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PII: S1386-1425(15)00684-8
DOI: http://dx.doi.org/10.1016/j.saa.2015.05.071
Reference: SAA 13739

To appear in: *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*

Received Date: 1 February 2015
Revised Date: 3 May 2015
Accepted Date: 23 May 2015

Please cite this article as: B. Jeragh, M.S. Ali, A.A. El-Asmy, Synthesis, crystal structure, characterization and biological activity of 2,5-hexanedione bis(isonicotinylhydrazone) and N-(2,5-dimethyl-1H-pyrrol-1-yl)isonicotinamide complexes, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2015), doi: http://dx.doi.org/10.1016/j.saa.2015.05.071

Synthesis, crystal structure, characterization and biological activity of 2,5-hexanedione bis(isonicotinylhydrazone) and N-(2,5-dimethyl-1H-pyrrol-1-yl)isonicotinamide complexes

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Abstract

The reaction between 2,5-hexanedione and isonicotinic acid hydrazide in EtOH gave two products. The ethanol insoluble product was identified as 2,5-hexanedione bis(isonicotinylhydrazone) [HINH] and the soluble ethanol product as N-(2,5-dimethyl-1H-pyrrol-1-yl)isonicotinamide [DINA]. A series of Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pd^{2+} complexes of HINH and Co^{2+}, Cu^{2+}, Zn^{2+} and Hg^{2+} complexes of DINA have been synthesized and structurally characterized. Based on the elemental analysis, mass spectra and molar conductance, the complexes have assigned the proposed imperical formulae. The crystal structures of N-(2,5-dimethyl-1H-pyrrol-1-yl)isonicotinamide and its Zn^{2+} and Hg^{2+} complexes have been solved by X-ray diffraction having $[Zn(DINA)_2Cl_2]$ and $[Hg(DINA)_2Cl_2]$ in a tetrahedral structure. In the DINH complexes, the ligand coordinates as a monodentate through the pyridine nitrogen. On the other hand, HINH behaves as a tetradentate (neutral or binegative) manner with the two metal ions. The magnetic moments and electronic spectra of all complexes provide tetrahedral, square-planar, trigonal biyramid and/or octahedral structure. The thermal decomposition of the complexes revealed the outer and inner solvents as well as the end product. The steady part of $[Zn(DINA)_2Cl_2]$ and $[Hg(DINA)_2Cl_2]$ thermograms till 303 and 286 ^{o}C indicates the absence of any outside solvents. All compounds have activity against bacteria more than fungi. $[Cd_4(HINH)Cl_8].3H_2O$ has the highest values.

Keywords: 2,5-Hexanedione bis(isonicotinylhydrazone); N-(2,5-Dimethyl-1H-pyrrol-1-yl)iso-nicotinamide; Biological activity; x-ray crystallography

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Introduction

A number of hydrazone derivatives have been developed and evaluated for their antibacterial activity. Also, their metal complexes have antimicrobial and antitumor activity due to the ability of the ligands to coordinate with the metal ions needed in the metabolism of fungus. Liu *et al*. synthesized and evaluated acetyl hydrazone derivatives for antitumor activity against A549, HCT11b, HepG2, PC-9 and A375 cell lines with an IC_{50} value of 4-17 μM. Aryl hydrazone derivatives synthesized by Vogel *et al.*were reported to have an IC_{50} of 6.7 nM against MDA-MB 231 and MCF-7 breast cancer cell lines [1]. Mono- and polynuclear Schiff base complexes were used as oxidants serving as models for galactose oxidase. The Cu(II) model has a special interest in some biological systems [2]. Much interest has been focused on the hydrazone complexes to show the coordinative behavior- antimicrobial activity relationship. Some hydrazones and their complexes have antitumor activity [3]: oximinohydrazones as antiparasitic, fungicidal and bactericidal properties [4]. Compounds containing oxime and amino groups were used for the separation and determination of some transition metal ions [5]. Aromatic heterocycles containing nitrogen act as ligands toward some metal ions [6]. Pyrroles belong to this class and are five-membered heterocyclic ligands containing nitrogen. They have a considerable attention due to their applicability in medicine [7–9] as antitumor, anti-inflammation, antipyretic, antiviral, antimicrobial, anticonvulsant, antihistaminic, antidepressant, insecticides, and fungicides [10-16]. In coordination chemistry, nitrogen ligands exhibit various coordination modes and have received considerable attention for the synthesis of transition metal complexes with various nuclear ties [17]. Complexes of some transition metal ions with 2-acetylpyridineisonicotinyl, pyrrolyl-2-carboxaldehydeisonicotinyl, 2,5-dihydroxyacetophenoneisonicotinoyl, isonicotinamidofurfur-aldimine, 2-thiophenecarbonyl and isonicotinoylhydrazones of 3-(N-methyl)isatin were reported [18-21].

On continuation to the work done on 2,5-hexanedione bis(isonicotinylhydrazone) as well as its metal complexes [22], the aim is to synthesize and characterize new keto-form complexes in which the method of preparation and conditions are changed. Also, the formation of N-(2,5-dimethyl-1H-pyrrol-1-yl)isonicotinamide during the preparation of the parent one in crystalline form pushed us to prepare its complexes.

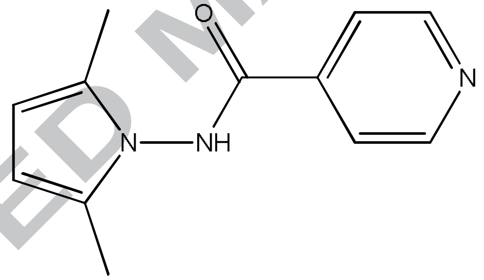
Experimental

Reagents

The starting materials, $CrCl_3.3H_2O$, $VOSO_4.H_2O$, $FeCl_3.3H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2.2H_2O$, $CdCl_2.2H_2O$, $HgCl_2$, K_2PdCl_4 and $ZrCl_4$, isonicotinic acid hydrazide, 2,5-hexanedione and solvents used for the synthesis of ligands and complexes were Sigma Chemicals and used as received.

Synthesis of HINH and DINH

HINH was prepared similar to our previous work [22]. On evaporating the mother liquor to its half volume, the precipitate formed was separated by filtration, recrystallized from ethanol and dried. It was confirmed as N-(2,5-dimethyl-1H-pyrrol-1yl)isonicotinamide (DINH) using elemental analysis, spectra (IR, NMR and MS) and single crystal structure (Structure 1).



