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Syntheses, crystal structures and antioxidant properties of four complexes derived from a new Schiff base ligand (N^1E,N^2E)-N^1,N^2-bis(1-(pyrazin-2-yl)ethylidene)ethane-1,2 diamine

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Four Ag(I), Cd(II) and Cu(II) complexes, $[Ag_2\mathbf{L}_2](ClO_4)_2$ (**1**), $[Cd\mathbf{L}(NO_3)_2]$ (**2**), $[Cd_2\mathbf{L}_2Cl_4]$ (**3**) and $[Cu_2\mathbf{L}_2(ClO_4)_3](ClO_4)$ (**4**), derived from the new Schiff base ligand (N^1E,N^2E)-N^1,N^2-bis(1-(pyrazin-2-yl)ethylidene)ethane-1,2 diamine (**L**) have been synthesized and crystallographically characterized. The crystal structural features of **1**–**4** show that **1** is a ligand-supported dinuclear silver complex, **2** is a mononuclear eight-coordinate complex, **3** is a dinuclear hepta coordinate species and **4**, interestingly, discloses two distinctly crystallographically independent groups of mononuclear $[Cu(ClO_4)_2\mathbf{L}]$ and a 1D $[Cu(ClO_4)\mathbf{L}](ClO_4)$ unit in one asymmetric group. Furthermore, $\pi\cdots\pi$ stacking and/or hydrogen bonding interactions seem to be effective in stabilizing these crystal structures. The antioxidant activities of **L** and complexes **1**–**4** have also been studied.

1. Introduction

Schiff bases, organic ligands, play a crucial role in the development of coordination chemistry because of their preparative accessibility and structural variety [1–3]. The finding that metal complexes based on Schiff base ligands can be widely applied in catalysis, magnetism and material chemistry [4–6], and that they are also ubiquitous in developing intriguing coordination models of main group and transition metals, is mainly due to their stability, easy preparation, structural variability and biological activity [7–14]. Especially, pyrazine-Schiff base ligands containing an additional nitrogen donor in the pyrazine unit can systematically be used to understand the features of the supramolecular architectures and to explore the fascinating properties of these supramolecular frameworks. For example, Hannon et al. [15] have reported a series of metallo-supramolecular architectures based on pyrazine-Schiff base ligands containing rigid spacers. In these structures, additional donor groups were introduced into the pyrazine-based ligand system to link the distinct architectures into larger arrays.

However, to the best of our knowledge, the study of coordination architectures based on pyrazine-Schiff base ligands containing a flexible spacer is still rare and unusual. So, in this work, we have designed and synthesized a new pyrazine-Schiff base ligand, (N^1E,N^2E)-N^1,N^2-bis(1-(pyrazin-2-yl)ethylidene)ethane-1,2 diamine (**L**), (Scheme 1) and four new complexes, $[Ag_2\mathbf{L}_2](ClO_4)_2$ (**1**), $[Cd\mathbf{L}(NO_3)_2]$ (**2**), $[Cd_2\mathbf{L}_2Cl_4]$ (**3**) and $[Cu_2\mathbf{L}_2(ClO_4)_3(H_2O)](ClO_4)$ (**4**). In addition, the antioxidant activities of **L** and **1**–**4** are also described.

2. Experimental

2.1. Materials and physical measurements

All the reagents were of the highest grade commercially available and used as received without any further purification. IR spectra were measured by an FTS 3000 (United States DIGILAB) spectrometer as KBr pellets in the range 4000–400 cm^{-1}. Elemental analyses of C, H and N were recorded on a VxRio EL Instrument. ^1H NMR spectra (400 MHz) were measured on a Varian Mercury Plus-400 spectrometer.

X-ray diffraction analysis data of **1**–**4** were collected with a Bruker SMART APEX II diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) by the θ scan mode. The structures were solved by direct methods with SHELXS-97 and refined with the full-matrix least-squares technique using the SHELXL-97 program [16]. All non-hydrogen atoms were refined anisotropically; all the hydrogen atoms were fixed geometrically at calculated

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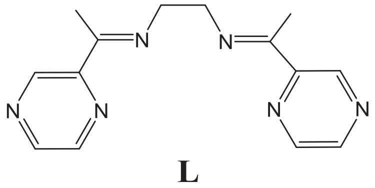

Scheme 1. The structure of the ligand **L**.

distances and refined isotropically. Detailed crystallographic data and structure refinement of complexes **1**–**4** are given in Table S1.

