Solid State Sciences 12 (2010) 795–802

Contents lists available at ScienceDirect

Solid State Sciences

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

Thiazolo[5,4-d]thiazole-2,5-dicarboxylic acid, $C_6H_2N_2O_4S_2$, and its coordination polymers

Alessia Aprea, Valentina Colombo, Simona Galli*, Norberto Masciocchi, Angelo Maspero*, Giovanni Palmisano

Dipartimento di Scienze Chimiche e Ambientali, Università dell'Insubria, via Valleggio 11, I-22100 Como, Italy

ARTICLE INFO

Article history:
Received 17 December 2009
Received in revised form
25 January 2010
Accepted 3 February 2010
Available online 11 February 2010

Keywords:
Coordination polymers
Powder diffraction
Thermal analysis
Crystal structure

ABSTRACT

Thiazolo[5,4-d]thiazole-2,5-dicarboxylic acid, $C_6H_2N_2O_4S_2$, was isolated as a polycrystalline material, and its crystal structure was determined by *ab-initio* X-ray powder diffraction (XRPD) methods. This species, upon deprotonation, was subsequently used in preparing the new coordination polymers $Ag_2(C_6N_2O_4S_2)$, $Mn(C_6N_2O_4S_2)(H_2O)_2$, $Co(C_6N_2O_4S_2)(H_2O)_2$, $Cu(C_6N_2O_4S_2)(H_2O)$ and $Zn(C_6N_2O_4S_2)(H_2O)_2$, fully characterized by analytical, thermal and XRPD structural methods – including *in situ* thermodiffractometry and simultaneous TGA and DSC. In the first-row transition metal derivatives, the $[C_6N_2O_4S_2]^{2-}$ anion systematically prefers the *N,O*-chelating, *vs.* the expected *O,O'*-bridging, coordination mode, not allowing the formation of porous 3D frameworks. Indeed, these species are dense 1D coordination polymers. At variance, the silver derivative possesses a complex, dense 3D framework, due to the presence of μ_6-$[C_6N_2O_4S_2]^{2-}$ ligands showing two μ_2-bridging carboxylates and two monohapto *N*-donor sites. When dehydration is viable, materials of $E_n(C_6N_2O_4S_2)$ formulation are irreversibly recovered ($n = 1$ for E = Mn, Co, Zn, Cu; $n = 2$, for E = H).

1. Introduction

In the last years, coordination polymers and metal-organic frameworks have been widely studied, and the number of new species belonging to these categories has impressively risen [1]. This is largely due to the extreme versatility of their chemistry: simple changes of metal ions, organic ligands, reactants stoichiometry and reaction conditions can lead to compounds differing in metal coordination geometry, framework topology, solvent trapping, thermal stability, polymorphic behavior and overall structural flexibility. Within this large list of chemically and structurally characterized species, some have shown very interesting functional aspects, ranging from catalytic [2], adsorptive [3], magnetic [4] and optical [5], to dielectric [6] and even antimicrobial [7] properties. These results have pushed many groups toward the preparation of novel systems, hopefully benefiting from the introduction of suitably tailored ligands in their crystalline frameworks.

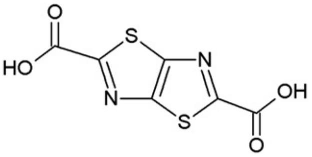
The main structural method for studying these materials is, and will remain, the conventional X-ray single-crystal diffraction technique which, however, must rely on not always available single-crystals of suitable size and quality. To overcome this problem, X-ray powder diffraction (XRPD) methods and suitably designed neutron and synchrotron radiation diffraction techniques have recently found vast diffusion and implementation, disclosing important structural features which would have otherwise remained inaccessible [8].

