



ISSN (PRINT) : 2320 -1967
ISSN (ONLINE) : 2320 -1975



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CHEMXPRESS 9(2), 178-182, (2016)

New metal complexes of oxadiazole-2-thione-based ligands; Synthesis and structural characterisation

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Received : 12th April, 2015 ; Revised : 03rd September, 2015 ; Accepted : 11th September, 2015

Abstract : New metal complexes of oxadiazole-2-thione-based ligands are reported. The reaction of 2-methyl-benzoic acid hydrazide, thiophen-2-yl-acetic acid hydrazide and isonicotinic acid hydrazide with carbon disulfide and potassium hydroxide in methanol resulted in the formation of the new ligands namely; 5-o-tolyl-3H-[1,3,4]oxadiazole-2-thione (L^1), 5-thiophen-2-ylmethyl-3H-[1,3,4]oxadiazole-2-thione (L^2) and 5-isoquinolin-3-yl-3H-[1,3,4]oxadiazole-2-thione (L^3), respectively. Monomeric metal complexes of the general formula $[M(L^n)(en)_2]$. (where $MCl_2 \cdot XH_2O = Co(II), Ni(II)$ and $Zn(II)$; $X = 6, 6, 0$ $en =$ ethylenediamine; $n = 1, 2, 3$) were achieved from the reaction of metal salt with

the appropriate ligand in presence of ethylenediamine as a coligand. Compounds were characterised by spectroscopic methods (NMR, mass spectra, FTIR and UV-Vis spectroscopy), elemental analyses, magnetic susceptibility, atomic absorption, chloride content, and melting point. Based on above analysis the suggested geometry about metal atoms is distorted octahedral. © Global Scientific Inc.

Keywords : 2-methyl-benzoic acid hydrazide; Thiophen-2-yl-acetic acid hydrazide and isonicotinic acid hydrazide; 5-o-tolyl-3H-[1,3,4]oxadiazole-2-thione.

INTRODUCTION

Heterocyclic ligands are an important class of compounds that play a vital role in the development of coordination chemistry^[1-3]. Multidentate heterocyclic ligands such as polyazoles, imidazoles and triazoles, with five-membered rings (azoles), are the core species in the design and fabrication of supramolecular structures^[4,5]. The geometrical structure and properties of metal complexes are depending on; (i)

type of metal ion and, (ii) the structure of the ligand and type of its donor atoms^[6]. Oxadiazole compounds such as 1,3,4-oxadiazole derivatives, are biologically important species and play a key role in the biological systems^[7]. These derivatives can be prepared from N-royl dithiocarbazates and their salts that could be converted to 1,3,4-oxadiazole derivatives^[8]. Ligands based on azole heterocycles, get a great interest due to their coordination ability and diverse coordination modes^[9-11]. Thio-azole hetero-

cycles are type of compounds exists as their thion- and/or thiol tautomeric forms. These types of compounds have drawn more attention due to their pharmacological applications, such as antiviral, analgesic, antimicrobial, antidepressant and antifungal effects^[12,13]. In addition, thiophene-based ligands have been used in the protection of metal corrosion^[14,15]. The formation of binary complexes of 1,3,4-oxadiazole-2-thiones and 1,2,4-triazole-3-thiones are well documented^[16-18]. However, little is known about the chemistry of mixed ligand complexes of this class of compounds. In this paper the preparation of new oxadiazole-2-thione-based ligands and their complexes in the presence of ethylenediamine are reported. Physico-chemical analyses revealed the formation of six coordinate monomeric complexes, in which the geometry about metal centre is distorted octahedral.

EXPERIMENTAL

Materials and methods

All reagents were obtained commercially (Aldrich) and used without further purification. Solvents used in the synthesis were distilled from appropriate drying agent immediately prior to use.

Physical measurements

Elemental analyses (C, H and N) were carried out on a Heraeus instrument (Vario EL). IR spectra were recorded as KBr discs using a Shimadzu 8400 S FTIR spectrophotometer from 4000-400 cm^{-1} . Electronic spectra were measured from 200-1100 nm for 10^{-3} M solutions in DMSO at 25°C using a Shimadzu 1800 spectrophotometer. ^1H - ^{13}C -NMR spectra were acquired in DMSO- d_6 solution using a Jeol 400 MHz spectrometer with tetramethylsilane (TMS) as an internal standard for ^1H NMR and mass spectroscopy analysis. Melting points were obtained on an Electro-thermal Stuart melting point SMP40 capillary melting point apparatus and are uncorrected. Metals were determined using a Shimadzu (A.A) 680 G atomic absorption spectrophotometer. Chloride content was determined using potentiometer titration method on a 686-Titrip processor-665Dosimat-Metrohm Swiss. Conductivity measure-

ments were made with DMSO solutions using a PW 9526 digital conductivity meter and room temperature magnetic moments were measured with a magnetic susceptibility balance (Johnson Matthey Catalytic Systems Division).

