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Two novel analogous Ni(II) and Cd(II) complexes of an imidazole based Schiff base obtained from imidazole-4-carbaldehyde and 2-aminophenol

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ABSTRACT

A new imidazole-based Schiff base, 2-((1H-imidazol-4-yl)methyleneamino)phenol and dichlorobis(2-((1H-imidazol-4-yl)methyleneamino)-phenol)metal(II) complexes (M: Ni, Cd) $[Ni(H_2L)_2Cl_2]$ (**1**) and $[Cd(H_2L)_2Cl_2]$ (**2**) have been prepared and characterized by X-ray diffraction, Elemental analyses, GC–MS and IR spectroscopy techniques. The structural properties of the title complexes have been further investigated by DFT calculations. The analogous complexes have been found to be configurationally different from each other. With the influences of intermolecular hydrogen bonds, complex **2**, in cis configuration has revealed an intriguing structural motifs with large solvent accessible voids that are otherwise absent in trans-configurated complex **1** which consists of the similar types of intermolecular contacts e.g. the similar intermolecular hydrogen bonds and C–H···π interactions. The structural properties of free ligand and the complexes have been significantly rationalized by DFT calculations and the general trends observed in the experimental data have been successfully reproduced by the calculated ones.

1. Introduction

Schiff base compounds obtained by the efficient condensation of aldehydes and amines and the metal complexes of these strong chelators have large potential applications in various areas such as medicine, agriculture, analytical chemistry, dye and polimer industry, catalysis, enzyme modeling, magneto-structural chemistry, and diverse miscellaneous studies. Within this form of compounds, the syntheses of aromatic Schiff bases with both aromatic aldehyde and aromatic amine precursors are generally resulted in higher yield and purity than these with aliphatic ones based on the strength of relative stability of imine bonds conferred by electron-rich aryl side groups on the nitrogen and carbon atoms. In aromatic Schiff bases, imidazole based ones and especially, their metal complexes have drawn special interest in the past few decades due to their powerful antimicrobial activities, their use in the design of molecular-based magnets as well as in the simulation of active sites of enzymes since imidazole presents in many natural enzymes and proteins. The short literature survey dealing with the metal complexes of imidazole-based Schiff bases has presented so far the effective in vitro antimicrobial, antibacterial and antifungal activities of Ag(I), Zn(II) and Sn(II) complexes [1–3], magnetic properties and electrochemistry of Zn(II), Ni(II), Cu(II) and Mn(II) complexes [4–7], spin crossover in Fe(II) and Fe(III) complexes [8,9], biomimetic modeling of copper(II) proteins [4], and catalytic activity of Pd(II) complexes for Heck coupling and precatalytic activities of V(III) and Cr(III) complexes for ethylene polymerization and higher olefin oligomerization [10]. As the first stage of our research, we have reported here synthesis, characterization and X-ray structures of mononuclear analogous Ni(II) and Cd(II) complexes of an imidazole based Schiff base ligand obtained by the condensation of 2-aminophenol and imidazole-4-carbaldehyde. Okamura and Maeda have reported Fe(III) complexes of monoanionic deprotonated form of the same ligand and investigated Mössbauer and magnetic properties of the complexes [11]. In the present study, The complexation of the ligand with the corresponding metal salts in neutral form yielded the analogous complexes **1** and **2**. We have also further studied the structural properties by Density Functional Theory (DFT) to probe the title complexes more qualitatively beyond the experimental findings.

2. Experimental

2.1. Materials and method

All reagents were purchased from commercial suppliers and used without further purification. Elemental analyses were performed on a LECO CHNS-932 elemental analyzer (USA). The IR

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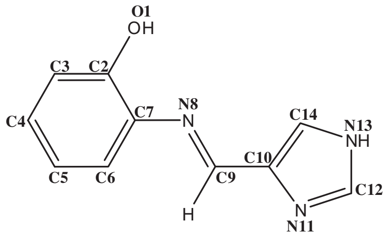

Scheme 1.

spectra were recorded on a Bruker Vertex-80V spectrometer (GERMANY) in the range of 4000–400 cm^{-1} using KBr pellets. UV–Vis spectra were recorded on a Unicam UV2 UV–Vis spectrometer (USA) within 200–800 nm range, in methanol medium. Mass spectrum was recorded on a Thermo Trace MS-GC (GERMANY) spectrometer using methanolic solutions.

2.2. Synthesis

2.2.1. Synthesis of 2-((1H-imidazol-4-yl)methyleneamino)phenol (H_2L)

Imidazole-4-carbaldehyde (2 mmol, 0.2 g) and 2-aminophenol (2 mmol, 0.220 g) were dissolved in 10 ml of absolute ethanol and refluxed for 3 h. The resulting reddish-orange solution was reduced to its half volume by slow heating and cooled to room temperature. The orange precipitate formed upon addition of 10 ml ethyl acetate-*n*-hexane mixture to the solution was filtered, washed with diethyleter and dried in air. Yield: 89%. *Anal.* Calc. C, 47.64; H, 3.57; N, 16.67. Found: C, 47.28; H, 3.91; N, 16.39%. IR (KBr, cm^{-1}): 3301 ν_{as}(OH); 3231 ν_{as}(NH–); 1634 ν(C=N); 1586 ν(C=C). GC–MS: m/z = 185.02 187.06 (H_2L, 55%). ^1H NMR (Scheme 1 and 200 MHz, ppm, $CDCl_3$): 10.02 (sb, H1, 1H) 8.62 (s, H9, 1H); 7.81 (s, H12, 1H); 7.62 (s, H14, 1H).

