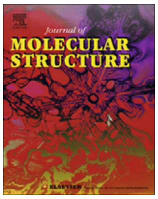
Journal of Molecular Structure 1006 (2011) 684–691

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

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



The new sulphur-containing ligand 4′-(4-methylthiophenyl)-3,2′:6′,3″-terpyridine (**L1**) and the supramolecular structure of the dinuclear complex $[Zn_2(\mu\text{-}\mathbf{L1})(acac)_4]$ (acac = acetylacetonato): The key role of non-covalent S···O contacts and C–H···S hydrogen bonds

Juan Granifo [a,*], Rubén Gaviño [b], Eleonora Freire [c,d,1], Ricardo Baggio [c]

[a] Departamento de Ciencias Químicas y Recursos Naturales, Facultad de Ingeniería, Ciencias y Administración, Universidad de La Frontera, Casilla 54-D, Temuco, Chile
[b] Instituto de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, Circuito Exterior Coyoacán, 04510 México, DF, Mexico
[c] Departamento de Física, Comisión Nacional de Energía Atómica, Av. Gral Paz 1499, 1650 San Martín, Pcia. de Buenos Aires, Argentina
[d] Escuela de Ciencia y Tecnología, Universidad Nacional de San Martín, Buenos Aires, Argentina

ARTICLE INFO

Article history:
Received 21 August 2011
Received in revised form 19 October 2011
Accepted 20 October 2011
Available online 28 October 2011

Keywords:
S···O interactions
C–H···S hydrogen bonds
Zinc(II) complexes
Acetylacetonate
4′-(4-Methylthiophenyl)-3,2′:6′,3″-terpyridine

ABSTRACT

The new terpyridyl ligand 4′-(4-methylthiophenyl)-3,2′:6′,3″-terpyridine (**L1**) combines with $Zn(acac)_2$ to form the dizinc complex $[Zn_2(\mu\text{-}\mathbf{L1})(acac)_4]$ (**1**) (acac = acetylacetonato). The single crystal structure of **1** shows the existence of two different $Zn(acac)_2$ centres bridged by the **L1** ligand through its two 3-pyridyl-nitrogen atoms. The acac and **L1** ligands allow the generation of a series of intra- and intermolecular hydrogen bonds of the C–H···N, C–H···O and C–H···π type. In addition, the presence of the CH_3–S group in **L1** plays a crucial role by providing the non-covalent S···O, S···H and $H(CH_3)$···O contacts, which permit to describe fully this unusual supramolecular network. The NMR spectra of **1** in $CDCl_3$ solution confirm the presence of the two zinc atoms joined by the bridging **L1** ligand, but, differently to the solid state, their environments are identical.

1. Introduction

The study of the coordination chemistry of 2,2′:6′,2″-terpyridine and its derivatives has been ascribed more widely to its action as chelating ligands, i.e., where they present a convergent disposition of its N-pyridyl donor atoms to link the metal centres [1,2]. In contrast, terpyridine-based ligands with the divergent mode able to bridge at least two metal centres are scarse; a few recent examples can be found mainly for functionalized 4,2′:6′,4″-terpyridines [3]. In this regard and only in two recent works, 3,3″ divergent and 4′-functionalized terpyridines [4′-phenyl-3,2′:6′,3″-terpyridine (**L2**, Scheme 1) and 4′-(4-pyridyl)-3,2′:6′,3″-terpyridine] involving the N 3-pyridyl atoms as linkers have been used [4]. More specifically, the reported examples that include one of these ligands are a coordination polymer [4b] and a dinuclear compound [4a]. This last complex, which incorporates the **L2** ligand, was formulated as $[Zn_2(\mu\text{-}\mathbf{L2})(acac)_4]\cdot H_2O$ (acac = acetylacetonato) (**2**). The supramolecular structure of **2** was described on the basis of the key role played by the acac and **L2** ligands and the guest water molecule by using a series of intermolecular hydrogen bonds: either conventional (of the O–H/O type) or non-conventional (C–H/O and CH/π [5,6]) including those CH/π arising between the coordinated acac ligand and phenyl rings, recently proposed by Zarić et al. [7]. Zarić et al. demonstrated that the chelating acac shows two types of interactions, one by using either its CH and/or CH_3 groups (hydrogen bond donor) and the other one involving the π-system of the chelate ring (as a hydrogen bond acceptor). With the aim on going further in the study of the bonding and supramolecular properties of this kind of systems, we replaced the **L2** ligand, with its phenyl ring, by the related **L1** ligand, with a 4-methylthiophenyl group instead (Scheme 1). The result of the reaction of **L1** with $Zn(acac)_2$ was the new dizinc complex $[Zn_2(\mu\text{-}\mathbf{L1})(acac)_4]$ (**1**) with the sulphur atom of the 4-methylthio substituent non-coordinated, but instead it appears involved in the singular non-covalent S···O and S···H interactions.