Structure 1. N-(2,5-dimethyl-1H-pyrrol-1-yl)isonicotinamide (DINA)

Synthesis of the metal complexes of HINH

The complexes were prepared by heating a mixture of HINH (3 mmol), dissolved in 20 mL ethanol and the metal salt (3 mmol) in 30 mL ethanol on a water bath for 1h. The binuclear complexes were prepared by heating a mixture of the ligand (3 mmol) dissolved in 20 mL ethanol and the metal salt (6 mmol) in 30 mL ethanol solution (v/v) under reflux on a water bath for 4 - 6 h. The precipitate was filtered off, washed with diethyl ether and finally dried in a vacuum desiccator over silica gel.

Synthesis of DINA complexes

A solution of N-(2,5-dimethyl-1H-pyrrol-1-yl)isonicotinamide (215 mg, 1mmol) in 20 ml ethanol was added slowly with continuous stirring to 10 ml ethanolic solution of $ZnCl_2{\cdot}2H_2O$ (0.375 mg, 1mmol); $HgCl_2$ (153 mg; 0.42 mmol), $CoCl_2.6H_2O$ or $CuCl_2.2H_2O$ and heated under reflux for 4 h. The product was collected by filtration and allowed to evaporate slowly at room temperature. The Zn(II) and Hg(II) salts formed white crystals after one week suitable for single crystal X-ray diffraction studies (Fig. 1).

Physical measurements

Carbon, hydrogen and nitrogen contents of HINH; DINA and their complexes were determined at the Microanalytical Unit (Varian Micro V1.5.8, CHNS Mode, 15073036) of Kuwait University. The metal content was determined using ICP-OES GBC Quantium Sequential at Kuwait University. The IR spectra were recorded a KBr disc on a FT/IR-6300 type A (400-4000 cm^{-1}). The electronic spectra of the complexes were recorded on Cary 5 UV-Vis Spectrophotometer, Varian (200-900 nm). The ^1H NMR spectra of the ligand and its diamagnetic complexes were recorded in DMSO d6, on a Bruker WP 200 SY spectrometer (300 MHz) at room temperature using tetramethylsilane (TMS) as an external standard. The mass spectra were recorded on a GC-MS Thermo-DFS (BG_FAB) mass spectrometer. Melting points were obtained on a Griffin melting point apparatus. The magnetic measurements were carried out on a Johnson-Matthey magnetic balance, UK. Thermogravimetric analysis (TGA) was measured (10-850 ^oC) on a Shimadzu TGA-60; the nitrogen flow and heating rate were 50 ml/min and 10^oC min^{-1}, respectively. The X-ray crystallographic data were collected on Rigaku R-AXIS RAPID diffractometer using filtered Mo-K α-radiation. The structure was solved by the direct methods and expanded using Fourier techniques at Kuwait University.

Results and discussion

Characterization of HINH and DINA

In the IR spectrum of HINH (Fig. 1), the bands at 3272 (vs), 1660 (vs), 1629 (s) and 1550 (s) cm^{-1} are assigned to $\upsilon(NH)$, $\upsilon(C{=}O)$, $\upsilon(C{=}N)_{Hy}$ and $\upsilon(C{=}N)_{Py}$, respectively. Its ^1H NMR spectrum showed a signal at 11.631 (d, 2H) due to the NH protons (disappeared on adding D_2O) and signals at 8.694 (d, 4H) and 7.350 (d, 4H) ppm for the CH protons of the pyridine rings and also signals at 8.694 (t, 4H); 7.350 (t, 4H) and 2.011-1.927 (d, 6H) for the CH_2 and CH_3 protons. On the other hand, the IR spectrum of DINA showed characteristic bands at 3226, 1672, 1594 and 1018 due to υ(NH), υ(C=O), υ$(C=N)_{Py}$, υ(N-N), respectively. Its ^1H NMR spectrum (Fig. 2) showed signals at 11.593 (s, 1H), 8.840 (d, 2H), 7.893 (d, 2H), 5.741 (s, 2H) and 2.062 (d, 6H) due to the protons of NH, CH of pyridine (six and five membered rings) and CH_3. Its ^{13}C NMR showed peaks at 164.84, 150.90, 140.58, 127.41, 122.07 and 103.91 assigned to C=O, C=N, C-N, C=C, C-N and C-C, respectively. The mass spectra of the two ligands revealed the molecular ion peak at m/z = 353.3 and 215.2 [Mol. Wt = 352.4 and 215.26].

Description of the crystal structure

The crystal structures of DINA, $[Zn(DINA)_2Cl_2]$ and $[Hg(DINA)_2Cl_2]$ with the atomic numbering scheme are shown in Fig. 3 while the crystal data and structure refinement are summarized in Table 1. DINH crystalized in a triclinic P-1 (#2) while the complexes in monoclinic and $P2_1/c$ (#14) space groups and the coordination geometry around the M(II) center is four (tetrahedral geometry); two nitrogen atoms from the two DINH molecules and two chlorine atoms completed the four coordination. The Zn-Cl_1 and Zn-Cl_2 are 2.2198(13) and 2.2117(14) while the Zn-N_1 and Zn-N_4 are 2.062(3) and 2.066(3)˚A, respectively. On the other hand, the Hg-Cl_1 and Hg-Cl_2 are 2.340(3) and 2.347(2) while the Hg-N_1 and Hg-N_4 are 2.452(5) and 2.422(5)˚A, respectively. The distances of M-N are considerably shorter than the M–Cl indicating the stronger ability of the nitrogen to bond to Zn or Hg than the chlorine atom. Furthermore, the longer M–Cl_1 distance compared to M–Cl_2 counterpart is consistent with other systems of this ligand type. The two chlorine atoms occupy the apical position. The Cl1-Hg-Cl2 (151.34^o) angle is larger than Cl1-Zn-Cl2 (122.88^o) indicating a larger distortion of the tetrahedral Hg(II) geometry. So, the bond angles in the Zn(II) complex are longer than the corresponding in Hg(II) and > 100^o indicating distortion of the tetrahedral structure. The Cl1–M–N4 bond angles vary from 95° to 100°. The N1-Zn-N4 (112.08^o) is similar to N1-Hg-N4 (112.42^o).

