Thiodipropionate Zn(II) complexes: Synthesis, DFT studies and X-ray structure of [Zn(phen)(H2O)2(μ-tdp)2]*3H2O

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Thiodipropionate Zn(II) complexes: Synthesis, DFT studies and X-ray structure of [{Zn(phen)(H₂O)}₂(μ-tdp)₂]·3H₂O

Abdessamad Grirrane,[a] Eleuterio Álvarez,[b] Antonio Pastor,*[a] and Agustín Galindo*[a]

Abstract. The zinc thiodipropionate complex [Zn(tdp)] (**1**) (tdp = $S(CH_2CH_2COO)_2^{2-}$) was obtained through reaction of aqueous zinc dichloride with 1:1 mixture of Na_2CO_3 and thiodipropionic acid. The bonding preferences of the tdp anion were studied by DFT methods. The reaction of **1** with *o*-phenanthroline (phen) gave the binuclear compound [{Zn(phen)(H₂O)}₂(μ-tdp)₂]·3H₂O (**2**), which was characterised by X-ray analysis.

Introduction

Thiodicarboxylic acids are interesting ligands due to their capacity to coordinate to metal centres through both carboxylate groups and the sulphur atom. Continuing our line of investigation into applications of the thiodiacetate ligand [1], we planned to explore the coordinating properties of the higher homologue of thiodiacetic acid, thiodipropionic acid $S(CH_2CH_2COOH)_2$, as investigations of structures containing the thiodipropionate ligand (tdp) are comparatively less extensive than those of the thiodiacetate [2]. Additionally, the tiodipropionate anion is more flexible than the thiodiacetate, possibly allowing the formation of novel topologies. Only a few examples of compounds containing tdp [3] or the hydrogenthiodipropionate anion has been X-ray characterised [4], although several structures are known for the parent thiodipropionic acid [5].

Results and Discussion

Synthesis and characterisation

Through reaction of aqueous zinc dichloride with a 1:1 mixture of Na_2CO_3 and thiodipropionic acid colourless crystals of [Zn(tdp)] (**1**) were obtained. Analytical and IR data were consistent with the proposed formula. Absence of water in the complex is confirmed by the absence of the O-H absorption in the IR spectrum and by analytical data. A very strong and broad absorption band at 1538 cm⁻¹, corresponding to the antisymmetric vibrations of the carboxylate groups, confirmed the presence of tdp coordinated to the Zn^{2+} through the O atoms [6].

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The reaction of **1** with *o*-phenanthroline gives the new complex [{Zn(phen)(H₂O)}₂(μ-tdp)₂]·3H₂O (**2**). The crystal structure of **2** was determined by X-ray diffraction (Fig. 1).
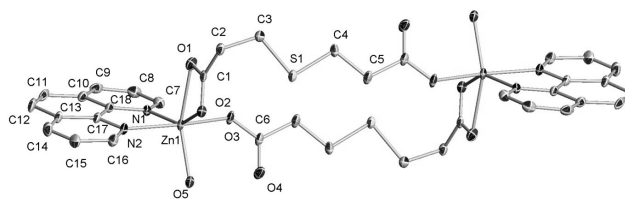

Fig. 1. ORTEP view of the dinuclear Zn(II) complex **2**. The displacement ellipsoids are drawn at a 50 % probability level.

The asymmetric unit contains one half of the dimeric complex, the other half being related by an inversion centre. The Zn atoms are each in a distorted octahedral coordination sphere defined by two N atoms of the phen ligand, three O atoms from the two carboxylate anions and the O atom of a water molecule *trans* to the O atom of the bidentate carboxylate group. Each thiodipropionate anion bridges the two Zn^{2+} ions in a different coordination mode. One terminal carboxylate group binds in a bidentate mode through two O atoms, whilst the other is bonded to the metal centre through just one O atom. This bonding mode is similar to that observed in polymeric related complex [Zn(tdp)(bipy)·(H₂O)]ₙ [3]. The Zn-O(carboxylate) bond lengths fall in the region 2.048-2.272 Å, and the Zn-N bond distances are 2.110(3) and 2.162(3) Å respectively. These distances are comparable to those found in [Zn(tdp)(bipy)·(H₂O)]ₙ [3], where the Zn-O (tdp) lengths are in the region 2.042-2.214 Å and the Zn-N distances are 2.112(2) and 2.198(2) Å. In the Zn-tdp-bipy compound and in complex **2** the thiodipropionate acts as bridge between the Zn atoms with the same coordination mode μ_2-$\kappa^2(O,O')$-$\kappa^1(O'')$. However, the formation of a binuclear compound in **2** or a polymeric complex in [Zn(tdp)(bipy)·(H₂O)]ₙ [3] is almost certainly due to the presence of water molecules of solvation in the former and the existence of π-stacking in the latter (see Supporting Information). Other selected structural parameters are collected in Table 1. In the crystal structure, the aqua ligand

forms an intermolecular hydrogen bond with the uncoordinated carboxylate oxygen atom (O4···O5 length 2.618(4) Å). Complex **2** is isostructural to the related adipate Zn compound [7].

