Polyhedron 38 (2012) 224–234

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Salicylaldimine Schiff bases – Generation of self-assembled and chiral complexes with Ni(II) and Zn(II) ions. An unusual antiferromagnetic interaction in a triply bridged Ni(II) dimer

Vimal K. Bhardwaj [b], Maninder Singh Hundal [b], Montserrat Corbella [a,*], Verónica Gómez [a,*], Geeta Hundal [b,*]

[a] Departament de Química Inorgànica, Universitat de Barcelona (UB), Av. Diagonal 645, 08028 Barcelona, Spain
[b] Department of Chemistry, Guru Nanak Dev University, Amritsar 143005, India

ARTICLE INFO

Article history:
Received 17 January 2012
Accepted 7 March 2012
Available online 28 March 2012

Keywords:
Schiff bases
Phenoxo/acetato/water bridging
X-ray crystal structures
Self-assembly
Antiferromagnetic coupling
Spontaneous resolution

ABSTRACT

Four new complexes of nickel(II) and zinc(II) with Schiff bases obtained from the condensation of salicylaldehyde and *N*,*N*-dimethyl-ethylene/propylenediamine and their reduced products have been synthesized and characterized by spectroscopic methods and single crystal X-ray structural analysis. Complex **1** is a six coordinated mononuclear complex of Ni(II), having a self assembled 2D structure with alternate cages and cavities running perpendicular to the *c* axis. The octagonal cavities are occupied by water molecules which are weakly hydrogen bonded to the eight oxygens lining the inner side of these cavities. Complex **2** is a phenoxo and aquo bridged dinuclear six coordinated complex of nickel(II) having two face sharing octahedra. Variable temperature magnetic susceptibility measurements of **2** show the presence of an antiferromagnetic coupling between the two nickel(II) centers. To the best of our knowledge it is the first dimeric complex of Ni(II), triply bridged by two phenoxo and one water molecule to show such a behavior. Complex **3** is a simple five coordinated monomer of Zn(II), whereas **4** is a chiral, dinuclear complex having zinc(II) ions with two different stereochemistries, which has been obtained by simultaneous resolution from achiral precursors.

1. Introduction

The chemistry of Schiff-base ligands and their metals complexes has received continuous and intensive attention in many fields of research because of their unique coordination and structural properties [1–6]. Among them, Salen type Schiff base complexes, derived from the condensation of salicylaldehyde and its derivatives with various primary amines, are gaining impetus for their varying denticity to form 1D, 2D and 3D complexes [7–11]. Their complexes have been put to use in various applications because of their importance with antitumor, antibacterial, antifungal and herbicidal activities [12–16], as inhibitors of xanthine oxidase [17], urease [18,19] and cancer [20,21]. Biologically they are potential catalysts for specific DNA/RNA cleavage reactions [22], and also for their catecholase activity [23–26]. They are used as luminescent probes [27] finding their use in OLEDs and information storage [28,29]. Schiff base complexes of transition metal ions have become a very important part of supramolecular chemistry by the formation of stable supramolecular architectures, by employing coordination bonding and/or hydrogen bonding and other intermolecular interactions, to self assemble complex molecules into multidimensional frameworks [30–34]. Much current effort is being devoted to the design and synthesis of such metal complexes [35–38] for the reason that such supramolecular materials not only display interesting structures, but also occasionally exhibit novel properties such as porosity, non-linear optical behavior [39] and magnetism [40–42]. Their complexes have also been used to combine the properties of liquid crystallinity with magnetism [43,44].

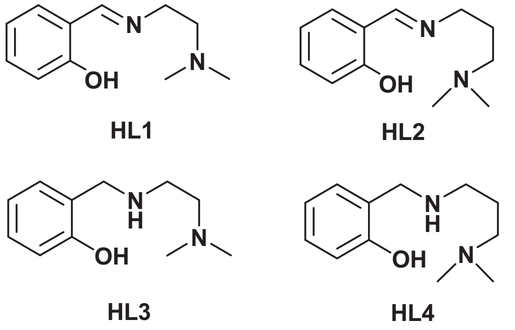
Earlier we reported copper(II) acetate complexes of these ligands (Scheme 1) and found them to have reasonable catecholase activity [26]. Extending our work we have synthesized four new complexes of the same ligands with Ni(II) acetate and Zn(II) acetate, and characterized them using spectroscopic and single crystal X-ray diffraction studies. The work is aimed towards creating supramolecular entities and to produce materials capable of showing magnetic alliances between the metal centers in the case of the Ni(II) ion and/or generating a chiral network or enantiomeric pairs using achiral precursors via spontaneous resolution. Our choice of ligands is based upon their facile synthesis and on the assumption that their low denticity and presence of phenoxo/acetato groups will require the involvement of the solvent/anion in the complex

---

* Corresponding authors. Tel.: +91 0183 2258804x3196, +91 9501114469; fax: +91 0183 2258820 (G. Hundal).