In the last decade, we have been interested in the rich structural chemistry of functional materials, putting particular emphasis on porous coordination polymers (PCP's) capable to selectively adsorb gases, liquids or ionic pairs under the appropriate conditions [9]. We have thus investigated manifold PCP's in which transition metal ions are bridged by geometrically stiff ligands possessing strong Lewis base capacity and high thermal stability. After having employed aromatic systems bearing negatively charged tetrazolyl [10], pyrazolyl [11] and *N*-aromatic oxo fragments [12], we have driven our attention to a *N,S*-heteroaromatic molecule, the thiazolo[5,4-d]thiazole-2,5-dicarboxylic acid, $C_6H_2N_2O_4S_2$ (**1**, see Scheme 1). Indeed, upon deprotonation, **1** affords the $[C_6N_2O_4S_2]^{2-}$ anion, a polydentate ligand which could behave as a long-spacer between transition metal ions, as recently demonstrated in the case of its alkaline earth coordination polymers [13]. In its bishydrated form, **1·2H₂O**, this ligand was initially isolated and studied *per se*, sagaciously combining analytical and structural techniques (TG, DSC, XRPD and

---

* Corresponding authors. Fax: +39 31 23866230.
E-mail addresses: simona.galli@uninsubria.it (S. Galli), angelo.maspero@uninsubria.it (A. Maspero).

1293-2558/$ – see front matter © 2010 Elsevier Masson SAS. All rights reserved.
doi:10.1016/j.solidstatesciences.2010.02.016



Scheme 1. Molecular connectivity of the $C_6H_2N_2O_4S_2$ species.

thermodiffractometry). Subsequently, **1** was coupled to first- and second-row transition metal ions, aiming at the formation of new PCP's. Of the many metal ions tested, only Ag(I), Mn(II), Co(II), Zn(II) and Cu(II) yielded analytically pure and polycrystalline coordination polymers, *i.e.* $Ag_2(C_6N_2O_4S_2)$, **2**, $Mn(C_6N_2O_4S_2)(H_2O)_2$, **3**, $Co(C_6N_2O_4S_2)(H_2O)_2$, **4**, $Zn(C_6N_2O_4S_2)(H_2O)_2$, **5** and $Cu(C_6N_2O_4S_2)(H_2O)$, **6**. As later shown, none of the prepared materials is adequate for gas adsorption. This behavior has been *ex post* explained by the tendency of the $[C_6N_2O_4S_2]^{2-}$ dianion to coordinate with the *N*,*O*-chelating [14], *vs.* the *O*,*O*′-bridging, mode, the latter being ubiquitous in polycarboxyarene ligands of highly porous, and chemically inert, 3D frameworks [15].

In the following, the preparation and the main structural features of **1** and of its transition metal derivatives **2–6**, derived by the less conventional *ab-initio* powder diffraction technique, are reported and discussed, including an extensive thermodiffractometric characterization.

2. Results and discussion

2.1. Synthesis and spectroscopy

The thiazolo[5,4-d]thiazole-2,5-dicarboxylic acid, **1**, has been reacted with several metallic salts. With the Ag(I), Mn(II), Co(II), Cu(II) and Zn(II) ions, microcrystalline species were isolated [16]. The reaction conditions required by **1** deserve a few comments. Due to its very limited solubility in many common solvents, all the reactions were carried out dissolving it in DMSO. **1** is also known to possess a limited thermal stability, as it may decarboxylate at low temperature [17]; thus, the reaction mixtures were initially kept at only 40 °C. Only at a later stage, *i.e.* after metal complexation occurred, the reaction vessels were heated further. Notably, the intrinsic acidity of the metal ions (assisted, in a few cases, by the presence of acetate groups) allowed ligand deprotonation and coordination polymers formation without the necessity of adding external bases.

The infrared spectra of complexes **3–6** are quite similar: their main features are a broad band at about 3190 cm^{-1}, attributed to the O–H stretching of the water molecules present in the crystal lattices, and a sharp band at about 1673 cm^{-1}, attributed to the C═O stretching of the carboxylate groups; if compared to that found in the free ligand (1746 cm^{-1}), this band is remarkably red shifted, due to the coordination to the metal ions (adopting, as later found by XRPD, a *N*,*O*-chelating mode). In the infrared spectrum of complex **2**, the C═O stretching determines a sharp band at even lower wavenumbers (1612 cm^{-1}), which is consistent with the significantly different ligand coordination mode in the silver derivative with respect to species **3–6** (*vide infra*). In agreement with the analytical and structural results, in the IR of **2** no O–H stretching mode of coordinated or hosted water molecules is observed.

