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Initial employment of pyridine-2-amidoxime in zinc(II) chemistry: Synthetic, structural and spectroscopic studies of mononuclear and dinuclear complexes

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ABSTRACT

The first employment of pyridine-2-amidoxime [(py)C(NH_2)NOH] in zinc(II) chemistry is reported. The syntheses, crystal structures, and spectroscopic characterization are described for complexes [Zn(O_2CR)$_2${(py)C(NH_2)NOH}$_2$] (R = Me; **1**, Ph; **2**), [Zn_2(acac)$_2${(py)C(NH_2)NO}$_2$] (**3**), and [Zn(NO_3){(py)C(NH_2)NOH}$_2$](NO_3) (**4**). The reactions between Zn(O_2CR)$_2$·$2H_2O$ (R = Me, Ph) or Zn(NO_3)$_2$·$5H_2O$ and two equivalents of (py)C(NH_2)NOH in MeOH led to mononuclear compounds **1**, **2** and **4**, respectively. All three complexes contain two neutral *N*,*N'*-chelating (η^2) (py)C(NH_2)NOH ligands, coordinated through the N_{pyridyl} and N_{oxime} atoms. In contrast, the use of Zn(acac)$_2$·H_2O in place of Zn(O_2CR)$_2$·$2H_2O$ gives the dinuclear compound **3**, which instead contains the anionic, η^1:η^1:η^1:μ bridging form of the organic ligand; the Zn^{II} atoms are doubly bridged by the diatomic oximate groups of the (py)C(NH_2)NO^- groups. Strong intra- and intermolecular hydrogen bonding interactions provide appreciable thermodynamic stability and interesting supramolecular chemistry for compounds **1**–**4**. The photoluminescence properties of complexes **1**–**4** recorded in the solid state at room temperature are also presented.

1. Introduction

The last two decades have witnessed an explosive growth of the interest in dinuclear and polynuclear complexes of 3d metals at moderate oxidation states with primarily oxygen- and/or nitrogen-based ligation [1–4]. In contrast to the paramagnetic 3d-metal ions, the analogous chemistry of diamagnetic Zn^{II} complexes with O- and/or N-based ligands is less developed. Mono-, di-, oligo- and polynuclear Zn^{II} complexes are being studied as polymerization catalysts, precursors to ZnO-based materials, models of active sites in zinc enzymes and molecular materials with interesting optical properties [5]. The synthetic methodology [6,7] and the nature of the organic ligands [8–14] are key issues for the preparation of such complexes [8–14].

A modern synthetic trend is the employment of two or even three ligands in the reaction systems (combination of ligands or "ligand blends"). The loss of a degree of the synthetic control [6] is more than compensated for by the vast diversity of structural types using the combination of ligands. Carboxylates (RCO_2^-), inorganic anions (e.g., NO_3^-, SO_4^{2-}, halides and pseudohalides) and/or β-diketonates ($RCOCHCOR^-$) are excellent ancillary terminal or/and bridging groups in 3d-metal chemistry when they are combined with suitable organic ligands (generally denoted as "L") [2,6,15]. Thus, we and others have been exploring various such binary (i.e., L/RCO_2^-, L/NO_3^-, L/$RCOCHCOR^-$) reaction schemes as potentially new routes to molecular species with unprecedented structural motifs.

As far as the nature of L is concerned, our group and others have had a longstanding interest in the reactivity of oxime ligands for the synthesis of mono-, oligo- and polynuclear 3d transition metal complexes [8b,12,16,17]. The monoanions of simple 2-pyridyl oximes, (py)C(R)NOH (R = H, Me, Ph, etc., i.e., a non-coordinating group; Fig. 1), are excellent sources of homo- and heterometallic complexes with beautiful structures and interesting physical properties. A logical extension of such studies is the investigation of the coordination chemistry of analogous organic molecules in which the non-donor R group is replaced by a donor group (i.e., pyridine, cyano, etc.; Fig. 1). When R is the amino group, the resulting ligand is pyridine-2-amidoxime (IUPAC name: *N*-hydroxy-pyridine-2-carboxamidine), (py)C(NH_2)NOH (Fig. 1), which belongs to the class of amidoximes. The presence of the amine functionality is expected to alter the coordination behaviour of this ligand (and hence the