Characterization of the metal complexes

Firstly, a series of metal complexes has been synthesized by the reaction of 2,5-hexanedione bis(isonicotinylhydrazone) and the metal salt. Three types of complexes were formed: mononuclear: $[Fe(HINH\text{-}2H)(H_2O)_2]Cl.3H_2O$; $[Cu(HINH)(H_2O)_2]Cl_2.H_2O$; binuclear $[Ni_2(HINH)(H_2O)_4Cl_2]Cl_2.2H_2O$, $[Co_2(HINH)(H_2O)_4Cl_4]$, $[Zn_2(HINH)Cl_4].6H_2O$, $[Cr_2(HINH)\text{-}(H_2O)_2Cl_6].2H_2O$, $[Hg_2(HINH\text{-}2H)Cl_2]$; $[Pd_2(HINH)(H_2O)_2Cl_4].5H_2O$ and tetranuclear $[Cd_4(HINH)Cl_8].3H_2O$ complexes. All complexes were formed in the keto form except $[Fe(HINH\text{-}2H)(H_2O)Cl].4H_2O$ and $[Hg_2(HINH\text{-}2H)Cl_2]$ which formed in the enol form. Secondly, four complexes were formed on the reaction of DINA with Co(II), Cu(II), Zn(II) and Hg(II). The analytical data confirm the formation of $[Hg(DINA)_2Cl_2]$, $[Zn(DINA)_2Cl_2]$, $[Co(DINA)_2(H_2O)Cl_2]$ and $[Cu(DINH)_2]Cl_2.5H_2O$. Most complexes are colored (Table 2) having high melting points (> 325 ^oC) except for $[Hg_2(HINH\text{-}2H)Cl_2]$ which has 201 - 203 ^oC. The complexes are insoluble in most common organic solvents but soluble in DMF. The molar conductance values (Table 2) of the complexes in DMF solution proved the electrolytic nature of $[Cu(HINH)(H_2O)_2]Cl_2.H_2O$, $[Ni_2(HINH)(H_2O)_4Cl_2]Cl_2.2H_2O$ and $[Cu(DINH)_2(H_2O)_2]Cl_2.5H_2O$ which have 1:2 except for $[Fe(HINH\text{-}2H)(H_2O)_2]Cl.3H_2O$ which has 1:1 electrolyte [23]. $[Co_2(HINH)(H_2O)_4Cl_4]$ is brown in solid and green in DMF. No change in color for the other complexes.

IR and ^{1}H NMR spectra of HINA complexes

On comparison of the IR spectra of $[Ni_2(HINH)(H_2O)_4Cl_2]Cl_2.2H_2O$, $[Co_2(HINH)(H_2O)_4Cl_4]$, $[Zn_2(HINH)Cl_4].6H_2O$, $[Cr_2(HINH)(H_2O)_2Cl_6].2H_2O$ and $[Pd_2(HINH)(H_2O)_2Cl_4].5H_2O$ with that of HINH, one can conclude that the ligand coordinates as a neutral tetradentate with the two metal ions according to the following (Table 3): i) the $\upsilon(C{=}N)_{Hy}$ and $\upsilon(C{=}O)$ bands observed at 1628 and 1659 cm^{-1} are shifted to lower wavenumbers by 11 - 33 cm^{-1} indicating their participation in bonding. In $[Pd_2(HINH)(H_2O)_2Cl_4].5H_2O$, the $\upsilon(C{=}N)_{Hy}$ band is shifted to higher wavenumber (1639 cm^{-1}). The shift of the iminic band can be assigned to the π-back bonding of metal to ligand [24]. The new band at 407 - 479 cm^{-1} is due to $\upsilon(M\text{-}N)$ [25]; the wide range may be due to a relatively strong bond with the metal ion. ii) The $\upsilon(C{=}N)_{py}$ band exists more or less at the same position (1552 cm^{-1}) indicating that the pyridine azomethine group is not participated in coordination. The new band observed at 485 - 570 cm^{-1} is due to $\upsilon(M\text{-}O)$ [26]. Two bands are observed in $[Cr_2(HINH)(H_2O)_3Cl_6].H_2O$ (512; 496 cm^{-1}) and $[Pd_2(HINH)(H_2O)_2Cl_4].5H_2O$ (537; 485 cm^{-1}) confirming the existence of the complex in a trans form. iii) In $[Ni_2(HINH)(H_2O)_4Cl_2]Cl_2.2H_2O$, $[Co_2(HINH)(H_2O)_4Cl_4]$, $[Zn_2(HINH)Cl_4].6H_2O$, $[Cr_2(HINH)(H_2O)_2Cl_6].2H_2O$, $[Pd_2(HINH)(H_2O)_2Cl_4].5H_2O$ and $[Cu(HINH)(H_2O)_2]Cl_2.H_2O$, the band observed at 3404–3509 cm^{-1} is attributed to the coordinated and/or hydrated water [27]. The ^1H NMR spectrum of $[Zn_2(HINH)Cl_4].6H_2O$ showed the signal of the NH protons at 11.623 confirming its presence without coordination or enolization (Table 4). The signals of the CH and CH_2 protons appeared at the same position as in the ligand spectrum. Also, the new signal observed at 2.33 is attributed to the coordinated water. In the spectrum of $[Cu(HINH)(H_2O)_2]Cl_2.H_2O$, the ligand coordinates as neutral but in a bidentate mannat through the two azomethine groups of the hydrazone moiety by the shift of the band to 1617 cm^{-1} and the appearance of new band at 404 cm^{-1} due to υ(M-N). The hydrated water appeared as a broad band at 3404 cm^{-1}. The C=O and $(C=N)_{py}$ are not taking part in coordination.

In the IR spectra of $[Hg_2(HINH\text{-}2H)Cl_2]$ and $[Fe(HINH\text{-}2H)(H_2O)Cl].4H_2O$, the ligand acts as a binegative tetradentate nature by the disappearance of the υ(NH) and υ(C=O) bands confirming the enolization of the amide group. The $υ(C=N)_{hy}$ appeared very weak at 1611 cm^{-1} while the $υ(C=N)_{py}$ exists at the same position. Also, the broad band at 416-453 cm^{-1} is due to υ(M-N). The ^1H NMR spectrum of $[Hg_2(HINH\text{-}2H)Cl_2]$ showed the disappearance of the NH signals.