Table 1. Selected bond distances (Å) and angles (°) for compound **2**

Zn(1)-O(3)	2.048(3)	N(1)-Zn(1)-N(2)	77.86(12)
Zn(1)-O(5)	2.063(3)	O(3)-Zn(1)-O(2)	97.75(11)
Zn(1)-N(1)	2.110(3)	O(5)-Zn(1)-O(2)	94.31(11)
Zn(1)-N(2)	2.162(3)	N(1)-Zn(1)-O(2)	150.05(11)
Zn(1)-O(2)	2.187(3)	N(2)-Zn(1)-O(2)	89.69(11)
Zn(1)-O(1)	2.272(3)	O(3)-Zn(1)-O(1)	83.28(11)
O(1)-C(1)	1.253(5)	O(5)-Zn(1)-O(1)	151.34(11)
O(2)-C(1)	1.273(5)	N(1)-Zn(1)-O(1)	95.28(11)
O(3)-C(6)	1.280(4)	N(2)-Zn(1)-O(1)	96.79(11)
O(4)-C(6)	1.241(5)	O(2)-Zn(1)-O(1)	58.88(10)
Zn(1)-C(1)	2.566(4)	O(3)-Zn(1)-C(1)	89.20(12)
O(3)-Zn(1)-O(5)	91.35(11)	O(5)-Zn(1)-C(1)	123.08(12)
O(3)-Zn(1)-N(1)	93.43(12)	N(1)-Zn(1)-C(1)	123.60(12)
O(5)-Zn(1)-N(1)	113.17(12)	N(2)-Zn(1)-C(1)	95.11(11)
O(3)-Zn(1)-N(2)	171.27(12)	O(2)-Zn(1)-C(1)	29.72(11)

Theoretical calculations

Due to the paucity of structural data for thiodipropionate compounds of transition metals [8], we decided to explore theoretically the bonding preferences of this ligand using the DFT approach. The first approach was to select the simplest neutral fragment [Zn(tdp)] and to optimize, without symmetry restrictions, the two models **I** and **II**, schematically depicted in Scheme 1. Model **I** displays the thiodipropionate ligand coordinated in $\kappa^3(O,S,O')$-fashion, which is the usual coordination mode for related thiodiacetate mononuclear compounds [1], with both carboxylate groups κ^1-bonded to the metal. In model **II** the thiodipropionate group is again tricoordinated, but now the sulphur atom is not bonded to the metal, while the two carboxylate moieties are κ^2 and κ^1 coordinated to zinc.

Scheme 1. Models of [Zn(tdp)] theoretically studied.

Fig. 2 shows the resulting optimised structures. Coordination of the sulphur atom to the Zn metal, moving from model **II** to **I**, is an exergonic process of -3.7 kcal·mol^{-1}. This low value suggests that such coordination is probably not essential in this type of compounds. If the sulphur atom is not bonded, the coordination of both carboxylates to different metal centres should be favoured over coordination to a single one. Confirmation of this assumption is provided by pimalate compounds (analogous to thiodipropionate with the S atom substituted for CH$_2$). In all structurally characterised pimalate complexes of transition metals each carboxylate group is bonded to a different metal centre [8].
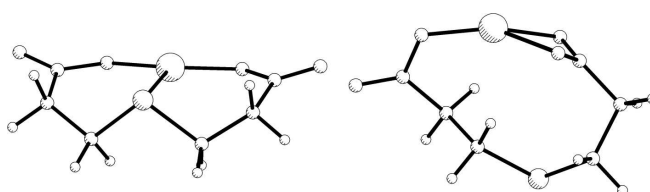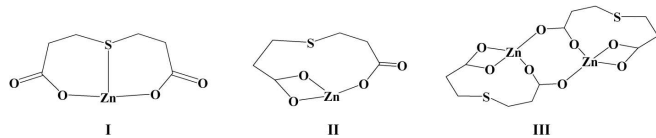

Fig. 2. Optimised structures of models **I-II**.