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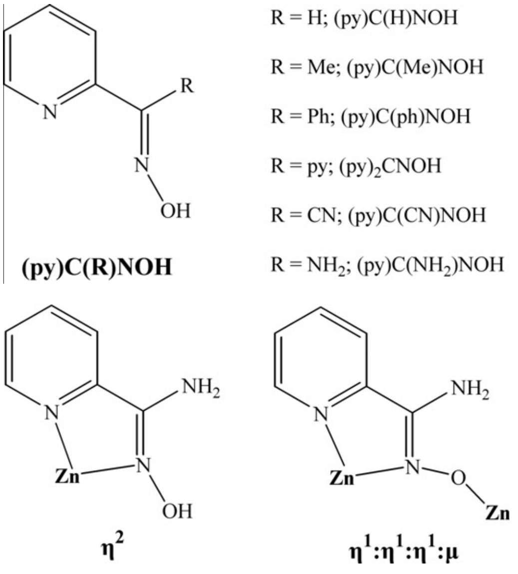

Fig. 1. General structural formula and abbreviations of simple 2-pyridyl oximes (top), including pyridine-2-amidoxime [(py)C(NH_2)NOH], and the crystallographically established coordination modes of the ligand's neutral [(py)C(NH_2)NOH] and anionic [(py)C(NH_2)NO^-] forms in complexes **1**–**4** (bottom left and right, respectively).

identity of the resultant metal complexes) in comparison with that of the (py)C(R)NOH (R = H, Me, Ph, etc.) ligands. Characteristics that differentiate the amino group are its coordination capability, potential for deprotonation, different electronic properties and hydrogen bonding effects.

In the present work, we report the first use of (py)C(NH_2)NOH in Zn(II) coordination chemistry by describing the syntheses, structures and spectroscopic characterization of three mononuclear compounds, featuring the neutral form of the ligand, and a dinuclear complex bearing the monoanion (py)C(NH_2)NO^-.

2. Experimental

2.1. General and physical measurements

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received. The free ligand (py)C(NH_2)NOH was synthesized according to the literature method [18]. $Zn(O_2CPh)_2\cdot 2H_2O$ was prepared as a white microcrystalline solid by the 1:2 reaction of $ZnSO_4\cdot 7H_2O$ and NaO_2CPh in H_2O.

Elemental analyses (C, H, N) were performed by the University of Ioannina (Greece) Microanalytical Laboratory using an EA 1108 Carlo Erba analyser. IR spectra (4000–450 cm^{-1}) were recorded on a Perkin-Elmer 16 PC FT spectrometer with samples prepared as KBr pellets; the spectra were also recorded as Nujol and hexachlorobutadiene mulls between CsI discs. Emission and excitation spectra were recorded using a Cary Eclipse spectrofluorometer.

2.2. Compound preparation

2.2.1. *[Zn(O_2CMe)$_2${(py)C(NH_2)NOH}$_2$]·2MeOH (**1**·2MeOH)*

To a colourless solution of $Zn(O_2CMe)_2\cdot 2H_2O$ (0.11 g, 0.50 mmol) in MeOH (10 mL) was slowly added a solution of (py)C(NH_2)NOH (0.14 g, 1.00 mmol) in the same solvent (10 mL). The resulting colourless solution was kept under stirring at room temperature for about 30 min, filtered, and the filtrate was layered with Et_2O (40 mL). Slow mixing gave after 4 days well-formed, X-ray quality colourless prismatic crystals of **1**·2MeOH. The crystals were collected by filtration, washed with cold MeOH (2× 3 mL) and Et_2O (2× 5 mL), and dried in air. Typical yields were in the 40–50% range. The air-dried solid was analyzed as solvent-free **1**. *Anal.* Calc. for $C_{16}H_{20}ZnN_6O_6$: C, 42.0; H, 4.4; N, 18.4. Found: C, 42.2; H, 4.5; N, 18.3%. IR data (KBr pellet, cm^{-1}): ν = 3430mb, 3198m, 1782w, 1676m, 1598m, 1552s, 1508m, 1408vs, 1340w, 1300w, 1262w, 1172w, 1098w, 1032m, 962w, 916w, 852w, 790m, 746m, 662m, 480w.