2. Results and discussion

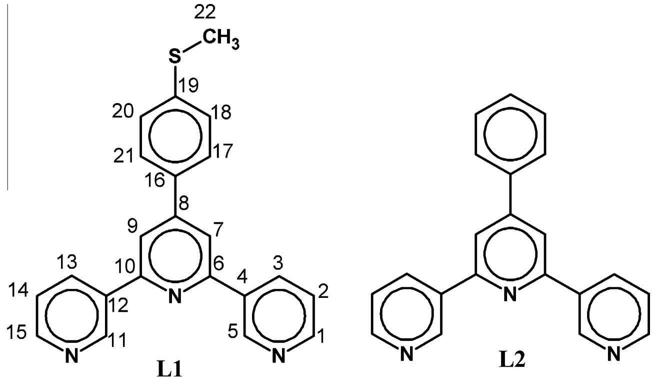
2.1. Synthesis

The **L1** ligand was prepared via the one-step general method by mixing 3-acetylpyridine, 4-(methylthio)benzaldehyde and NH_3 in

---

* Corresponding author.
E-mail address: jgranifo@ufro.cl (J. Granifo).
[1] Member of CONICET.

0022-2860/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2011.10.038



Scheme 1. The sketches of the ligands **L1** and **L2**. For **L1** the numbering of carbon atoms (hydrogen atoms where correspond) is indicated.

a EtOH solution. The newly synthesized ligand was characterized by elemental analysis, ^{1}H, ^{13}C and 2D NMR experiments, mass spectrometry and IR spectroscopy. Complex **1** was prepared by the reaction of an excess of $Zn(acac)_2$ with **L1** in a hot acetonitrile solution, from which colourless blocks suitable for single crystal X-ray analysis were obtained.

*2.2. The NMR spectra of **L1** (performed through COSY, DEPT, PND)*

The NMR results in $CDCl_3$ solution of the **L1** molecule are in good agreement with the expected molecular structure (Scheme 1 and Section 5.1). Thus, the ^{13}C NMR spectrum shows one solitary methyl group (15.13 (C22) ppm) and the corresponding signals of the aromatic region: four due to quaternary carbons [134.00 (C16 superimposed with C4/C12), 140.76 (C19), 149.69 (C8), 155.00 (C6/C10) ppm] and seven due to CH carbons [116.83 (C7/C9), 123.38 (C2/C14), 126.34 (C17/C21), 127.10 (C18/C20), 134.22 (C3/C13), 148.13 (C1/C15), 149.95 (C5/C11) ppm]. Similarly, the ^{1}H NMR is characterized for a high field singlet (2.48 ppm) due to the three protons of the thiomethyl group. The four phenyl protons can be readily distinguished from the other for the characteristic AA′BB′ pattern of H18/H20 (7.30 ppm) and H17/H21 (7.57 ppm). The two protons of the central pyridine ring H7/H9 appear as a sharp singlet (7.79 ppm). Those four protons of the 3-pyridyl groups next to the electronegative N atoms, H5/H11 (9.29 ppm) and H1/H15 (8.63 ppm), together with the two H3/H13 (8.39 ppm) protons, show the largest displacement towards low field. The two remaining protons H2/H14 (7.36 ppm) of the 3-pyridyl rings appear in a predictable manner as a multiplet.

