

Synthesis and structural characterizations of mononuclear zinc complexes with an unprecedented terminal bidentate coordination mode of the flexible 1,1,3,3-tetrakis(3,5-dimethyl-1-pyrazolyl)propane ligand



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ABSTRACT

Four new complexes, $[\text{Zn}(\text{tdmpp})_2\text{H}_2\text{O}](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**), $[\text{Zn}(\text{NCS})\text{Cl}(\text{tdmpp})]$ (**2**), $[\text{ZnI}_2(\text{tdmpp})]$ (**3**) and $[\text{ZnCl}_2(\text{tdmpp})]$ (**4**), were prepared and structurally characterized. The 1,1,3,3-tetrakis(3,5-dimethyl-1-pyrazolyl)propane (tdmpp) ligand in the above compounds represents the first example of a flexible tetradentate nitrogen donor ligand in which the ligand is coordinated to the metal center as a terminal chelating ligand. The perchlorate ion in **1** acts as an uncoordinated anion, while in **2** the SCN and chlorine ligands and in **3** the iodine ligand participate in the coordination sphere of the metal center. The coordination ability of these anions and significant effects of non-covalent C–H \cdots π and C–H \cdots X (X = O, Cl and I) interactions play a major role in the crystal packing of these compounds. In **1**, the zinc atom adopts a distorted trigonal bipyramidal geometry and the $[\text{Zn}(\text{tdmpp})_2\text{H}_2\text{O}]^{2+}$ cations are linked by C–H \cdots O hydrogen bonds to give a 1-D chain structure. In the structures of **2** and **3**, the mononuclear neutral molecules form a 1-D chain structure along the *b*-axis through C–H \cdots Cl and C–H \cdots I hydrogen bonds, respectively. These chains are linked by intermolecular C–H \cdots π interactions to generate a three-dimensional network. Crystals of compound **4** were not suitable for X-ray diffraction studies and therefore its structure could only be investigated in the solid state by infrared spectroscopy and elemental analysis.

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1. Introduction

Structural studies of Zn(II) complexes are of particular interest due to its importance in biological systems [1]. Zn(II) is a borderline acid with versatile coordination properties. It can interact with oxygen, nitrogen and sulfur donor ligands to form coordination compounds in which the most common coordination geometry of zinc is tetrahedral, which is clearly connected with the fact that the octet rule is obeyed in these cases. Nevertheless, five and six-coordinated complexes of zinc(II), comparable to those of the other transition elements, are not rare [2–15]. Zinc coordination compounds such as $\text{Zn}(\text{NR}^1\text{R}^2)_2$ ($\text{R}^1 = \text{CMe}_3$, $\text{R}^2 = \text{SiMe}_3$) with the coordination number of two are rare [16]. In these compounds the steric hindrance of the bulky amide ligands prevent the formation of compounds with a coordination number higher than two. Crystal-engineering studies show that the flexibility and steric

hindrance of the ligands play a significant role in the construction of metal–organic frameworks. Thus, a comparison between the coordination modes of rigid and flexible tetradentate–nitrogen donor ligands can provide valuable information about the differences between these ligands. Rigid tetrakis(pyrazolyl)borate $[\text{pz}^-\text{Tp}^x]^-$ derivatives tend to act only as chelating bidentate or tridentate ligands through the imine nitrogen atoms of the pyrazolyl rings. Coordination of the fourth pyrazolyl ring and formation of polymeric compounds with these ligands have not been reported in the literature so far. This could be due to the fact that there are few or no conformational changes when a rigid ligand is coordinated to a metal ion [17]. In contrast to the $[\text{pz}^-\text{Tp}^x]^-$ anions, the rigid tetratopic 3,3',5,5'-tetra(1H-imidazol-1-yl)-1,1'-biphenyl (L) and 1,2,3,4-tetra-(4-pyridyl)-butane (TPB) ligands are unable to act as chelating agents when they participate in the construction of Zn(II) and Cd(II) coordination polymers [18–20]. In these frameworks, each metal ion is coordinated to two nitrogen atoms from two different ligands. On the other hand, the flexibility of a ligand such as 1,1,3,3-tetrakis(3,5-dimethyl-1-pyrazolyl)propane

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(tdmpp), with an alkyl spacer (Scheme 1), significantly affects the structure of the resultant coordination compounds because the flexibility of the spacer group allows the backbone of the ligand to bend and rotate freely when coordinating to a metal center [21]. This ligand can act either as a terminal bidentate or bridging tetradentate ligand. To the best of our knowledge, there are no examples of a flexible tetradentate nitrogen donor ligand, such as tdmpp, in which the ligand is coordinated to a metal center as a terminal chelating ligand. The absence of mononuclear metal complexes of the tdmpp ligand in the literature in which a single metal ion is coordinated to all four donor atoms of the ligand could be due to the flexibility and steric requirements of the ligand, which increases its tendency to form coordination compounds with different coordination architectures [22,23]. The object of this study is to design and synthesise coordination compounds of Zn(II) containing the tdmpp ligand in order to obtain complexes with an unprecedented terminal bidentate coordination mode of this ligand. All the synthesized compounds have been structurally characterized by X-ray crystallography, infrared spectroscopy and elemental analysis.

2. Experimental

2.1. Materials and physical measurements

All experiments were carried out in air. The starting materials were purchased from commercial sources and used without further purification. Tdmpp was prepared by the published method [21]. The infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded from KBr discs with a Bomem MB-102 FT-IR spectrometer. The elemental analyses for C, H and N were performed on a Thermo-Finnigan Flash EA 1112 CHNS analyzer.