Table 1
Crystallographic data for **1** and **2**.

Complex	(**1**)	(**2**)
Formula	$C_{20}H_{18}N_6O_2Cl_2Ni$	$C_{20}H_{18}N_6O_2Cl_2Cd$
Molecular weight (g/mol)	503.71	557.41
T (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
Unit cell dimensions		
a (Å)	7.9712(5)	13.8899(5)
b (Å)	12.9977(10)	25.058(2)
c (Å)	10.5370(7)	7.5601(5)
β (°)	96.647(6)	98.368(4)
V ($Å^3$)	1084.37(13)	2603.4(3)
Z	3	8
D_{calc} (mg/mm^3)	1.544	1.423
M (mm^{-1})	1.171	1.069
$F(000)$	516	1112
θ (°)	3.40–28.95	3.25–27.56
Reflections collected	4400	5047
Independent reflections	2462	2581
Reflections observed (>2σ)	1939	1552
Absorption correction	integration	integration
Data/restraints /parameters	2462/0/146	2581/1/145
Goodness-of-fit (GOF) on F^2	1.039	1.120
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0557$	$R_1 = 0.2376$
	$wR_2 = 0.1048$	$wR_2 = 0.0688$
R indices (all data)	$R_1 = 0.0392$	$R_1 = 0.1208$
	$wR_2 = 0.0918$	$wR_2 = 0.0688$

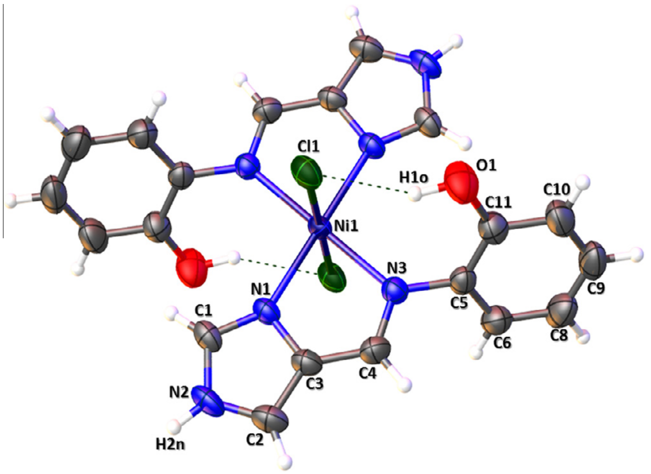

Fig. 1. Molecular structure of **1**.

2.2.2. Complex **1**

$NiCl_2 \cdot 6H_2O$ (1 mmol, 0.238 g) dissolved in 10 ml of absolute ethanol was gradually added to a 10 ml ethanolic solution of H_2L (2 mmol, 0.380 g) and the obtained mixture was refluxed for 5 min. The resulted light green precipitate was filtered, wahsed with cold ethanol and resolved in excess ethanol by heating at 50 °C. The final green solution was left to stand undisturbed at room temperaure for crystallization. Upon slow evaporation of the solvent within 2 days, X-ray quality block crystals collected on the wall of the vessel were washed with cold ethanol and dried in air. Yield: 28%. *Anal.* Calc. C, 47.64; H, 3.57; N, 16.67. Found: C, 47.28; H, 3.91; N, 16.39%. IR (KBr, cm^{-1}): 3277 ν_{as}(OH); 3133 ν_{as}(-NH–); 1625 ν(C=N); 1586 ν(C=C).

2.2.3. Complex **2**

$CdCl_2 \cdot 2H_2O$ (1 mmol, 0.200 g) dissolved in 10 ml of absolute ethanol was gradually added to a 10 ml ethanolic solution of H_2L (2 mmol, 0.380 g) and the obtained mixture was refluxed for a day. The resulting orange solution standing at room temperature for one day provided well-developed X-ray quality orange crystals. Yield: 42%. *Anal.* Calc. C, 43.06; H, 3.23; N, 15.07. Found: C, 42.83; H, 3.80; N, 14.26%. IR (KBr, cm^{-1}): 3300 ν_{as}(OH); 3136 ν_{as}(NH–); 1623 ν(C=N); 1596 ν(C=C).

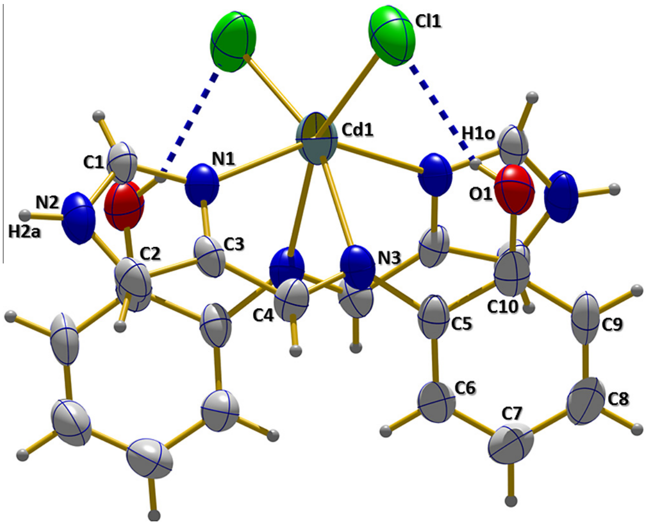

Fig. 2. Molecular structure of **2**.