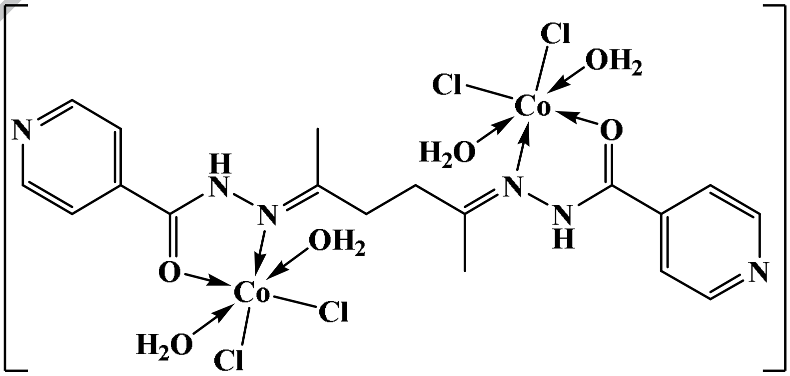
IR and ^{1}H NMR spectra of DINA complexes

In the IR spectra of DINA complexes, the $υ(C=N)_{py}$ at 1594 in the spectrum of the ligand is shifted to higher wavenumber (1608 - 1617 cm^{-1}) due to its sharing in bonding. One only band is observed in the low frequency region due to υ(M-N) vibration [25]. The υ(C=O) vibration still more or less at the same position. The $[Co(DINA)_2Cl_2(H_2O)]$ and $[Cu(DINA)(H_2O))_2]Cl_2.3H_2O$ spectra showed the hydrated or the coordinated water band at 3421 or 3443 cm^{-1}, respectively; this band is not observed in $[Hg(DINA)_2Cl_2]$ and $[Zn(DINA)_2Cl_2]$. Thus, the IR spectra of the compounds are found in good agreement with their respective structural features. The ^1H NMR spectrum of $[Hg(DINA)_2Cl_2]$ showed the same signals as in the spectrum of its ligand (Table 4) confirming the nonparticipation of the NH group in bonding. Also, in its ^{13}C NMR spectrum, the peaks of C=O and $C=N_{py}$ exist at the same position.

Electronic spectra and magnetic moments

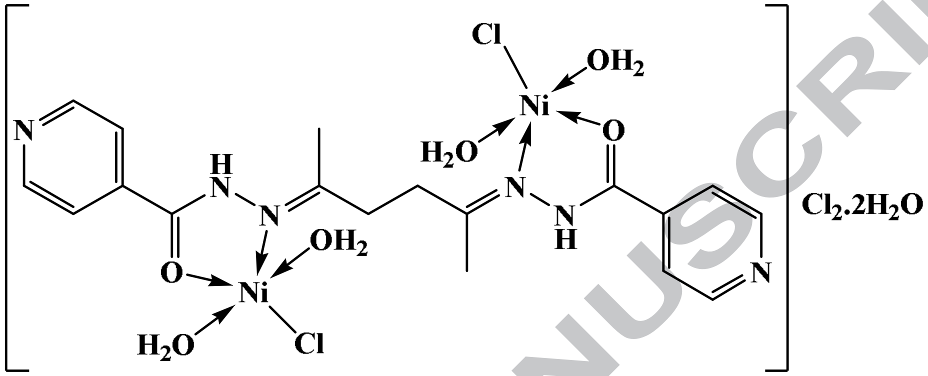
Table 5 showed the electronic spectral bands of the complexes as well as their magnetic moments. The colors of the solid complexes are similar to those in DMSO solution. HINH spectrum showed three absorption bands at 47170, 44640 and 42370 cm^{-1} assigned to the π→π* transitions of $C=N_{Py}$, $C=N_{Hy}$ and C=O groups. The n→π* bands are observed collectively at 37595 cm^{-1}. The observation of the bands as broad may be due to the existence of the carbonyl and azomethine groups in two opposite sides [28]. The bands at 27025–226350 and 22220-21730 cm^{-1} in the spectra of the metal complexes may be due to NMCT and OMCT [29].

The electronic spectrum of $[Co_2(HINH)(H_2O)_4Cl_4]$ (Fig. 4) revealed three bands with maxima at 14730, 16260 and 22200 cm^{-1} assigned to the $^4T_{1g}\rightarrow^4T_{2g}$ (ν_2), $^4T_{1g}\rightarrow^4T_{2g}$ (ν_3) and charge transfer transitions, respectively. The first two bands are characteristic for octahedral geometry (Structure 1) [30] around each cobalt ion. The 10Dq (Δ_o), B and β are calculated to be 10350 cm^{-1}, 788.62 cm^{-1} and 0.81, respectively; values at 8690 cm^{-1}, 869 cm^{-1}` and 0.895 were calculated for the Co(II) complex of 2,5-hexanedione bis(salicyloylhydrazone) [31]. The μ_{eff} is 4.05 BM for each cobalt atom which is slightly lower than the values reported for the octahedral geometry (4.7 - 5.2 BM) and higher than the spin only moment (3.87 BM) for the three electrons. This may be due to strong interactions between the two central atoms. In the electronic spectrum of $[Co(DINA)(H_2O)Cl_2]$, the d-d bands are observed at 20530 and 16920 cm^{-1} which resemble the spectra of five-coordinate Co(II) complexes [32]. A square-pyramid structure may be assigned for this complex. Its magnetic moment (3.59 BM) supports the presence of three unpaired electrons with sp^3d hybridization (outer complex).



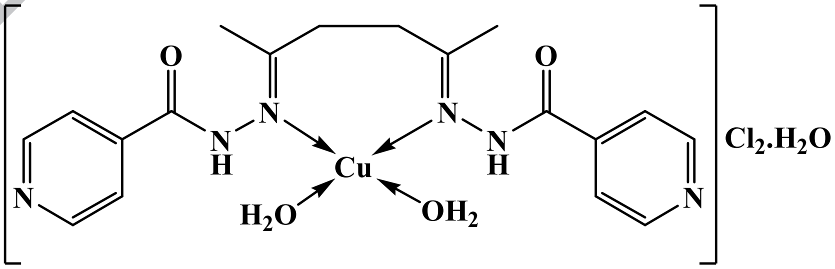
Structure 1. Proposed structure of $[Co_2(HINH)(H_2O)_4Cl_4]$

The magnetic moment value, for each atom, of $[Ni_2(HINH)(H_2O)_4Cl_2]Cl_2.2H_2O$ is 2.83 BM. The value lies within the range reported for five or six coordination containing two unpaired electrons. Its electronic spectrum showed one main broad band at 21140 cm^{-1} in trigonal biyramid geometry (Structure 2) with sp^3d hybridization [33]. Ni(II) complex with 2,5-hexanedione bis(salicyloylhydrazone) [31] was found mononuclear and adopted octahedral structure.



Structure 2. Proposed structure of $[Ni_2(HINH)(H_2O)_4Cl_2]Cl_2.2H_2O$

Cu(II) complexes with square-planar geometry have three spin allowed transitions assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ [34]. The electronic spectrum of $[Cu(HINH)(H_2O)_2]Cl_2.H_2O$ exhibits one band with maximum at 20080 cm^{-1} characteristic for CuN_2O_2 chromophore and assigned to the $^2B_{1g} \rightarrow {}^2E_g$ transition in a square–planar geometry (Structure 3) [35]. The band position and the magnetic moment (1.97 BM) are consistent with this geometry.