E-mail addresses: montse.corbella@qi.ub.es (M. Corbella), veronica.gomez@qi.ub.es (V. Gómez), geetahundal@yahoo.com (G. Hundal).

0277-5387/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.poly.2012.03.029



Scheme 1. Showing the ligands used in this study.

formation, increasing the chances of getting bridged dimeric/polymeric complexes. The reduction of **HL2** to give **HL4** has been done to see the effect of increased flexibility of the ligand on the structure. Although some complexes of **L1** and **L2** are known with Ni(II) and Zn(II) (CSD search), none of the complexes have acetate as the counter anion and also their structures are totally different. There is as yet no crystal structure report of any complex with **L4** except the one of Cu(II) reported by us [26]. We give here structural evidence of a self assembled supramolecular architecture from a mononuclear nickel(II) complex with water molecules as guests in the cavities, an antiferromagnetically coupled nickel(II) dimer and spontaneous resolution of a chiral dinuclear zinc(II) complex from achiral precursors, having Zn(II) ions with different stereochemistries.

2. Experimental

2.1. General experimental

All solvents were dried by standard methods. Unless otherwise specified, chemicals were purchased from commercial suppliers and used without further purification. TLC was performed on glass sheets pre-coated with silica gel. The elemental analyses were performed on a Flash EA 1112 elemental analyzer. FTIR spectra were recorded on a Shimadzu 8400S IR spectrometer for the compounds in the solid state as KBr discs or as neat samples, in the range 400–4000 cm^{-1}. The electronic absorption spectra were recorded on a Shimadzu Pharmaspec UV-1700 UV–Vis spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL 300 MHz instrument with TMS as the reference. Magnetic susceptibility measurements (2–300 K) and magnetization measurements at 2 K (0–50000 G), were carried out in a Quantum Design MPMP SQUID magnetometer at the *Unitat de Mesures Magnètiques* (Universitat de Barcelona). Two different magnetic fields were used for the susceptibility measurements, 415 G (2–5 K) and 7000 G (2–300 K), with superimposable $\chi_M T$ vs. T graphs. Pascal's constants were used to estimate the diamagnetic corrections for the compounds. The fit was performed by minimising the function $R = \Sigma[(\chi_M T)_{exp} - (\chi_M T)_{calc}]^2/\Sigma[(\chi_M T)_{exp}]^2$. The ligands **HL1**–HL4 were prepared by methods similar to those reported in the literature [45–47].

2.2. Synthesis of the complexes

2.2.1. $[(Ni\,L1)(CH_3COO)(H_2O)_2]_4{\cdot}H_2O$ (**1**)

A methanolic solution of nickel(II) acetate (2.48 g, 10 mmol) was added to a solution of **HL1** (1.92 g, 10 mmol) in $CHCl_3$. The solution was stirred for two hours. After completion of the reaction, the solution was filtered. After evaporation of the solvent, a green colored compound was obtained which was washed with methanol and dried under vacuum. Green colored crystals were obtained on recrystallization from methanol. Yield: 66%. M.p.: 186 °C. *Anal.* Calc. for $C_{13}H_{24}N_2NiO_6$: C, 43.01; H, 6.66; N, 7.72. Found: C, 42.57; H, 6.41; N, 7.58%. Selected IR (KBr, cm^{-1}): 3132 ν_{O-H}, 3012 $\nu_{aromatic\ C-H}$, 2925 $\nu_{aliphatic\ C-H}$, 1649 (s) $\nu_{C=N}$, 1599, 1537 $\nu_{asym\ OCO}$, 1411, 1323 $\nu_{sym\ OCO}$, 1188 ν_{C-N}, 1149 (m) ν_{C-O}. UV–Vis λ_{max} (nm), ε ($M^{-1}cm^{-1}$) in CH_3OH: 886 (154), 600 (54), 368 (13170). μ_B 3.39 BM. Conductivity (nitrobenzene, 1 mM solution at 298 K): $\Lambda = 4.8\ \Omega^{-1}cm^2 mol^{-1}$.

2.2.2. $[\{(Ni(\mu\text{-}L2)(CH_3COO)\}_2(\mu\text{-}H_2O)]$ (**2**)