*2.3. Coordination geometry and bonding in **1***

The crystal and molecular structure of **1** was determined by single crystal X-ray diffraction at 273 K and it consists of a bis-monodentate **L1** ligand bridging the Zn1 and Zn2 atoms from two different $\{Zn(acac)_2\}$ fragments, through its 3-pyridyl N atoms (Fig. 1 and Table 1). Even if crystallizing in the non-centrosymmetric space group Cc, the molecular assembly presents a strongly-pseudo twofold rotation axis in a way that the whole symmetry ends up mimicking the C2/c space group; the whole molecular body abides to this pseudo operation, while the terminal $PhSCH_3$ group, which would not possible respond to this C2 operation, appears disordered into two almost equally populated halves (occupancies: higher, 0.532; lower, 0.468), thus complying with the pseudosymmetry. Refinement in the centrosymmetric space group, however, resulted in much higher R indices, for what a constrained refinement in Cc was preferred, and it is the one herein reported.

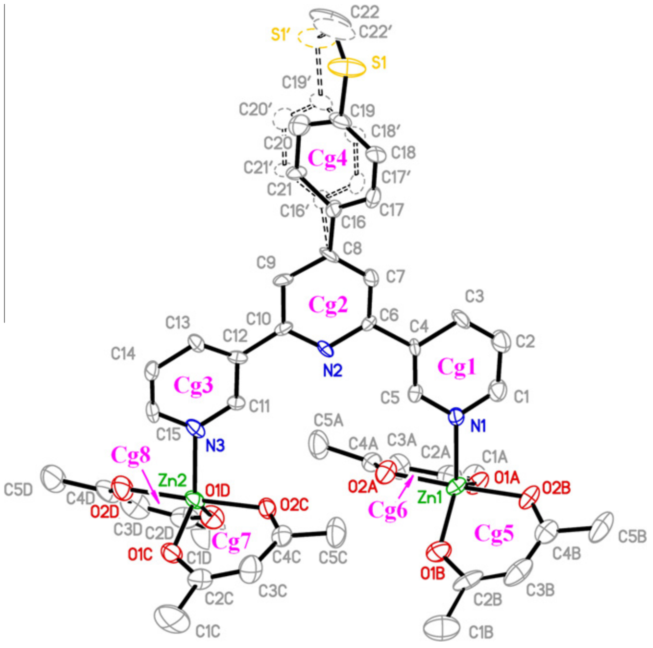


Fig. 1. Molecular diagram of **1**, with anisotropic displacement ellipsoids drawn at a 40% probability level. The disordered $PhSCH_3$ end shown in full/broken lines. H atoms removed, for clarity.

Table 1
Selected bond lengths (Å) and bond angles (°) for **1**.

Bond distances	
Zn1–O1A	1.948(3)
Zn1–O1B	1.986(3)
Zn1–O2A	2.009(4)
Zn1–O2B	2.061(4)
Zn1–N1	2.091(2)
Zn2–O1C	2.010(3)
Zn2–O1D	1.941(3)
Zn2–O2C	2.055(4)
Zn2–O2D	2.067(4)
Zn2–N3	2.099(3)
Bond angles	
O1A–Zn1–O1B	119.19(14)
O1A–Zn1–O2A	90.15(14)
O1B–Zn1–O2A	92.95(15)
O1A–Zn1–O2B	88.97(14)
O1B–Zn1–O2B	89.54(15)
O2A–Zn1–O2B	177.49(14)
O1A–Zn1–N1	112.84(12)
O1B–Zn1–N1	127.96(13)
O2A–Zn1–N1	87.36(13)
O2B–Zn1–N1	90.81(12)
O1C–Zn2–O1D	119.57(14)
O1C–Zn2–O2C	91.43(14)
O1D–Zn2–O2C	91.31(14)
O1C–Zn2–O2D	90.15(15)
O1D–Zn2–O2D	89.09(16)
O2C–Zn2–O2D	177.91(13)
O1C–Zn2–N3	113.27(12)
O1D–Zn2–N3	127.15(13)
O2C–Zn2–N3	88.64(13)
O2D–Zn2–N3	89.49(14)

Each Zn centre (Zn1/Zn2) has a NO_4 coordination sphere; four sites are provided by two different acac groups coordinated in the usual chelating form through their carbonyl O donor, the planar groups subtending to each other angles of 61.6/60.2° for Zn1/Zn2, respectively. The fifth site of the coordination polyhedron is occupied by a 3-pyridyl N atom from the **L1** ligand. The geometry around each Zn atom is an almost perfect trigonal bipyramid, with apical O2A–Zn1–O2B/O2C–Zn2–O2D angles of 177.5/177.9° and the apical bonds deviating by less than 1.9/0.9° from the normal