Structure 3. Proposed structure of $[Cu(HINH)(H_2O)_2]Cl_2.H_2O$

The electronic spectrum of $[Cr_2(HINH)(H_2O)_2Cl_6].2H_2O$ showed two bands at 15455 and 22170 cm^{-1} assigned to $^4A_{2g} \longrightarrow {}^4T_{2g}(\nu_1)$ and $^4A_{2g} \longrightarrow {}^4T_{1g}(\nu_2)$ in an octahedral geometry [36].

The $^4A_{2g} \longrightarrow {}^4T_{1g}(P)(\nu_3)$ band is expected to be at 30915 cm^{-1} generally covered by the broad charge transfer band. The B value is 656.69 cm^{-1} calculated by the equation: $B = (2\ \nu_1^2 - 3\ \nu_1\nu_2 + \nu_2^2)/(15\ \nu_2 - 27\ \nu_1)$. The values of Dq and β are 1834 cm^{-1} and 0.729. These values as well as the magnetic moment (4.1 BM) confirm the octahedral structure.

The electronic spectrum of $[Fe(HINH\text{-}2H)(H_2O)_2]Cl.3H_2O$ showed three bands at 21830 and 29960 cm^{-1} attributed to $^6A_{1g} \longrightarrow {}^4T_{1g}(G)$, $^6A_{1g} \longrightarrow {}^4T_{2g}$ (G) and $^6A_{1g} \longrightarrow {}^4E_g(G)$ in an octahedral configuration [37]. The magnetic moment value (6.39 BM) is in the range reported for the high-spin configuration containing four unpaired electrons.

Thermal Studies

The thermogram of $[Co_2(HINH)(H_2O)_4Cl_4]$ showed seven decomposition steps at 46, 220, 334, 401, 668, 800 and > 800 ^oC corresponding to the removal of the lattice water (% Found 2.03; % Calcd. 2.78); the removal of one coordinated water (% Found 3.05; % Calcd. 2.78); the removal of the other coordinated waters with $2Cl_2$ (% Found 23.03; % Calcd. 21.29), C_6H_{10} (% Found 12.59; % Calcd 12.31), $2C_5H_4N$ (% Found 23.67; % Calcd 23.42), H_2N_4 (% Found 8.99; % Calcd. 8.70) leaving 2CoO (% Found 25.79; % Calcd. 22.52 %), respectively.

The TG curve of $[Cu(HINH)(H_2O)_2]Cl_2.H_2O$ showed interesting property in which the chelating ring $[CuN_2O_2]$ still remain as residue and unchanged up to 800 ^0C. The first step (50 ^oC) removed the outside water and Cl (% Found 8.94; % Calcd. 9.99 %). The second step (195 ^oC) corresponds to loosing of $2H_2O$+Cl (% Found 13.2; % Calcd. 13.11). The third step represents the repulsion of $2C_5H_4N$ (% Found 30.23; % Calcd. 28.867). The fourth step (Found 22.80; % Calcd. 24.80) corresponds to the removal of $C_7H_{22}N_2$. The moiety remains unchanged because it forms stable rings up to 800 ^oC.

However, $[Cu(DINH)_2(H_2O)_2]Cl_2.5H_2O$ showed four steps ending with the loss of the complex at > 400 ^oC (Table 6). On the other hand, $[Co(DINA)_2(H_2O)Cl_2]$ shows two decomposition steps at 261.9 and > 300 ^oC corresponding to the removal of one ligand molecule + Cl_2 + H_2O in the first step and one ligand molecule + Co in the second step. The steady part of the thermograms of $[Zn(DINA)_2Cl_2]$ and $[Hg(DINA)_2Cl_2]$ till 303 and 286 ^oC, respectively, indicating the absence of any outside solvents. No remaining residue above 600 ^oC.

Biological Activity

Inspection of the data in Table 7 which includes the biological activity of HINH, DINA and their Co(II), Ni(II), Cd(II) and Pd(II) complexes against ten types of bacteria (1-10) and three types of fungi (11-13), one can observe the following: the compounds have activity against bacteria more than fungi. The complexes have more activity than the ligands. The $[Cd_4(HINH)Cl_8].3H_2O$ has the highest values. The activity against Saccharomyces cerevisiae is the highest. All compounds have activity against Staphylococcus aureus PA 129 more than Staphylococcus aureus PA 128. All compounds have no activity against Pseudomonas aeruginosa Ps-8 except $[Co_2(HINH)(H_2O)_4Cl_2]Cl_2.H_2O$. The compounds have low activity against E. Coli PA151 less than E. Coli PA149. The more potent for Bacillus sp. M3017 is $[Cd_4(HINH)Cl_8].3H_2O$. The more potent for Candida albicans PA48 are HINH and $[Cd_4(HINH)Cl_8].3H_2O$. The activity of $[Cu(HINH)(H_2O)_2]Cl_2.H_2O$ against Saccharomyces cerevisiae is the highest one. The order of activity for all compounds against Saccharomyces cerevisiae is: $[Cd_4(HINH)Cl_8].3H_2O$ > $[Co_2(HINH)(H_2O)_2Cl_2]Cl_2.H_2O$ > HINH > $[Ni_2(HINH)(H_2O)_4Cl_2]Cl_2.2H_2O$ > DINA. The high activity of $[Cd_4(HINH)Cl_8].3H_2O$ may be due to the high content of cadmium and chlorine in the complex.

Conclusion

The reaction between isonicotinic acid hydrazide and 2,5-hexanedione gave two compounds (also, the same reaction was adopted in 2,5-hexanedione bis(salicyloylhydrazone) [31]). The soluble one is N-(2,5-dimethyl-1H-pyrrol-1-yl)isonicotinamide (DINA) and confirmed by X-ray crystallography. The insoluble is 2,5-hexanedione bis(isonicotinylhydrazone) (HINH). Aim to extend our earlier work on HINH and its complexes have been achieved. The synthesis and characterization of the new complexes have been described by spectroscopy. The complexes of HINH have been formed in the keto-form; the previous complexes were formed in the enol-form. Two complexes of DINA with Zn(II) and Hg(II) were analyzed by single crystal X-ray diffraction and found tetrahedral.

Further Materials

Crystallographic data for the structures reported in this paper have been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC-968028 for DINH; CCDC 967825 for Zn(II) complex and 967823 for Hg(II) complex.

Acknowledgment

This work was supported financially by the research sector, Kuwait University (Project No. SC06/12). The authors acknowledge this support and all service labs (GS 01/01; GS 01/03; GS 01/05). The authors thank also Dr. Ismail Al-Saleh, Associate Professor, Department of Biology, Faculty of Science, Kuwait University, Kuwait for helping in antimicrobial part.