2.2. Synthesis

2.2.1. Synthesis of the ligand L

To a stirring solution of 1-(pyrazin-2-yl)ethanone (0.244 g, 2 mmol) in absolute methanol (25 ml), 1,2-ethanediamine (0.06 g, 1 mmol) dissolved in 5 ml absolute methanol was added dropwise. The mixture was heated under reflux for 8 h and then cooled to room temperature. A yellow solid was collected by vacuum filtration and washed with cold methanol. Yield, 83%. Melting Point: 178 °C. *Anal.* Calc. for $C_{14}H_{16}N_6$ (268.32): C, 62.67; H, 6.01; N, 31.32. Found: C, 62.55; H, 5.93; N, 31.52%. Selected IR data (cm^{-1}): 3440w, 2912w, 1647s, 1568m, 1398m, 1131m, 1020w, 866m, 776w, 621w. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 9.36 (s, 2H), 8.49 (s, 4H), 4.05 (s, 4H), 2.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 15.3, 66.9, 148.3, 157.3, 166.8.

2.2.2. Synthesis of $[Ag_2L_2](ClO_4)_2$ (1)

An acetonitrile solution of **L** (0.2 mmol, 0.0536 g) was added to $AgClO_4{\cdot}6H_2O$ (0.2 mmol, 0.0414 g) with constant stirring. After 30 min, the precipitate that formed was filtered. After 2 weeks, yellow crystals were grown by slow diffusion of diethyl ether. Yield, 92%. *Anal.* Calc. for $C_{28}H_{32}Ag_2Cl_2N_{12}O_8$ (951.30): C, 35.35; H, 3.39; N, 17.67. Found: C, 35.24; H, 3.43; N, 17.55%. Selected IR data (cm^{-1}): 3446w, 2931w, 2008w, 1627s, 1576w, 1402m, 1171m, 1094s, 1029m, 865m, 756w, 623s.

2.2.3. Synthesis of $[CdL(NO_3)_2]$ (2)

Complex **2** was synthesized by a method similar to that for **1**, except with the use of $Cd(NO_3)_2{\cdot}4H_2O$ instead of $AgClO_4{\cdot}6H_2O$. Colorless crystals suitable for X-ray analysis were obtained within 1 week. Yield: 84.62%. *Anal.* Calc. for $C_{14}H_{16}CdN_8O_6$ (504.75): C, 33.31; H, 3.20; N, 22.20. Found: C, 33.08; H, 3.12; N, 22.35%. Selected IR data (cm^{-1}): 3457w, 1655s, 1581w, 1474m, 1283m, 1136w, 1032s, 943w, 858m.

2.2.4. Synthesis of $[Cd_2L_2Cl_4]$ (3)

To a hot stirring solution of **L** (0.2 mmol, 0.0536 g) in 15 ml CH_3CN, $CdCl_2$ (0.2 mmol, 0.0366 g) in 15 ml CH_3OH was added dropwise and the mixture was stirred for 2 h. Colorless crystals suitable for X-ray analysis were obtained by the slow diffusion of diethyl ether into a solution of the complex in CH_3CN/CH_3OH (v/v = 1:1) within 2 weeks. Yield: 79.16%. *Anal.* Calc. for $C_{14}H_{16}CdCl_2N_6$ (451.63): C, 37.23; H, 3.57; N, 18.61. Found: C, 37.04; H, 3.64; N, 18.54%. Selected IR data (cm^{-1}): 3537w, 3492w, 1830w, 1763m, 1655s, 1582w, 1444m, 1291s, 1033s, 942w, 857w, 818m.

2.2.5. Synthesis of $[Cu_2L_2(ClO_4)_3](ClO_4)$ (4)

Complex **4** was synthesized by a method similar to that for **1**, except with the use of $Cu(ClO_4)_2{\cdot}7H_2O$ instead of $AgClO_4{\cdot}6H_2O$. Brown single crystals suitable for X-ray analysis were obtained within 2 weeks. Yield: 82.92%. *Anal.* Calc. for $C_{14}H_{32}Cl_4Cu_2N_{12}O_{16}$ (1061.54): C, 18.82; H, 3.61; N, 18.81. Found: C, 18.67; H, 3.49; N, 18.71%. Selected IR data (cm^{-1}): 3446w, 1627s, 1576w, 1474w, 1402m, 1360w, 1312m, 1101s, 865m, 623s.