SYNTHESIS

Preparation of potassium 5-o-tolyl-3H-[1,3,4]oxadiazole-2-thione (L^1)

Ligand was prepared using a standard method^[8,19], as follows:

CS_2 (0.5 g, 6.5 mmol) was added dropwise with stirring to a solution of 2-methyl-benzoic acid hydrazide (1 g, 6.6 mmol) and potassium hydroxide (0.37 g, 6.5 mmol) in methanol (30 mL). After the addition, the solution was allowed to reflux for 4 h, and then solvent was removed under reduced pressure. The remaining residue was redissolved in water (5 mL), and a precipitate was formed by pouring the aqueous solution into an ice containing hydrochloric acid (5 mL, 5%). The solid was filtered off, washed with 10% (v/v) mixture of EtOH/ether, and then dried in vacuo. Yield: 0.73 g (57%), mp= 189 °C. IR (KBr, cm^{-1}): (see supporting information(SI), Figure SI:1): 3152 $\nu(\text{NH})$, 1622 $\nu(\text{C}=\text{N})$, 1350 $\nu(\text{C}-\text{O}-\text{C})$, 1103 $\nu(\text{N}-\text{N})$ and 1151 $\nu(\text{C}=\text{S})$. ^1H NMR (300 MHz, DMSO- d_6): (see supporting information(SI), Figure SI:25): $\delta_{\text{H}} = 2.032$ (s, 3H, $\text{C}_9\text{-H}$), 6.719 ($\text{C}_5\text{-H}$), 7.325 ($\text{C}_7\text{-H}$), 7.792 ($\text{C}_4\text{-H}$), 7.964 ($\text{C}_6\text{-H}$), 11.838 (s, 1H, N-H); ^{13}C NMR (DMSO- d_6 , TMS) (see SI:Figure:26): $\delta_{\text{C}} = 16.529$ (C_9), 154.179 (C_1), 147.00 (C_2), 112.101 (C_5), 127.471 (C_7), 135.625(C_6), 145.930 (C_3), 146.477 (C_8), 147.003 (C_4). The mass spectrum of L^1 : (see SI:Figure: 31: showed several peaks corresponding to successive fragmentations of the molecule. Peak detected at m/z 193.1 (71 %) ($\text{M}+1$)⁺ represent the molecular ion peak of the ligand. Other distinct peaks were observed in the spectrum at m/z 178.0 (10 %), 100.98 (15 %), assigned to the $[\text{M}-\text{CH}_3]^+$ and $[\text{M}-(\text{CH}_3)+(\text{C}_6\text{H}_6)]^+$ fragments, respectively.

Preparation of L^2 and L^3

The method used to prepare L^2 and L^3 was analogous to the procedure given for the L^1 , but thiophene-

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2-carboxylic acid hydrazide and isonicotinic acid hydrazide were used in place of 2-methyl benzoic acid hydrazide. The quantities of other reagents used were adjusted accordingly, and an identical work-up procedure was used to give a pale-yellow solid for L². Yield: 0.79 g (62%), mp= 258 °C. IR (KBr, cm⁻¹): (see SI:Figure:2: 3148 ν(NH), 1619 ν(C=N), 1352 ν(C-O-C), 1121 ν(N-N) and 1142 ν(C=S)).

NMR and mass spectral data for L²; ¹H NMR (300 MHz, DMSO-d₆): (see SI:Figure:27: δ_H = 2.683 (CH₂), 6.713 (C₅-H), 6.329 (C₆-H), 7.897 (C₇-H), 8.745 (s, 1H, N-H)); ¹³C NMR (DMSO-d₆, TMS): (see SI:Figure:28 δ = 31.074 (C₃), 112.575 (C₇), 115.579 (C₅), 127.943(C₆), 136.074(C₄), 146.454 (C₂), 147.496 (C₁). The mass spectrum of L²: (see SI:Figure:32: showed several peaks corresponding to successive fragmentations of the molecule. Peak detected at m/z 182.6 (47 %) (M-1)⁺ represent the molecular ion peak of the ligand. Other distinct peaks were observed in the spectrum at m/z 99.7 (30 %), 32.4 (17%), assigned to the [M-C₄H₃S]⁺ and [M-(C₄H₃S)+ S) fragments, respectively.