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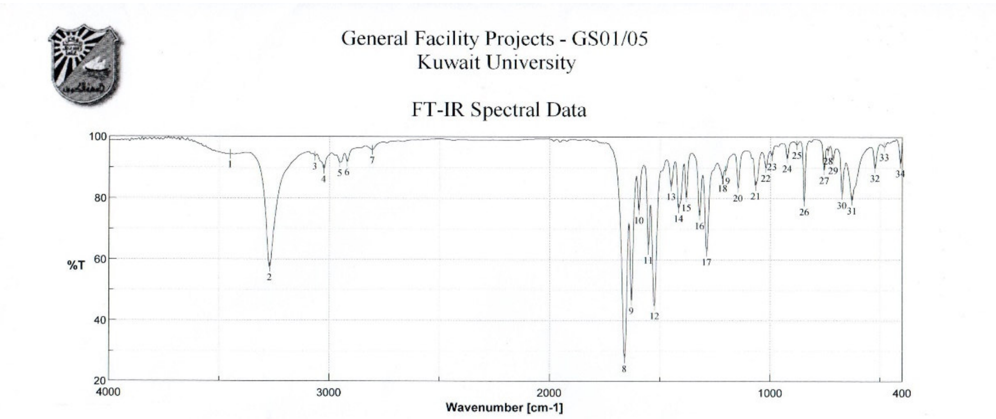
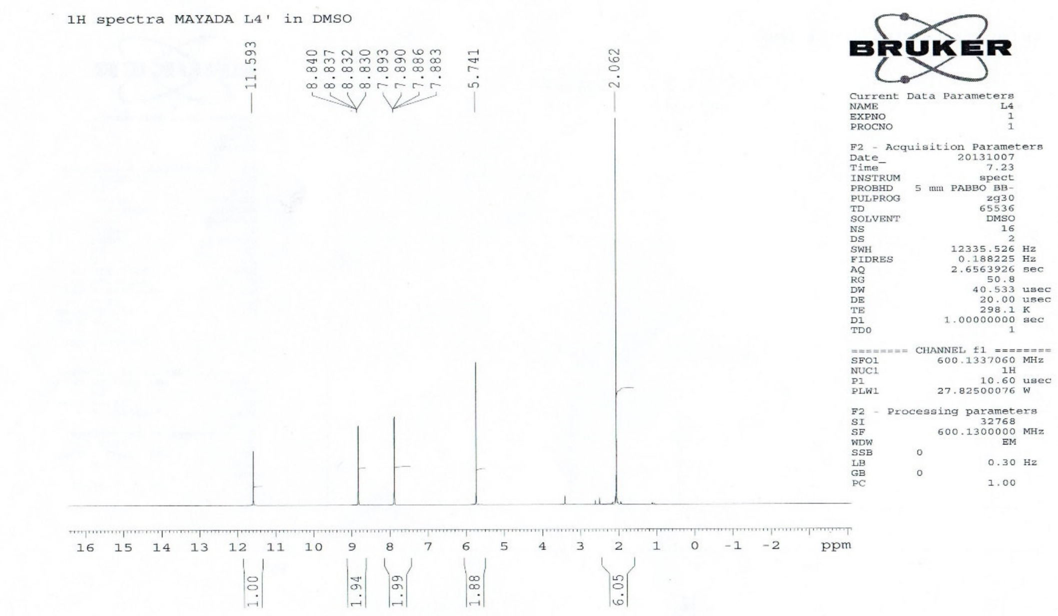


Fig. 1. IR spectrum of 2,5-hexanedione bis(isonicotinylhydrazone) [HINH]`



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EXPNO                    1
PROCNO                   1

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PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                      16
DS                       2
SWH              12335.526 Hz
FIDRES            0.188225 Hz
AQ               2.6563926 sec
RG                    50.8
DW                  40.533 usec
DE                   20.00 usec
TE                   298.1 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           600.1337060 MHz
NUC1                    1H
P1                   10.60 usec
PLW1           27.82500076 W

F2 - Processing parameters
SI                   32768
SF             600.1300000 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
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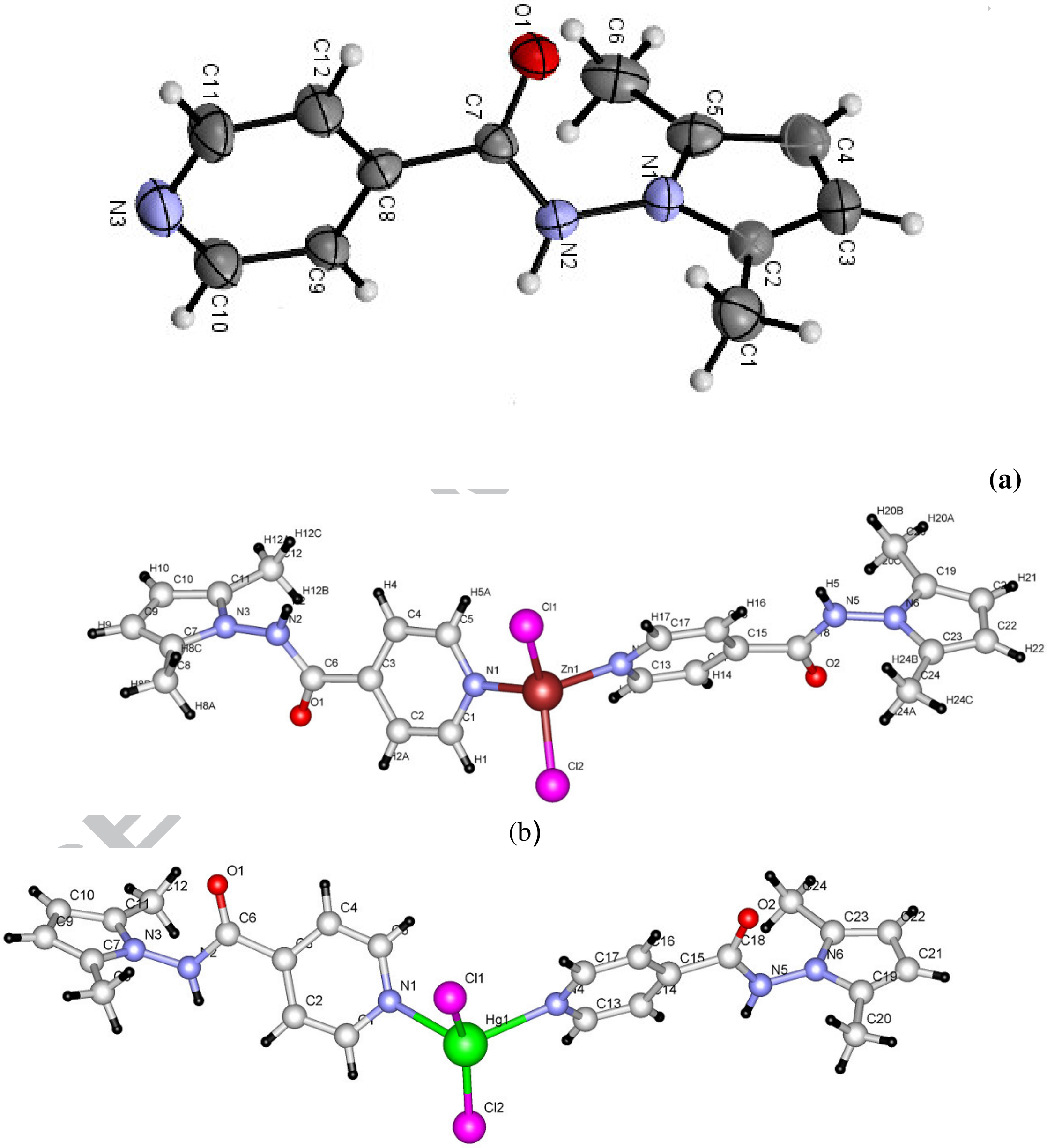
Fig. 2. 1H NMR specrtrum of N-(2,5-dimethyl-1H-pyrrol-1-yl)isonicotinamide [DINA]