2.2. Crystal structure of $C_6H_2N_2O_4S_2\cdot 2H_2O$, $\mathbf{1\cdot 2H_2O}$

The crystal structure of this species, shown in Fig. 1, is monoclinic, $P2_1/c$, and contains $C_6H_2N_2O_4S_2$ moieties (located on inversion centres) and water molecules, interacting with the organic species by evident hydrogen bonds (see caption to Fig. 1). As far as the organic $C_6H_2N_2O_4S_2$ moiety is concerned, the freely refined torsion angle of the carboxylic residue slightly deviates from planarity [6.8(3)°, *syn*-S–C–C–O sequence], thus maintaining a largely delocalized π-system. Hydrogen atoms cannot be detected by XRPD. Yet, given the observed coordination geometry, we propose that the acidic proton on the organic acid resides on the carboxylic oxygen O1; the two hydrogen atoms of the water molecule interact with the remaining basic sites with slightly longer distances. Taking into account the hydrogen bond interactions, the overall connectivity is three-dimensional. Moreover, as expected for thia-aromatic moieties with markedly flat shapes, significant S···S contacts are present (3.42–3.48 Å), which, in similar systems, have been associated with interesting electronic conduction processes [18]. For comparison, the strictly related molecule 2,5-di-2-thienylthiazolo[4,5-*d*]thiazole [19] shows intermolecular S···S contacts of 3.58 Å and a twist of the aromatic rings of 1.69(8)°, comparable to the values found in $\mathbf{1\cdot 2H_2O}$.

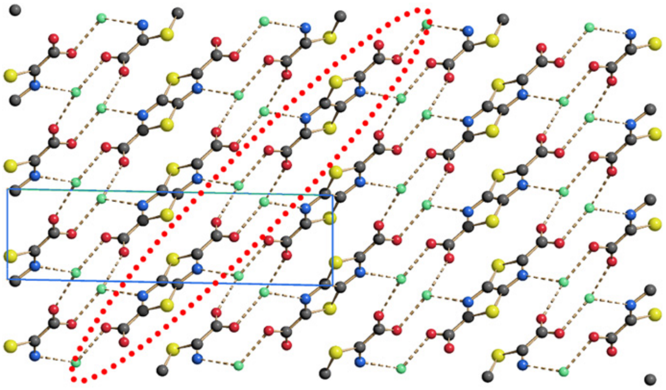


Fig. 1. Crystal structure of $C_6H_2N_2O_4S_2\cdot 2H_2O$, $\mathbf{1\cdot 2H_2O}$, viewed down **b**. Horizontal axis, **c**; vertical axis, **a**. Carbon, grey; nitrogen, blue; carboxylic oxygen, red; water oxygen, light green; sulfur, yellow. Hydrogen bonds are drawn as fragmented lines. The red ellipse highlights the molecular ribbons described in the text. Relevant intermolecular distances: Ow···O1 2.58(1), Ow···O2 2.73(1), Ow···N1 3.03(2) Å.

2.3. Crystal structure of $Ag_2(C_6N_2O_4S_2)$, **2**

This species crystallizes in the monoclinic $P2_1/n$ space group. The asymmetric unit features one crystallographically independent Ag(I) ion and half $C_6N_2O_4S_2$ moiety, the whole ligand being located on an inversion centre (see Fig. 2). Each silver ion is coordinated to five different atoms: a rather distorted digonal coordination [Ag–O1 2.241(7) Å, Ag–O2 2.268(6) Å and O1–Ag–O2 135.8(5)°] is completed by three ancillary longer interactions (Ag–N1 2.54 Å, Ag–O2′ 3.04 Å and Ag–S1 2.88 Å). This rich connectivity generates a rather dense three-dimensional polymer, with no cavities capable of hosting water (or other small) molecules. The tendency of Ag(I) ions to afford dense structures with polytopic aza-aromatic systems has already been observed for the $Ag_2(btb)$ species (H_2btb = 1,4-bis(5-tetrazolyl)benzene), in which each metal ion is tetracoordinated and the btb fragment behaves as a rare μ_8-ligand [10]. Whether in the present case a μ_4- or a higher connectivity for the dicarboxylate anion is present, it depends on the distance cut-off set for the long Ag–X interactions. As in $\mathbf{1\cdot 2H_2O}$, also in **2** the COO^- groups are only slightly rotated off the average molecular plane of the organic ligand, by a mere 1.7(6)° [*syn*-S–C–C–O sequence]. Interestingly, and at variance with $\mathbf{1\cdot 2H_2O}$, no S···S contacts are present in **2**.