And brown solid powder for L³ yield (0.83 g, 68%), mp= 244°C. IR (KBr, cm⁻¹): (see SI:Figure: 3: ν(NH) 3347, ν(C=S) 1616, ν(C-O-C) 1362, ν(N-N) 1144, ν(C=S) 1101. NMR data for L³; ¹H NMR (300 MHz, DMSO-d₆): (see SI:Figure:29: δ = 7.293 (C₇-H), 8.344 (C₈-H), 7.405 (C₆-H), 7.927 (C₅-H), 9.555 (C₄-H), 9.775 (s, 1H, N-H)); ¹³C NMR (DMSO-d₆, TMS): (see SI:Figure:30: δ_C = 111.18 (C₄), 112.46 (C₅), 115.15 (C₇), 116.04(C₈), 126.28(C₆), 126.73 (C₁₀), 147.25 (C₁₁), 148.54 (C₃), 148.93 (C₉), 149.51 (C₂) 154.55 (C₁).

Synthesis of complexes

The complexes were prepared in a similar method and as follows: To a solution of Lⁿ (2 mmol) (where n = 1-3) dissolved in water (20 mL), was added a solution of MCl₂.nH₂O (1 mmol) where (M= Co(II), Ni(II), n= 6 and Zn(II),; n= 0) in water (15 mL). The mixture was stirred for 15 min, upon which time a solid was formed. This was filtered off, washed with a mixture of methanol/water (50:50), and then dried in air. A solution of ethylenediamine (4 mmol) in methanol (10 mL) was added to a methanolic solution of the oxadiazole-2-thione ligand

complex. The reaction mixture was stirred vigorously for 20 min, and then the resulting mixture was, filtered off, and then allowed to evaporate at RT to yield the title compound. Elemental analysis data, colours, and yields for the complexes are given in (TABLE 1).

RESULTS AND DISCUSSION

Chemistry

The new heterocyclic ligands L¹-L³ were obtained in good yields from the reaction of carbon disulfide, potassium hydroxide and aromatic carboxylic acid hydrazide (Scheme 1). The ligands contain more than one donor atoms; therefore it may act, upon coordination with metal centre, as monodentate or bidentate ligands. The ligands were characterised by elemental analysis (TABLE 1), IR (TABLE 2), UV-Vis (TABLE 3), mass and ¹H-, ¹³C-NMR. Monomeric complexes of the ligands with Co(II), Ni(II) and Zn(II) were synthesised from the stirring (2 mmol) of the ligand with (1 mmol) of metal chloride and (4 mmol) of ethylenediamine using a mixture of water/methanol. Neutral complexes^[20] of the general formula [M(Lⁿ)₂(en)₂], (where M = Co(II), Ni(II) and Zn(II), L = L¹-L³, n = 1, 2 or 3); were obtained (Scheme 2).

The complexes are air-stable solids, soluble only in DMF and DMSO, and not soluble in other common organic solvents. The coordination geometries of the complexes were deduced from their spectra. The analytical data (TABLE 1) agree well with the suggested formulae. The most important infrared bands of the ligands and their complexes together with their assignments are collected in (TABLE 2).

IR and NMR Spectra

The prominent infrared bands for the ligands and their complexes together with their assignments are listed in (TABLE 2). The IR spectra for the free ligands (L¹ – L³): (see SI:Figures:1-3: show peaks around 3347-3152, 1616-1622, 1103-1144 and 1101-1142 cm⁻¹, which assigned to ν_{as}(NH), ν(C=N), ν(N-N) and ν(C=S), respectively. The IR spectra of the complexes exhibited L¹-L³ bands with the appropri-