(a)

(b)

(c)

Fig. 3. Crystal structure of a) DINH;l b)Zn(II) complex and c) Hg(II) complex)ؤ(

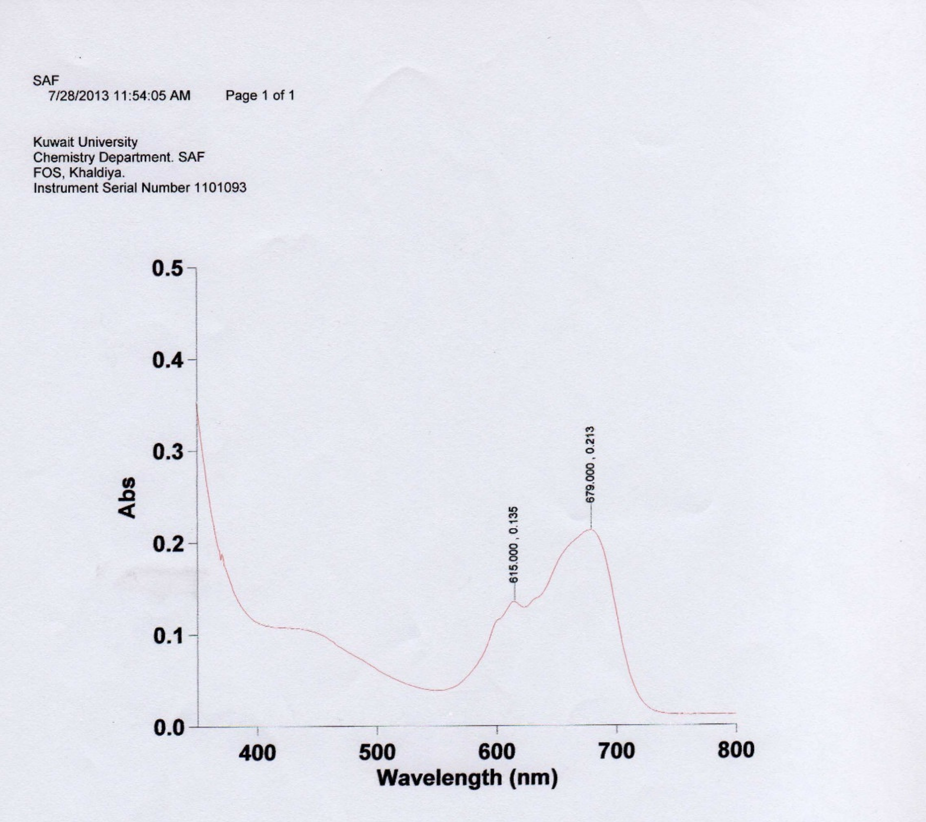


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Fig. 4 . Electronic spectrum of [Co_2(HINH)(H_2O)$_4$$Cl_4$]

Table 1
Crystal structure data of DINH and its Zn(II) and Hg(II) complexes

Property	DINH	$[Hg(DINH)_2Cl_2]$	$[Zn(DINH)_2Cl_2]$
Empirical Formula	$C_{12}H_{13}N_3O$	$C_{24}H_{26}Cl_2N_6O_2Hg$	$C_{24}H_{26}Cl_2N_6O_2Zn$
Formula Weight	215.25	702.00	566.79
Crystal Color, habit	colorless, platelet	colorless, block	colorless, block
Crystal dimensions	0.200 X 0.100 X 0.040 mm	0.200 X 0.100 X 0.050 mm	0.200 X 0.060 X 0.050 mm
Crystal System	triclinic	monoclinic	monoclinic
Lattice Type	Primitive	Primitive	Primitive
Lattice Parameters	a = 13.523(2) Å b = 14.106(2) Å c = 18.811(2) Å α = 99.776(7) ^{o} β = 98.121(7) ^{o} γ = 91.421(7) ^{o}	a = 13.0357(7) Å b = 11.5586(6)Å c = 18.868(2) Å β = 102.641(8) ^{o}	a = 12.4133(8) Å b = 11.8437(7) Å c = 18.929(2) Å β = 103.687(8) ^{o}
Volume	V = 3496.4(7) Å^3	V = 2773.9(3)Å^3	V = 2703.8(3) Å^3
Space Group	P-1 (#2)	$P2_1/c$ (#14)	$P2_1/c$ (#14)
Z value	12	4	4
D_{calc}	1.227 g/cm^3	1.681 g/cm^3	1.392 g/cm^3
F_{000}	1368.00	1368.00	1168.00
μ(MoKα)	0.815 cm^{-1}	7.868 cm^{-1}	11.377 cm^{-1}

Table 2

Empirical formula, molecular weight, color and elemental analysis of HINH, DINH and their complexes