2.3. Scavenger measurements of superoxide and hydroxyl radicals

The superoxide radicals were measured in a test system using NBT/VitB_2/MET [17]. **L** and **1**–**4**, dissolved in DMF ($C_{i(1-5)}$ = 0.2, 1.0, 2.0, 3.0, 4.0 μM) respectively, were added to a solution containing MET (0.01 mol L^{-1}), NBT (4.6×10^{-5} mol L^{-1}), VitB_2 (3.3×10^{-6} mol L^{-1}) and phosphate buffer (0.067 mol L^{-1}). After incubating the solution mixture at 30 °C for 10 min and illuminating with a fluorescent lamp for 3 min, the absorbance (A_i) of these samples was measured at 560 nm. The suppression ratio was calculated using the following equation:

$$\text{Suppression ratio}(\%) = [(A_0 - A_i)/(A_0)] \times 100\%$$

where A_i is the absorbance in the presence of **L** and **1**–**4**, and A_0 is the absorbance in the absence of **L** and **1**–**4**.

The hydroxyl radical scavenging study was prepared through the Fenton reaction [18]. **L** and **1**–**4** were dissolved in DMF ($C_{i(1-5)}$ = 2.0, 4.0, 6.0, 8.0, 10.0 μM) respectively. Then, 0.5 mL 114 μM Safranine, 1 mL 945 μM EDTA–Fe(II), 1 mL 3% H_2O_2 and 2.5 mL 0.15 M phosphate buffer (pH 7.4) were added to the 30 μL above tested solution. The sample without the tested compounds was used as a control. The resulting mixture was incubated for 1 h at 37 °C. Then a UV spectrophotometer was used to measure the absorbance at 520 nm (A_i, A_0, A_c). The suppression ratio was calculated by using following equation:

$$\text{Suppression ratio}(\%) = [(A_i - A_0)/(A_c - A_0)] \times 100\%.$$

where A_i is the absorbance in the presence of **L** and **1**–**4**, A_0 is the absorbance in the absence of **L** and **1**–**4**, and A_c is the absorbance in the absence of **L** and **1**–**4**, EDTA–Fe(II) and H_2O_2.

The antioxidant activity was described as the 50% inhibitory concentration (IC_{50}). The IC_{50} values were calculated from regression lines where x is the concentration of **L** and **1**–**4** in μM and y is the percent inhibition of **L** and **1**–**4**.

3. Results and discussions

The structures of **1**–**4** were characterized by infrared (IR) spectra, which showed valuable information about the counterions in their respective coordination environments. In the IR spectra of **1** and **4**, the strong peaks at 1094 (**1**) and 1101 (**4**) cm^{-1} should be ascribed to the presence of free perchlorate ions [19,20]. The spectrum of **2** reveals strong bands at 1474, 1283 and 1032 cm^{-1}, suggesting the nitrate groups act in the monodentate coordination mode in this complex [19,20].

3.1. Crystal structure of $[Ag_2L_2](ClO_4)_2$ (1)

A single-crystal X-ray diffraction study of **1** shows that the crystal lattice consists of the double helical cation $[Ag^2L^2]^{2+}$ and two uncoordinated perchlorate counter anions (Fig. 1). In the dinuclear cation $[Ag^2L^2]^{2+}$, the ligands act as neutral tetradentate chelating ligand units, binding two silver atoms, and wrap around a helical axis through the Ag1 and Ag2 atoms. Each silver atom is four-coordinated by two imine nitrogen atoms and two nitrogen atoms of different pyrazinyl groups. The distance between the metal centers (Ag1···Ag2) is 3.1374 Å, which is significantly shorter than the sum of the van der Waals radii of two silver atoms (3.44 Å), suggesting the presence of a ligand-supported weak Ag···Ag metallic binding interaction. The coordination geometry around any of the two central Ag atoms can be described as a distorted trigonal bipyramid. Two pyrazinyl nitrogen atoms and another silver atom form the