $[Cd(S_2P(OCy)_2)_2(3\text{-}NC_5H_4C(H){=}NN{=}C(H)C_5H_4N\text{-}3)\cdot(CHCl_3)_2]_\infty$ is shown in Fig. 3 and selected bond distances and angles are included in Table 1. The cadmium atom is situated on a crystallographic centre of inversion, at ½ ½ ½, and is coordinated in a *trans*-N_2S_4 donor set. The 3-pyridinealdazine is also disposed about a centre of inversion, located at 1 1 ½. The dithiophosphate ligand coordinates the cadmium centre forming essentially equivalent Cd–S bond distances, as they differ by only 0.021 Å; the equivalence extends to the associated P–S bond distances, as expected. The greatest