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Synthesis, characterization, X-ray crystal structure and conductometry studying of a number of new Schiff base complexes; a new example of binuclear square pyramidal geometry of Cu(II) complex bridged with an oxo group

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ABSTRACT

Three new binuclear Cu(II), Mn(II), Co(II) complexes $[Cu_2(L)(ClO_4)](ClO_4)_2$ (**1**), $[Mn_2(L)(ClO_4)](ClO_4)_2$ (**2**), and $[Co_2(L)(ClO_4)](ClO_4)_2$ (**3**), {L = 1,3-bis(2-((Z)-(2-aminopropylimino)methyl)phenoxy)propan-2-ol} have been synthesized. Single crystal X-ray structure analysis of complex **1** showed that the complex is binuclear and all nitrogen and oxygen atoms of ligand (N_4O_3) are coordinated to two Cu(II) center ions. In addition, the crystal structure studying shows, a perchlorate ion has been bridged to the Cu(II) metal centers. However, two distorted square pyramidal Cu(II) ions are bridged asymmetrically by a perchlorate ion and oxygen of hydroxyl group of Schiff base ligand. In addition, the conductometry behaviors of all complexes were studied in acetonitrile solution.

1. Introduction

Polynuclear systems with three or more metal ions bridged by oxo, chloro and acetato groups have recently attracted considerable attention due to the existence of oxo-bridged tri- and multinuclear metal constellations in metallo proteins and enzymes [1–5]. The presence of two or trinuclear active sites in enzymes has been established by crystal structures. Synthesis of model complexes can be achieved by the self-assembly of simple ligands but the reproducibility is less compared to other methods [6]. Alternatively preformed ligands are useful for these synthesis in addition to their utility in reactions with metals inert to template reactions [7]. A variety of different Schiff base ligands containing N or O as donor atoms have been employed for preparation of polynuclear coordination complexes, aiming at understanding the structural and chemical factors that govern the exchange coupling between paramagnetic centers. Among the different metal complexes, Copper complexes with hybrid ligands have been widely studied in the past few decades as they afford numerous useful materials having unique properties such as magnetic exchange, photoluminescence, electrical conductivity, nonlinear optical property etc. [1–20]. Some metal complexes have been extensively utilized in clinics for centuries and have attracted numerous inorganic chemists to analyze them, with the main focus being medical applications [13,14]. Copper, an essential trace element with an oxidative nature and bioessential activity in human metabolism, does not exist in an ionic form in biological systems. Thus, measurement of copper in the body is evaluated in the form of complexes with organic compounds [11]. Herein we report the synthesis and characterization of three new Schiff base complexes of Copper (II), Cobalt (II) and Manganese (II). Schiff bases are a critical class of compounds in medical chemistry that have demonstrated significant chemotherapeutic and antibacterial application [16–20]. We have been involved in the synthesis and characterization of different cocrystal [21], macrocyclic [22] and macroacyclic [23] Schiff base complexes and in addition to notes above, in some cases we have reported their theoretical studying [24]. As mentioned earlier in this work, we report the synthesis and characterization of three new Cu(II), Co(II) and Mn(II) Schiff base complexes. The complexes were synthesized

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with the template condensation of two different amine and aldehyde (L, Fig. 1) in the presence of Cu(II), Co(II) and Mn(II) salts. The X-ray crystal structure of complex Cu(II) shows that, this compound is binuclear and both of the metal centers are square pyramidal.

2. Experimental

2.1. General information

Hydrated metal salts were obtained from Aldrich and was used without further purification. IR and UV spectra were measured on measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo Ka radiation. For compound **1** a blue prismatic crystal with dimensions of 0.35 × 0.35 × 0.20 mm was mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 47917 unique reflections. Data were collected at a temperature of 298(2) K to a maximum 2θ value of 53.48°, in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA [25] software package.

The numerical absorption coefficient, μ, for Mo Kα radiation is 0.700 mm^{-1}. A numerical absorption correction was applied using X-RED [26] and X-SHAPE [27] software. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct methods [28] and a subsequent difference Fourier map and then refined on F2 by a full-matrix least-squares procedure using anisotropic displacement parameters [28]. All of the hydrogen atoms were located in ideal positions and then refined isotropically. Subsequent refinement then converged with R factors and parameter errors significantly better than for all attempts to model the solvent disorder. Atomic factors are from International Tables for X-ray Crystallography [29]. All refinements were performed using the X-STEP32 crystallographic software package [30].

2.2. Synthesis

2.2.1. Preparation of $[Cu_2(L)\ (ClO_4)](ClO_4)_2$, **1**

1,2-diaminopropane (0.49 g, 066 mmol) was heated under reflux for 15 min in EtOH (15 ml). Then this solution was added to a mixed solution of 2-[3-(formyl phenoxy)-2-hydroxy propoxy] benzaldehyde (0.10 g, 0.33 mmol) and $Cu(ClO_4)_2{\cdot}6H_2O$ (0.122 g, 0.33 mmol) in dry MeOH (40 ml) with continuous stirring. The mixture was stirred at 60C° for 8 h. The solution was filtered and the filtrate was reduced to ca 10 cm^3. After about 48 h blue crystals were formed with a 61% yield. Anal. Calc. for $C_{23}H_{31}Cl_3Cu_2N_4O_{15}$: C, 33.01; H, 3.73; N, 6.69. Found: C, 33.14; H, 3.41; N, 6.41%. IR (KBr, cm^{-1}): 1654, (ν C=N Schiff base), 1240, (ν C–O), 1092, (ν ClO_4, Sterching), 624, (ν ClO_4, Bending), 3258, 3319, (ν NH_2).