To confirm the preferentiality of the coordination mode we extended the DFT calculations to a third model, **III** (see Scheme 1), in which the thiodipropionate bridges two zinc ions. It is actually a binuclear species [Zn(tdp)]$_2$ where one carboxylate group is κ^2-bonded to a Zn atom, with the other carboxylate acting as bridge in a syn,anti-μ_2-$\kappa^1(O),\kappa^1(O')$ coordination. Fig. 3 shows the optimised structure. From an energetic point of view, the dimerisation process from **II** to **III** is clearly favourable because the conversion is very exergonic (-72.4 kcal·mol^{-1}). Consequently, the coordination of tdp as a bridge is evidently favoured over tricoordination to a single metal. This indicates that thiodipropionate most likely behaves as a bridge ligand in compound **1**, the compound probably being polymeric in nature [Zn(tdp)]$_n$.
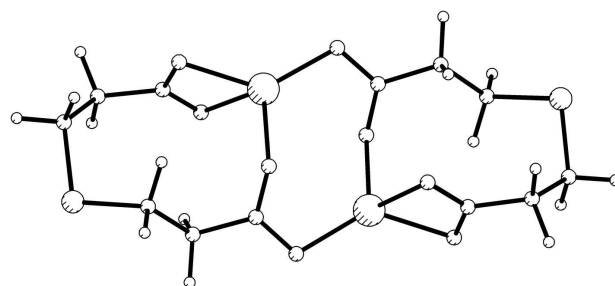

Fig. 3. Optimised structure of model **III**.

Compound **1** is soluble in water and it is probable that a hydrate species exists when in solution. For this reason two other model compounds were considered, [Zn(tdp)(H$_2$O)$_3$] **IV** and [{Zn(H$_2$O)$_3$}$_2$(μ-tdp)$_2$] **V**. Both compounds were optimised, without symmetry restrictions and the resulting structures are shown in Fig. 4. It was again calculated that the dimerisation reaction from **IV** to **V** is an exergonic process of -32.7 kcal·mol^{-1}. Therefore, the bridging nature of tdp is evidently favoured over $\kappa^3(O,S,O')$ tricoordination to a single metal and **V** is probably the solution structure of **1**.

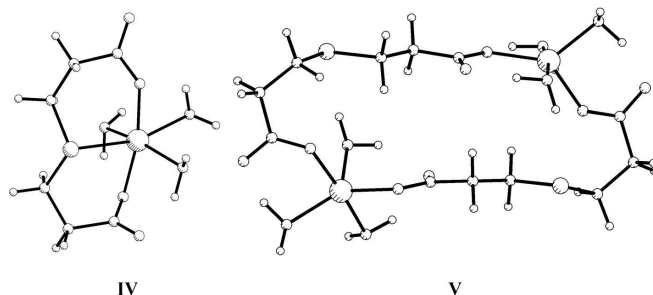Fig. 4. Optimised structures of [Zn(tdp)(H$_2$O)$_3$] **IV** and [{Zn(H$_2$O)$_3$}$_2$(μ-tdp)$_2$] **V**.

Experimental Section

General

All preparations and other operations were carried out under aerobic conditions. Thiodipropionic acid and other chemicals were obtained from commercial sources and were used without further purification. Infrared spectra were recorded on Perkin-Elmer Model 883 spectrophotometer (KBr pellets). [1]H spectra were run on Bruker AMX-300 spectrometer. Microanalyses (C, H, N) were performed on an Elemental LECO CHNS 93 analyzer by the "Servicios Generales de Investigación" (CITIUS) of the University of Sevilla.

Synthesis of [Zn(tdp)] (1)

To a solution of $S(CH_2CH_2COOH)_2$ (0.53 g, 3 mmol) in water (15 ml) Na_2CO_3 (0.32 g, 3 mmol) was added and the mixture stirred until evolution of CO_2 ceased. This was then mixed with $ZnCl_2$ (0.41 g, 3 mmol) dissolved in water (15 ml), the resulting solution stirred for 10 minutes. Acetone was added and the solution was kept at room temperature overnight. Colourless crystals of **1** formed, which were filtered off, washed with acetone and diethyl ether and air dried (0.55 g, 75 % yield). IR (cm^{-1}): 1538 s, 1451 s, 1413 s, 1327 m, 1316 m, 1211 m, 1167 w, 1063 w, 955 m, 785 s, 742 m, 698 s, 576 w, 512 w. ^{1}H NMR (300 MHz, D_2O): δ 2.59 (t, $^3J_{HH}$ = 7.2 Hz, CH_2), 2.30 (t, $^3J_{HH}$ = 7.2 Hz, CH_2). Elemental analysis for $C_6H_8O_4SZn$ (Mw = 241.4): calcd. C, 29.82; H, 3.31; found C, 29.87; H, 3.20 %.