2.2.2. *[Zn(O_2CPh)$_2${(py)C(NH_2)NOH}$_2$]·0.5H_2O (**2**·0.5H_2O)*

To a colourless solution of $Zn(O_2CPh)_2\cdot 2H_2O$ (0.34 g, 1.00 mmol) in MeOH (20 mL) was slowly added a solution of (py)C(NH_2)NOH (0.28 g, 2.00 mmol) in the same solvent (20 mL). The resulting white slurry was refluxed for 1 h, during which time all solids dissolved and the colour of the solution turned to pale yellow. The latter solution was then allowed to slowly concentrate by solvent evaporation at room temperature for a period of 3–4 days. Well-formed colourless prismatic crystals of **2**·0.5H_2O appeared that were collected by filtration, washed with cold MeOH (2× 3 mL) and Et_2O (2× 5 mL), and dried in air. Typical yields were in the 75–80% range. The air-dried solid was analyzed as solvent-free **2**. *Anal.* Calc. for $C_{26}H_{24}ZnN_6O_6$: C, 53.7; H, 4.2; N, 14.4. Found: C, 53.5; H, 4.0; N, 14.6%. IR data (KBr pellet, cm^{-1}): ν = 3464mb, 3310m, 3182m, 3062m, 2712mb, 1678s, 1596s, 1534vs, 1444w, 1398vs, 1304m, 1178m, 1098m, 1024s, 872w, 830m, 790m, 746m, 722s, 674s, 634w, 470w.

2.2.3. *[Zn_2(acac)$_2${(py)C(NH_2)NO}$_2$] (**3**)*

To a colourless solution of $Zn(acac)_2\cdot H_2O$ (0.26 g, 1.00 mmol) in MeOH (10 mL) was slowly added a solution of (py)C(NH_2)NOH (0.14 g, 1.00 mmol) in the same solvent (10 mL). The resulting pale yellow solution was kept under stirring at room temperature for about 30 min, filtered, and the filtrate was layered with Et_2O (40 mL). Slow mixing gave after 10 days well-formed, X-ray quality yellow prismatic crystals of **3**. The crystals were collected by filtration, washed with cold MeOH (2× 3 mL) and Et_2O (2× 5 mL), and dried in air. Typical yields were in the 80–85% range. *Anal.* Calc. for $C_{22}H_{26}Zn_2N_6O_6$: C, 44.0; H, 4.4; N, 14.0. Found: C, 44.1; H, 4.6; N, 13.9%. IR data (KBr pellet, cm^{-1}): ν = 3280m, 3244m, 3078m, 2918m, 1634vs, 1600vs, 1556s, 1516vs, 1484m, 1446s, 1394vs, 1294m, 1260m, 1192w, 1174w, 1156m, 1098m, 1032s, 1020vs, 922s, 896w, 842w, 796m, 764m, 750m, 696m, 666w, 644m, 570w, 548m, 518m, 475w.

2.2.4. *[Zn(NO_3){(py)C(NH_2)NOH}$_2$](NO_3) (**4**)*

To a colourless solution of $Zn(NO_3)_2\cdot 4H_2O$ (0.13 g, 0.50 mmol) in MeOH (10 mL) was slowly added a solution of (py)C(NH_2)NOH (0.14 g, 1.00 mmol) in the same solvent (10 mL). The resulting colourless solution was kept under stirring at room temperature for about 30 min, filtered, and the filtrate was layered with Et_2O (40 mL). Slow mixing gave after 2 days well-formed, X-ray quality colourless prismatic crystals of **4**. The crystals were collected by filtration, washed with cold MeOH (2× 3 mL) and Et_2O (2× 5 mL), and dried in air. Typical yields were in the 70–75% range. *Anal.* Calc. for $C_{12}H_{14}ZnN_8O_8$: C, 31.1; H, 3.0; N, 24.2. Found: C, 31.2; H, 3.2; N, 24.1%. IR data (KBr pellet, cm^{-1}): ν = 3434mb, 3370m, 3314m, 3200m, 3086m, 2796m, 1674vs, 1608s, 1492m, 1448m, 1382vs, 1326vs, 1174m, 1090m, 1026s, 1006m, 834m, 794m, 744w, 680m, 642w, 570w, 502m.

2.3. Single-crystal X-ray crystallography

The crystallographic data and structure refinement details for the four complexes are summarized in Table 1. Selected prismatic colourless crystals of **1**·2MeOH, **2**·0.5H_2O and **4**, and a yellow prismatic crystal of **3** were mounted in air. Diffraction measurements for all four complexes were performed on a Crystal Logic Dual