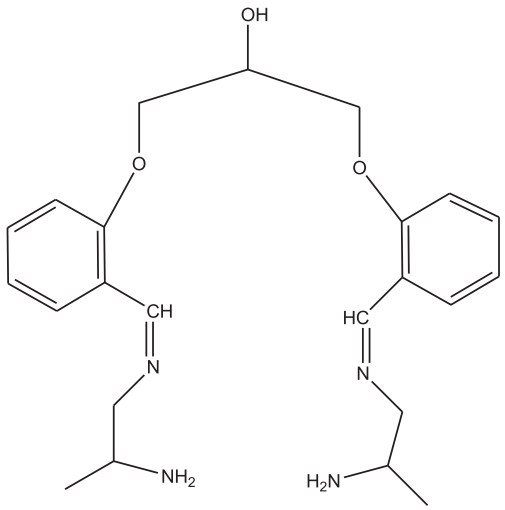

Fig. 1. The structure of Schiff base ligand (L).

2.2.2. Preparation of $[Mn_2(L)\ (ClO_4)](ClO_4)_2$, **2**

Compound **2** was synthesized in an analogue manner to the **1**. Yield, 54%. Anal. Calc. for $C_{23}H_{31}Cl_3Mn_2N_4O_{15}$: C, 33.70; H, 3.81; N, 6.83. Found: C, 32.91; H, 3.27; N, 6.04%. IR (KBr, cm^{-1}): 1655, (ν C=N Schiff base), 1103, (ν C–O), 1092, (ν ClO_4, Sterching), 624, (ν ClO_4, Bending), 3213, 3234, (ν NH_2).

2.2.3. Preparation of $[Co_2(L)\ (ClO_4)](ClO_4)_2$, **3**

Compound **3** was synthesized in an analogue manner to the **1**. Yield, 48%. Anal. Calc. for $C_{23}H_{31}Cl_3Co_2N_4O_{15}$: C, 33.37; H, 3.77; N, 6.77. Found: C, 32.74; H, 3.81; N, 6.20%. IR (KBr, cm^{-1}): 1645, (ν C=N Schiff base), 1243, (ν C–O), 1106, (ν ClO_4, Sterching), 625, (ν ClO_4, Bending), 3248, 3282, (ν NH_2).

3. Result and discussion

All complexes, **1**–**3** were readily synthesized by the template condensation of a new aldehyde and an amine in the presence of Cu(II), Mn(II) and Co(II) metal ions respectively. These compounds are quite stable in air and can be stored in a desiccator for long periods of time without decomposition. The resulting compounds were characterized by IR and elemental analysis in all cases and X-ray diffraction in the case of complex **1**. Condensation of all the primary amino group is confirmed by the lack of N–H stretching bands in the IR reign (3150–3450 cm^{-1}) [31] and the presence of strong C=N (Schiff base) stretching bands at 1654, 1655 and 1645 cm^{-1} for complexes **1**, **2** and **3**, respectively. A splatted intense band at ca. 1100 cm^{-1} due to ClO_4^- shows splitting [32,33], indicating the coordination of ClO_4^- for all complexes. The electronic spectra of all complexes in acetonitrile (10^{-4} M) show three intense bands in the UV region (Fig. 3), at 200–300 nm as expected for aromatic rings [34]. In addition, the molar conductivity (Λ_M) values of the complexes were measured at 25 °C using 10^{-3} M solutions in CH_3CN solvent (Table 3). These values indicate that all complexes are electrolytes [35,36]. Hence, in the addition to Schiff base ligand one molecule of perchlorate is probably coordinated with the metal centers. In addition to coordinated ClO_4^-, there are two perchlorate as counter ions.

3.1. X-ray crystal structure analysis

Template condensation reaction of an amine and an aldehyde in the presence of copper perchlorate under the conditions described in section 2 gave analytically $[Cu_2(L)\ (ClO_4)](ClO_4)_2$, **1**. Suitable crystals of **1** were obtained by slow diffusion of diethyl ether vapor into a mixture of methanol/ethanol solution of the corresponding complex. A summary of the details of the crystal data, data collection and refinement details is given in Table 1. ORTEP diagram of the molecular structure of **1** is shown in Fig. 2 with the atomic numbering. Selected bond lengths and bond angles are listed in Table 2. The Cu–O and Cu–N bond lengths are within the normal range.

As can be seen in Fig. 2, both Cu(II) centers are five coordinate, best described as (SP) square pyramidal (Figs. 2 and 3). The Cu–N bond lengths are in the expected range from 1.93 to 1.98 Å as well as expected for Cu–O bond lengths (1.93–2.60 Å). The longest bond lengths are located at the pyramidal position (Cu(1)–O(6)