A methanolic solution of nickel(II) acetate (2.48 g, 10 mmol) was added to a solution of **HL2** (2.06 g, 10 mmol) in $CHCl_3$. The solution was refluxed for two hours and then filtered. After evaporation of the solvent, a dark-green compound was obtained which was washed with methanol and dried under vacuum. Dark-green colored crystals were obtained by the vapor diffusion method of crystallization using $CHCl_3$ as the solvent and petroleum ether as the precipitant. Yield: 68%. M.p.: 198 °C. *Anal.* Calc. for $C_{28}H_{42}N_4Ni_2O_7$: C, 50.64; H, 6.38; N, 8.44. Found: C, 50.99; H, 6.91; N, 8.70%. Selected IR (KBr, cm^{-1}): 3431 ν_{O-H}, 2970 $\nu_{aromatic\ C-H}$, 2864 $\nu_{aliphatic\ C-H}$, 1631 $\nu_{C=N}$, 1600, 1542 $\nu_{asym\ OCO}$, 1407 $\nu_{sym\ OCO}$, 1317 δ_{C-H}, 1230, 1195 ν_{C-N}, 1147(m) ν_{C-O}. UV–Vis λ_{max} (nm), ε ($M^{-1}cm^{-1}$) in CH_3OH: 1032 (31), 634 (72), 364 (11200). μ_B 2.90 BM. Conductivity (nitrobenzene, 1 mM solution at 298 K): $\Lambda = 5.2\ \Omega^{-1}cm^2 mol^{-1}$.

2.2.3. $[(ZnL2)(CH_3COO)]$ (**3**)

A methanolic solution of zinc (II) acetate (2.19 g, 10 mmol) was added to a solution of **HL2** (2.06 g, 10 mmol) in CH_3OH. The solution was stirred for two hours. After evaporation of the solvent, an off-white colored compound was obtained which was washed with methanol and dried under vacuum. Pale-white colored crystals were obtained on recrystallization from methanol. Yield: 65%. M.p.: 174 °C. *Anal.* Calc. for $C_{14}H_{20}N_2O_3Zn$: C, 51.00; H, 6.11; N, 8.50. Found: C, 51.16; H, 6.18; N, 8.66%. Selected IR (KBr, cm^{-1}): 2899 $\nu_{aromatic\ C-H}$, 2837 $\nu_{aliphatic\ C-H}$, 1639 (s) $\nu_{C=N}$, 1556 $\nu_{asym\ OCO}$, 1442, 1419 $\nu_{sym\ OCO}$, 1325 δ_{C-H}, 1242, 1207 ν_{C-N}, 1157 ν_{C-O}. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.89–1.96 (m, $-CH_2$, 2H), 2.07 (s, $-CH_3COO^-$, 3H), 2.46 (s, $-NCH_3$, 6H), 2.97 (broad s, $-NCH_2$, 2H), 3.89 (broad s, $-NCH_2$, 2H), 6.65 (t, Ar, 1H, $J = 7.2$ Hz), 6.68 (d, Ar, 1H, $J = 8.2$ Hz), 7.07 (broad s, Ar, 1H), 7.21–7.27 (m, Ar, 1H), 8.10 (s, $-CH{=}N$, 1H). UV–Vis λ_{max} (nm), ε ($M^{-1}cm^{-1}$) in CH_3OH: 357 (4820), 268 (7930), 232 (17440). Conductivity (nitrobenzene, 1 mM solution at 298 K): $\Lambda = 4.5\ \Omega^{-1}cm^2 mol^{-1}$.

2.2.4. $[Zn_2(\mu\text{-}L4)(\mu\text{-}CH_3COO)_2(CH_3COO)]$ (**4**)

A methanolic solution of zinc(II) acetate (2.19 g, 10 mmol) was added to a solution of **HL4** (1.04 g, 5 mmol) in CH_3OH. The solution was stirred for three hours. After completion of the reaction, the solution was filtered. On slow evaporation of the solvent, off-white colored crystals were obtained. Yield: 72%. M.p.: 204 °C. *Anal.* Calc. for $C_{18}H_{27}N_2O_7Zn_2$: C, 42.04; H, 5.29; N, 5.45. Found: C, 41.92; H, 5.34; N, 5.62%. Selected IR (KBr, cm^{-1}): 3236 ν_{N-H}, 3018 $\nu_{aromatic\ C-H}$, 2917, 2846 $\nu_{aliphatic\ C-H}$, 1591 (s) $\nu_{asym\ OCO}$, 1444, 1403 (s) $\nu_{sym\ OCO}$, 1277 ν_{C-N}, 1033 ν_{C-O}. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.25 (broad, $-NCH_2$, 2H), 1.73 (broad s, $-CH_2$, 2H), 1.84 (s, $-CH_3COO^-$, 3H), 2.05 (s, $-NCH_3$, 6H), 2.37–2.40 (broad s, $-CH_2$, 2H), 3.08 (broad s, $-NCH_2$, 2H), 3.48–4.17 (broad s, $-NH$, 1H), 6.65 (t, Ar, 1H, $J = 7.2$ Hz), 6.90 (d, Ar, 1H, $J = 7.5$ Hz), 6.99 (d, Ar, 2H, $J = 6.3$ Hz), 7.17 (m, Ar, 2H). UV–Vis λ_{max} (nm), ε ($M^{-1}cm^{-1}$) in CH_3OH: 286 (3020) 236 (8150) 211 (7340). Conductivity (nitrobenzene, 1 mM solution at 298 K): $\Lambda = 3.6\ \Omega^{-1}cm^2 mol^{-1}$.