Synthesis of [{Zn(phen)(H₂O)}₂(μ-tdp)₂]·3H₂O (2)

A solution of *o*-phen·H_2O (0.099 g, 0.5 mmol) in 10 ml of water was added to a suspension of **1** (0.121 g, 0.5 mmol) in 20 ml of water. The mixture was heated at 80 ºC for 1 h, then concentrated to about 20 ml. Slow evaporation of the solvent resulted in the formation of colourless crystals of [{Zn(phen)(H₂O)}₂(μ-tdp)₂]·3H₂O (**2**), which were collected by filtration, washed with water, acetone and diethyl ether and dried in air (0.160 g, 68 %). IR (cm^{-1}): 3461-3033 v br, 1574 s, 1518 m, 1453 w, 1403 s, 1308 s, 1280 w, 1222 w, 1207 m, 1185 m, 1136 m, 1101 m, 1060 w, 1020 w, 970 w, 877 m, 868 m, 846 s, 783 w, 725 s, 698 m, 672 m, 648 m, 539 w, 424 m. ^{1}H NMR (300 MHz, D_2O): δ 8.94, 8.60, 8.57, 8.53, 8.00, 7.97, 7.87, 7.74 (8 H, phen), 2.52 (t, $^3J_{HH}$ = 4 Hz, CH_2), 2.24 (t, $^3J_{HH}$ = 8 Hz, CH_2). Elemental analysis for $C_{18}H_{21}N_2O_{6.5}SZn$ (Mw = 466.8): calcd. C, 46.31; H, 4.53; N, 6.00; found C, 46.37; H, 4.28; N, 5.91 %.

X-ray structural study of 2

A summary of the crystal data of compound **2** is given in Table 2. The X-ray data were collected at 100 K on a Bruker-Nonius X8APEX-II CCD diffractometer equipped with a graphite monochromator and Mo-K$_\alpha$ radiation. The data were reduced [9] and corrected for Lorentz polarisation effects and absorption by multiscan method applied by SADABS [10]. The structure was solved by direct methods (SIR-2002 [11]) and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12 [12]). All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters.

Computational details

The electronic structure and geometries of the model complexes **I-V** were computed within the density functional theory at the B3LYP [13,14] level. The basis set used for all the atoms

was 6-311G**. All the optimised geometries were characterised as local energy minima by diagonalisation of the analytically computed Hessian (vibrational frequencies calculations). The DFT calculations were performed using the Gaussian 98 suite of programs [15]. Cartesian coordinates for the optimised molecules are available from the authors upon request.

Table 2. Crystallographic data for **2**

Empirical formula	$C_{36}H_{42}N_4O_{13}S_2Zn_2$
Formula weight	933.60
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.2136(12) Å
	b = 10.4602(13) Å
	c = 11.7097(15) Å
	α= 66.880(4)°.
	β= 71.629(4)°.
	γ = 72.505(4)°.
Volume	964.6(2) Å^3
Z	1
Density (calculated)	1.607 Mg/m^3
Absorption coefficient	1.423 mm^{-1}
F(000)	482
Crystal size	0.30 x 0.15 x 0.15 mm^3
Theta range (data collection)	2.16 to 30.57°.
Index ranges	-12 ≤ h ≤ 13, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	21743
Independent reflections	5646 [R(int) = 0.0297]
Completeness to theta = 30.57°	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8149 and 0.6748
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5646 / 0 / 262
Goodness-of-fit on F^2	1.071
Final R indices [I>2σ(I)]	R1 = 0.0542, wR2 = 0.1575
R indices (all data)	R1 = 0.0586, wR2 = 0.1600
Largest diff. peak and hole	2.084 and -1.251 e·Å^{-3}

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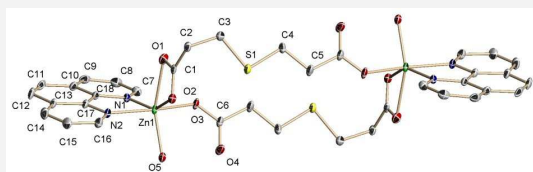
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Agustín Galindo* **…….. Page No. – Page No.**

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Supporting Information

Figure S1. Comparison of the crystal packing of complex **2** and [Zn(tdp)(bipy)·(H$_2$O)]$_n$ [reference 3].