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Note

Binuclear copper and zinc complexes based on polypyridyl ligand 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz): Synthesis, spectral and structural characterization

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ABSTRACT

The reaction of $MCl_2 \cdot 2H_2O$ (M = Cu, Zn) with 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz) (referred hereafter as L) in 2:1 molar ratio in acetonitrile at room temperature afforded binuclear complexes $[M_2(\kappa^3\text{-L})Cl_4]$ [Cu (**1**), Zn (**2**)] where the ligand is bis-tridentate manner. The complexes have been characterized by elemental analyses, FAB-MS, IR, EPR, NMR and electronic spectral studies. Solid state structures of both the $[Cu_2(\kappa^3\text{-L})Cl_4] \cdot 5H_2O$ (**1**), $[Zn_2(\kappa^3\text{-L})Cl_4] \cdot H_2O$ (**2**) have been determined by single crystal X-ray analyses. A well-resolved uudd cyclic water tetramer and water monomer were reported in the crystal host of $[Cu_2(\kappa^3\text{-L})Cl_4] \cdot 5H_2O$ (**1**) and $[Zn_2(\kappa^3\text{-L})Cl_4] \cdot H_2O$ (**2**) showing the contribution of the water cluster to the stability of the crystal host **1** and **2**.

1. Introduction

The design of binuclear metal complexes incorporating suitable bridging ligands which lead to the formation of stable mixed valence states has attracted considerable research interest in recent years [1]. This has been primarily due to their relevance for biological processes, molecular electronics and for theoretical studies of electron transfer kinetics [2]. Since the discovery of the pyrazine-mediated strong intermetallic coupling in the Creutz–Taube complex [3,4], polyazine-based heterocyclic bridging ligands capable of mediating intermetallic electronic communication through the π-symmetry orbitals have been investigated [5–9]. 2,3,5,6-Tetrakis(2-pyridyl)pyrazine (tppz) was first reported in 1959 by Goodwin and Lions [10], has been found to be a suitable mediator for intermetallic coupling almost of the order of the Creutz–Taube ion [9]. The coordination modes of tppz ligand toward metal ions has shown its great versatility as bidentate [11], terdentate [12], bis-bidentate [11a,13], tris-bidentate [11a] and bis-terdentate [9f,9g,12a,12f,14].

In 1989 Escuer et al. first reported a hexafluoroacetylacetonate binuclear copper complex of tppz $[Cu_2(tppz)(hfacac)_4]$ (hfacac = hexafluoroacetylacetonate) [15]. Ruminski et al. have synthesized and characterized mono and bimetallic Ru(II) [9a], Rh(II) [16] and Fe(II) [17] complexes of tppz. However, structurally characterized complexes of binuclear copper and mononuclear zinc containing tppz in bis-tridentate were reported by Stoeckli-Evans and coworkers [12a]. The ability of tppz ligand to mediate magnetic interactions between paramagnetic centers separated by more than 6.4 Å in the tppz-bridged metal complexes has renewed the interest in this ligand [12f,12g]. More recently, structural and magnetic studies on tppz-bridged metal complexes have been reported [12f,12h,12i,12j].

Because of our interests in polypyridyl ligands [18] we have examined reactivity of 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz) with Cu(II), and Zn(II) salts. We describe herein the synthesis, spectral and structural characterization of five-coordinate binuclear copper $[Cu_2(\kappa^3\text{-L})Cl_4] \cdot 5H_2O$ (**1**), and zinc $[Zn_2(\kappa^3\text{-L})Cl_4] \cdot H_2O$ (**2**) complexes containing 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz) ligand.

2. Results and discussion

2.1. Syntheses

Reactions of $MCl_2 \cdot 2H_2O$ (M = Cu, Zn) with L in acetonitrile in 2:1 molar ratio with stirring at room temperature gave the neutral

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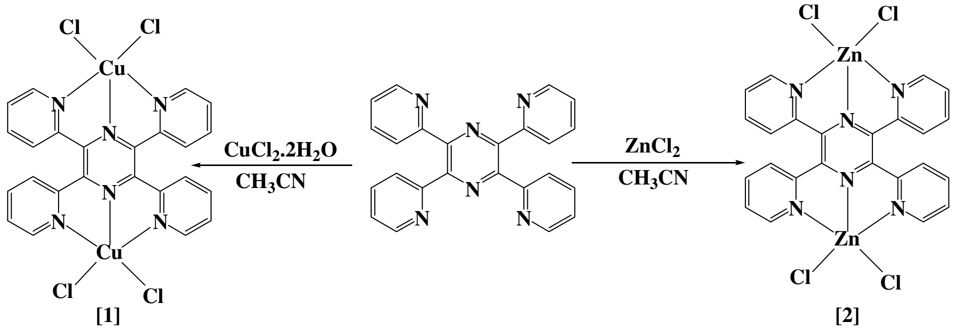

Scheme 1.