2.2. Synthesis of $[\text{Zn}(\text{tdmpp})_2\text{H}_2\text{O}](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (1)

$\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.062 g, 1 mmol) was dissolved in methanol (20 mL). After stirring for ca. 5 min. at room temperature, tdmpp (0.14 g, 2 mmol) was added to this solution and the resulting solution was stirred for a further 4 h, then filtered. Colorless crystals of **1** were obtained from the freshly made sample in the reaction solvent by the slow evaporation method over a period of two days. Yield: 0.094 g (50% based on Zn). *Anal. Calc.* for $\text{C}_{46}\text{H}_{64}\text{Cl}_2\text{N}_{16}\text{O}_{10}\text{Zn}$: C, 48.53; H, 5.63; N, 19.69. Found: C, 48.11; H, 5.59; N, 19.42%. Selected IR ($\text{KBr}, \text{cm}^{-1}$): 2923(m), 3129 (m), 1557(s), 1463(m), 1420(m), 1391(m), 1250(m), 1096(s), 967(m), 885(m), 805(m), 624(s), 568(m).

2.3. Synthesis of $[\text{Zn}(\text{NCS})\text{Cl}(\text{tdmpp})]$ (2)

ZnCl_2 (0.051 g, 1 mmol) was added to a methanol solution (30 mL) of KSCN (0.072 g, 2 mmol) and the mixture was heated under reflux for 30 min. The resulting colorless mixture was cooled to room temperature and then tdmpp (0.15 g, 1 mmol) was added into the mixture, which was stirred for 4 h and filtered. This compound was crystallized from the methanol solution in a manner similar to that for **1**. Yield: 0.11 g, (54% based on Zn). *Anal. Calc.* for $\text{C}_{24}\text{H}_{34}\text{ClN}_8\text{OSZn}$: C, 48.24; H, 5.73; N, 21.09. Found: C, 48.17; H, 5.40; N, 20.40%. Selected IR ($\text{KBr}, \text{cm}^{-1}$): 2923(m), 3129(m), 2073(s), 1558(s), 1467(m), 1344(m), 1312(m), 1286(m), 1241(m), 1196(m), 1048(m), 958(m), 803(m), 707(m), 565(m).

2.4. Synthesis of $[\text{ZnI}_2(\text{tdmpp})]$ (3)

A methanol solution (10 mL) of tdmpp (0.15 g, 1 mmol) was slowly added to an aqueous solution (10 mL) of ZnI_2 (0.11 g, 1 mmol) in a test tube. Colorless crystals suitable for X-ray crystallography were obtained after one week. Yield: 0.15 g, (61% based on Zn). *Anal. Calc.* (%) for $\text{C}_{23}\text{H}_{32}\text{I}_2\text{N}_8\text{Zn}$: C, 37.34; H, 4.36; N, 15.14. Found: C, 37.57; H, 3.90; N, 14.77%. Selected IR ($\text{KBr}, \text{cm}^{-1}$): 2922(m), 3129(m), 1558(s), 1460(m), 1415(m), 1319(m), 1286(m), 1042(m), 958(m), 816(m), 688(m).

2.5. Preparation of $[\text{ZnCl}_2(\text{tdmpp})]$ (4)

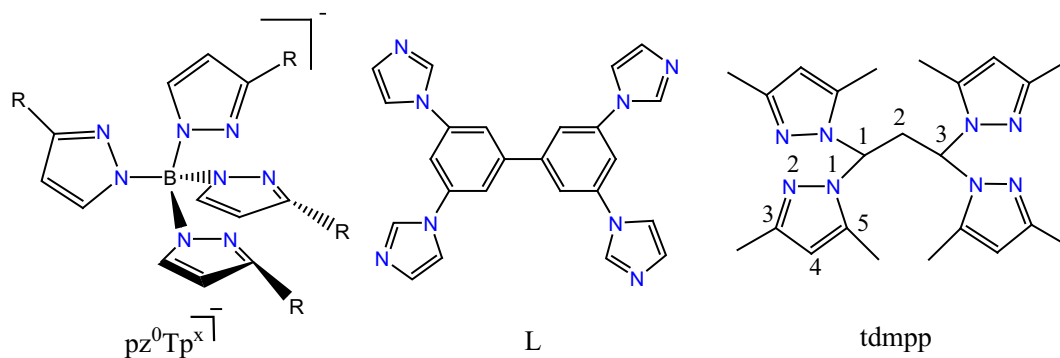
ZnCl_2 (0.014 g; 0.10 mmol) was dissolved in water (10 mL) and slowly added to a methanolic solution (10 mL) of tdmpp (0.044 g; 0.10 mmol) and stirred at room temperature for 8 h. The colorless crystalline precipitate of $[\text{Zn}(\text{tdmpp})\text{Cl}_2]$ (**4**) was filtered off and dried in air (0.06 g, 57% based on Zn). Attempts to obtain single crystals of this compound were not successful. *Anal. Calc.* for $\text{C}_{23}\text{H}_{32}\text{Cl}_2\text{N}_8\text{Zn}$: C, 49.60; H, 5.79; N, 20.12. Found: C, 49.26; H, 5.51; N, 19.80%. IR data (cm^{-1}): 3125(m), 2923(m), 1558(s), 1466(m), 1345(m), 1313(m), 1285(m), 1043(m), 959(m), 810 (m), 709(m).

2.5.1. Caution

Perchlorate compounds are potentially explosive and should be handled with care.

2.6. X-ray crystallography

The crystallographic data for the three compounds were collected at room temperature with a Bruker APEX II CCD area-detector diffractometer using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$).



L = 3,3',5,5'-tetra(1H-imidazol-1-yl)-1,1'-biphenyl

Scheme 1.

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