ate shifts and the M-N frequencies due to complex formation (TABLE 2). The $\nu_{\text{as}}(\text{NH})$ vibration at *ca.* 3150 cm^{-1} in the free ligands is disappeared, and new bands that can be attributed to $\nu(\text{NH})$ of ethylenediamine is appeared around 3402-3262, 3445-3220 and, 3331-3200 cm^{-1} for L^1 , L^2 and L^3 complexes, respectively^[21]. The appearance these bands, that assigned to $\nu(\text{NH}_2)$ moiety, indicated the coordination of the amine group of ethylenediamine to the metal atoms^[22, 23]. Peaks around 1589-1600 1589-1616 and 1604-1622 cm^{-1} attributed to $\nu(\text{C}=\text{N})$ in the complexes of L^1 , L^2 and L^3 , respectively. These bands were shifted to lower frequency compared with that in the free ligands, except $[\text{Ni}^{\text{II}}(\text{L}^3)_2(\text{en})_2]$ complex (see SI:Figure:11) which shifted to higher frequency. This can be attributed to delocalisation of metal electron density (t_{2g}) to the π -system of the ligand^[24, 25]. The small shift in $\nu(\text{C}=\text{S})$, indicated the exocyclic sulfur is not bonding. This shift may be attributed to the formation of hydrogen bonding with NH_2 group^[26]. At lower frequency the complexes exhibited bands around 505-524 cm^{-1} can be assigned to $\nu(\text{M}-\text{N})$ for the complexes^[27].

^1H , ^{13}C NMR spectra of L^1 , L^2 and L^3 show the expected signals (see Experimental). ^1H NMR of the ligands L^1 and L^2 (see SI:Figure: 25, 27) show peaks at chemical shifts *ca.* 2.032 (s, 3H, CH_3) and 2.683 (s, 2H, CH_2) ppm, assigned to methyl and methylene group in L^1 and L^2 , respectively. Resonances detected at 11.838, 8.754 and 9.775 ppm, equivalent to one proton (s, 1H), were assigned to the $\text{N}-\text{H}_{\text{triazole}}$ of L^1 , L^2 and L^3 . The deshielding of this group and its shifted to downfield may be attributed to hydrogen bonding with the $\text{DMSO}-d_6$ NMR solvent, which lead to decrease of the density of electrons on the N-H group. Signals between 6.719-7.792, 6.713-7.897 and 7.293-9.555 ppm were assigned to protons of aromatic ring in L^1 , L^2 and L^3 , respectively. The NMR show only thion form in solution and no signal was detected to thiol form, such as IR spectrum show only thion form, the compounds show only thion form in solid and solution.

Electronic spectra, magnetic moments and conductivity measurements

The UV-Vis spectra of L^1 , L^2 and L^3 (see

SI:Figure:13-15) exhibits an intense absorption peaks at 255, 259 and 263 nm assigned to overlap of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The electronic spectra of the complexes of L^1 exhibited various extents of hypsochromic shift of the bands related to the intra-ligand $\pi \rightarrow \pi^*$ transition in Co(II), Ni(II) and Zn(II) complexes (see SI:Figures:16-18), respectively (TABLE 3). Bands related to the (CT) transition were observed in the Zn spectrum of the complexes (TABLE 3),^[28, 29]. The spectrum of the Co(II) complex showed the $\pi \rightarrow \pi^*$ and d-d band which could be attributed to spin forbidden transition in an octahedral geometry^[28]. The magnetic moment of this complex is typical for a high spin octahedral structure^[30]. The Ni(II) complex is paramagnetic suggesting an octahedral geometry^[22]. The electronic spectrum of this complex was consistent with this assignment. The spectrum of the Zn(II) complex exhibited bands assigned to intra-ligand $\pi \rightarrow \pi^*$ ^[29]. The electronic spectra of the complexes of L^2 exhibited bands related to the intra-ligand $\pi \rightarrow \pi^*$ and the (CT) transitions (see TABLE 3). The spectra of the Co(II) and Ni(II) complexes (see SI:Figures:19, 20, 22 and 23) of L^2 and L^3 showed similar behaviour to those of L^1 suggesting octahedral geometries for the complexes. The magnetic moment values were consistent with the octahedral structures. The spectra of Zn(II) complex of L^2 and L^3 (see SI:Figures: 21 and 24) showed similar behaviour to those of L^1 suggesting octahedral geometries^[28]. The magnetic moment values were consistent with the octahedral structures. The molar conductivities indicate that the Co(II), Ni(II) and Zn(II) complexes are non-electrolyte. (TABLE 1)^[20].

CONCLUSION

In this paper, the synthesis and coordination chemistry of metal complexes obtained from the reaction of oxadiazole-thion-based ligands with some metal ions are explored. The mode of bonding and overall structure of the complexes was determined through physic-chemical and spectroscopic methods, which revealed the formation of six coordinate complexes.

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