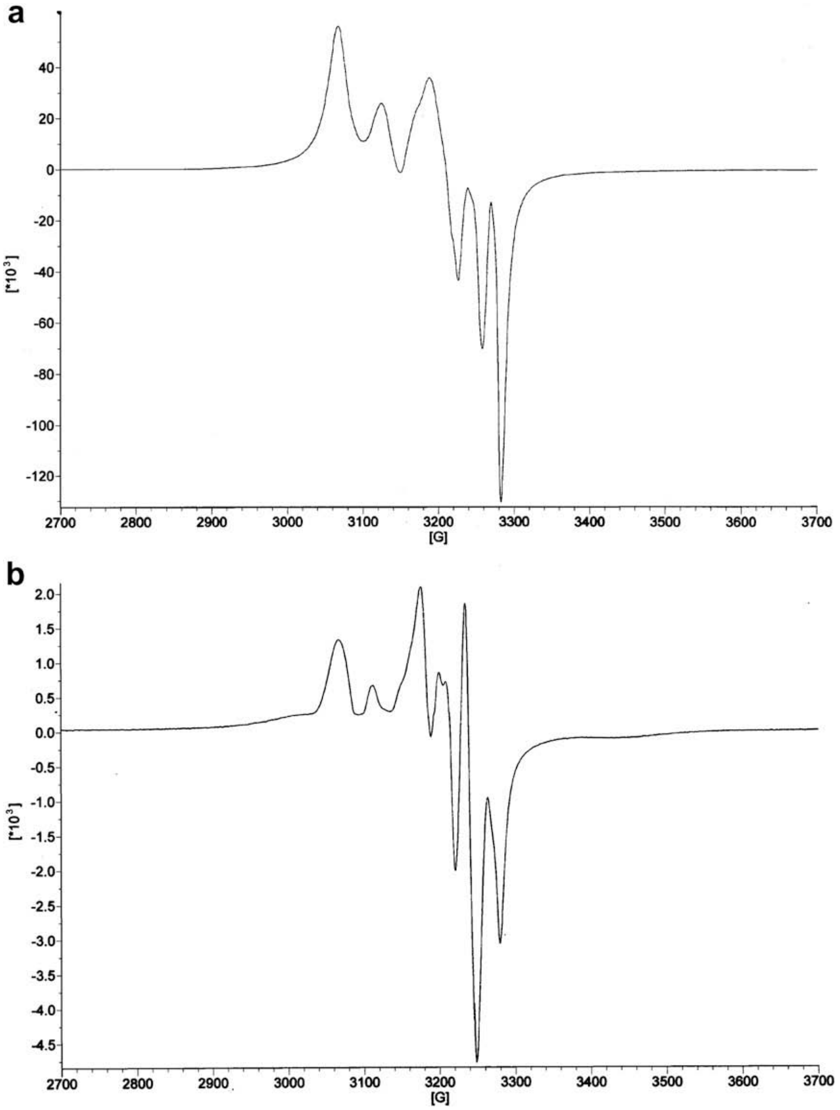

Fig. 1. (a) EPR spectra of [**1**] in CH_3CN at rt; (b) at LNT.

complexes $[Cu_2(\kappa^3\text{-}L)Cl_4] \cdot 5H_2O$ (**1**), $[Zn_2(\kappa^3\text{-}L)Cl_4] \cdot H_2O$ (**2**) in excellent yield. Synthesis of **1** has been previously described by Stoeckli-Evans et al. following a quite different procedure [12g]. A reaction Scheme 1 showing the synthesis of the complexes is given below .

2.2. Characterization

The complexes **1** and **2** are air stable, non-hygroscopic shiny crystalline solids, soluble in common organic solvents, and insoluble in diethyl ether and petroleum ether. The complexes were fully