

[1] D. Braga, F. Grepioni, *Chem. Soc. Rev.* **2000**, 29, 229-238. [2] P. Seiler, J. Dunitz, *Acta Cryst.* **1979**, B35, 2020-2032. [3] P. Seiler, J. Dunitz, *Acta Cryst.* **1982**, B38, 1741-1745. [4] G.M. Sheldrick, SHELXL-97 – A program for Crystal Structure Refinement, University of Goettingen, Germany, 1997.

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A thallium intermediate compound trapped in a crystal and its SCSC evolution

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The identification and isolation of intermediate compounds are of importance in chemistry for understanding reaction mechanisms, and because of their special reactivities and sometimes for their special bonding or structural characteristics. However, the isolation of these species is in general rare due to their exceptional chemical reactivity and/or lower thermodynamic stability in relation to other species.

We present the identification of a CoTl compound (**1**) which is an intermediate in the formation of a heterometallic CoTl polymer with bridging acetates (**2**). Compound **1**, which is also a polymer, has been trapped as a minor species in crystals of the CoTl coordination polymer (**2**) and evolves to (**2**) when heated.

The crystal structures of the compounds and their evolution when heated have been studied using the same single crystal for all measurements. The Tl atoms are bonded to oxygen from the carboxylate groups in both polymers. The carboxylate groups are also bonded to the cobalt centers, thus acting as bridges between the Tl and the Co. However, both metals (Co and Tl) are ligated by the same oxygen atom [O(1)] in compound **1**, Fig. 1, while in compound **2**, the metals are bonded to different oxygen atoms of the carboxylate group, [O(1), O(2)], Fig. 2.

When heated, the Tl atom in compound **1** moves away from O(1) [from 2.798(3) Å to 3.044(3) Å] and gets closer to O(2) [from 3.348(3) Å to 2.735(3) Å], Fig. 3, thereby changing the nature of the bridge acetate between Co and Tl.

There are few heterometallic compounds of Co and Tl and in the only carboxylate derivative to have been characterized structurally, the carboxylate group bridges only Co atoms[1]. The thallium atom in the intermediate compound (**1**) is three coordinated, with a nearly planar geometry around the thallium center, quite distinct from the usual pyramidal geometry found for three-coordinate Tl(I).

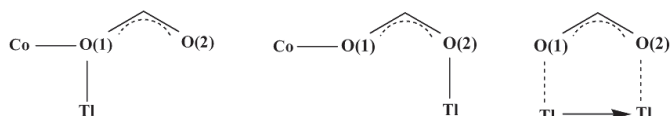


Fig. 1

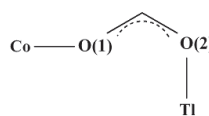


Fig. 2

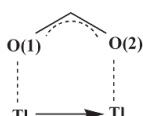


Fig. 3

[1] T.J. Mizoguchi, J. Kuzelka, B. Spingler, J.L. Dubois, R.M. Davydov, B. Hedman, K.O. Hodgson, S.J. Lippard, *Inorganic Chemistry* **2001**, 40, 4662-4673

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Di- and Tetranuclear Zinc(II)-complexes of a new ditopic-hydrazone ligand

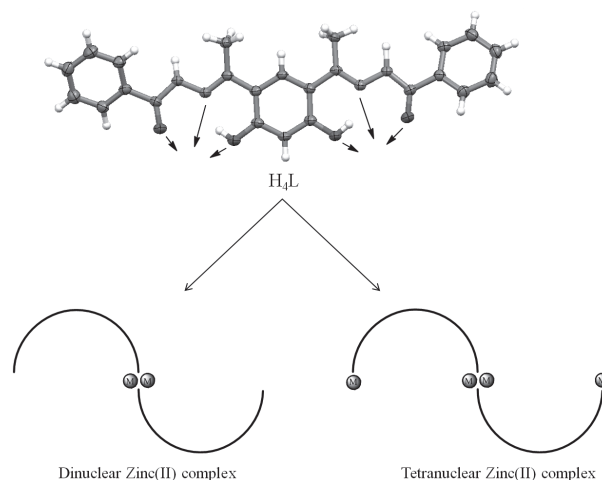
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Coordination chemistry of polytopic-hydrazone ligands is an interesting area of research [1]. These kind of organic compounds are useful to coordinate more than one metal center into $[n \times n]$ grid complexes [1, 2] or polymeric structures [3]. Moreover, magnetic and/or optical and structural properties are in continuous investigation [4].

Herein, we report the synthesis and structural characterization of a new ditopic hydrazone ligand, **H₄L**, a dinuclear zinc(II)-complex **1** ($[\text{Zn}(\text{H}_2\text{L})(\text{dmsO})_2]$) and a tetranuclear one, **2**, ($[\text{Zn}_2(\text{L})(\text{dmsO})_3]_2 \cdot 2\text{dmsO}$) (Scheme 1). Both compounds were obtained by reaction of equimolar amounts of zinc(II) acetate and **H₄L** using conventional and solvothermal mediated reactions, respectively. Formation of an hydrolyzed-ligand-zinc-complex was also obtained ($[\text{Zn}(\text{HL}^*)(\text{H}_2\text{O})_2](\text{dmf})$, **3**) when an excess of zinc(II) nitrate was used.

Ligand **H₄L** contains two ONO-binding pockets capable of coordinate one or two metal ions. This structural versatility has been shown in complexes **1** and **2**. Free and coordinated pockets co-exist together in the dinuclear complex **1** and all the pockets are occupied in complex **2**.

In addition, oxygen atom of the hydroxyl group bridges two metal centers forming a Zn_2O_2 diamond core.



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[1] L.N. Dawe, K.V. Shuvaev, L.K. Thompson, *Chem. Soc. Rev.* **2009**, 38, 2334-2359. [2] Y.S. Moroz, L. Szyrwił, S. Demeshko, H. Kozłowski, F. Meyer, I. Fritsky, *Inorg. Chem.* **2010**, 49, 4750-4752. [3] S. Sen, C.R. Choudhury, P. Talukder, S. Mitra, M. Westerhausen, A.N. Kneifel, C. Desplanches, N. Daro, J.-P. Sutter, *Polyhedron* **2006**, 25, 1271-1278. [4] A. R. Stefankiewicz, G. Rogez, J. Harrowfield, M. Drillon, J. Lehn, *Dalton Trans.* **2009**, 29, 5787-5802.

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