Compound, Empirical formula	M.W Calcd (Found)	Color	**M.P., °C**	**Λ***	**C** Calcd (Found)	**H** Calcd (Found)	**N** Calcd (Found)	**M** Calcd (Found)
HINH $C_{18}H_{20}N_6O_2$	352.41 (353.30)	White	169-171	5.3	61.50 (61.72)	5.72 (5.78)	23.84 (23.03)	--
$[Ni_2(HINH)(H_2O)_4Cl_2]Cl_2.2H_2O$ $C_{18}H_{32}N_6Ni_2O_8Cl_4$	719.81	Pale yellow	>325	95.3	30.03 (29.50)	4.48 (3.92)	11.68 (11.60)	16.43 (16.52)
$[Cu(HINH)(H_2O)_2]Cl_2.H_2O$ $C_{18}H_{26}N_6O_5CuCl_2$	540.91	Reddish brown	> 325	122.8	39.96 (39.97)	4.84 (4.47)	15.53 (15.41)	11.74 (11.34)
$[Co_2(HINH)(H_2O)_4Cl_4]$ $C_{18}H_{26}N_6O_5Co_2Cl_4$	666.16	Brown	322	10.0	32.45 (32.53)	3.93 (3.35)	12.61 (12.76)	17.69 (17.65)
$[Zn_2(HINH)Cl_4].6H_2O$ $C_{18}H_{32}N_6O_8Zn_2Cl_4$	733.03	Yellowish white			29.49 (29.31)	3.57 (3.36)	11.46 (11.17)	17.83 (17.44)
$[Cr_2(HINH)(H_2O)_2Cl_6].2H_2O$ $C_{18}H_{28}N_6O_4Cr_2Cl_6$	741.23	Pale green	> 325	45.1	29.16 (28.88)	3.81 (3.83)	11.34 (11.98)	14.03 (13.78)
$[Hg_2(HINH\text{-}2H)Cl_2]$ $C_{18}H_{20}N_6O_2Hg_2Cl_2$	824.52	Yellow	201-203	28.7	26.22 (27.16)	2.20 (2.52)	10.19 (9.75)	
$[Pd_2(HINH)(H_2O)_2Cl_4].5H_2O$ $C_{18}H_{34}N_6O_9Pd_2Cl_4$	833.18	Yellow			25.94 (25.65)	4.11 (3.56)	10.08 (9.62)	
$[Fe(HINH\text{-}2H)(H_2O)_2]Cl.3H_2O$ $C_{18}H_{28}N_6O_7FeCl$	534.91 (524)	Dark brown	> 325	81.4	40.41 (40.71)	5.27 (4.48)	15.71 (15.85)	

$[Cd_4(HINH)Cl_8].3H_2O$	1139.754	Yellowish white			18.96 (18.20)	2.30 (2.09)	7.37 (9.84)	
DINH $C_{12}H_{13}N_3O$	215.270 (215.3)	Orange	123-125	4.9	66.33 (66.35)	6.95 (6.09)	19.34 (19.35)	-
$[Zn(DINH)_2Cl_2]$ $C_{24}H_{26}N_6O_2ZnCl_2$	566.784	Yellow			50.86 (51.39)	4.62 (5.05)	14.83 (15.20)	11.53 (11.78)
$[Hg(DINH)_2Cl_2]$ $C_{24}H_{26}N_6O_2HgCl_2$	702.800	Yellow			40.89 (39.78)	3.72 (3.91)	11.92 (11.04)	28.49 (28.95)
$[Co(DINH)_2(H_2O)Cl_2]$ $C_{24}H_{28}N_6O_3CoCl_2$	580.206	Reddish	> 325		49.69 (49.54)	4.86 (4.76)	14.48 (14.77)	10.16 (10.34)
$[Cu(DINH)_2(H_2O)_2]Cl_2.3H_2O$ $C_{24}H_{36}N_6O_7CuCl_2$	657.070	Brown	> 325	105.4	43.87 (42.93)	5.52 (4.94)	12.79 (12.74)	9.67 (9.80)

***Molar conductance in 10^{-3} mol L^{-1} DMF solution**

Table 3
IR spectral data (cm^{-1}) of HINH; DINH and their metal complexes

Compound	ν(NH)	ν(C=N)$_{Hy}$	ν(C=N)$_{Py}$	ν(C=O)	υ(M-O)	υ(M-N)
HINH	3270(s)	1628 (s)	1552 (s)	1659 (s)	-	-
$[Ni_2(HINH)(H_2O)_4Cl_2]Cl_2.2H_2O$	3375*(br); 3232 (w); 3144 (w)	1595 (s)	1549 (s)	1653 (s)	570 (w)	479 (w)
$[Cu(HINH)(H_2O)_2]Cl_2. H_2O$	3404*(br)	1617 (w)	1546 (w)	1659 (w)	-	404 (w)
$[Co_2(HINH)(H_2O)_4Cl_4]$	3261(m); 3209(m) 3186(w)	1603 (s)	1549 (s)	1653(s)	542(m)	428 (w)
$[Zn_2(HINH)Cl_4].6H_2O$	3489*(br); 3236(br); 3159(br)	1599 (s)	1549 (s)	1656(s)	553(w)	473 (w)
$[Cr_2(HINH)(H_2O)_2Cl_6].2H_2O$	3450*(br); 3267(m); 3214(m) 3180(w)	1604 (m)	1552 (m)	1652 (s)	512 (br) 496	407 (w)
$[Hg_2(HINH\text{-}2H)Cl_2]$	-	1611 (w)	1550 (m)	-	532 (w) 474 (w)	416 (w)
$[Pd_2(HINH)(H_2O)_2Cl_4].5H_2O$	3449**(br); 3321(m); 3235 (m)	1639(m)	-	1671 (s)	537 (w0 485 (w)	457 (w)
$[Fe(HINH\text{-}2H)(H_2O)_2]Cl.3H_2O$	3397* (br); 3225 (vw)	1611 (w)	1552 (m)	-	509 (m)	453 (w)

					485 (m)	
$[Cd_4(HINH)Cl_8].3H_2O$	3509 (br) 3266 (m)	1611 (w)	1540 (s)	1649 (m)	498 (s)	
DINH	3226 (s)		1594 (m) 1536 (m)***	1672 (s)	-	-
$[Zn(DINH)_2Cl_2]$	3273 (s)		1617 (m) 1588 (w)***	1678 (s)	-	426 (w)
$[Hg(DINH)_2Cl_2]$	3225 (br)		1608 (w) 1536 (w)***	1671 (s)	-	454 (w)
$[Co(DINH)_2(H_2O)Cl_2]$	3421**(br); 3262 (s)		1619 (m) 1541 (m)***	1682 (s)	527 (w)	440 (vw)
$[Cu(DINH)_2]Cl_2.5H_2O$	3443*(br); 3216 (br)		1617 (w) 1508 (w)***	1698 (m)		452 (w)

hydrated water; **coordinated water; ** ν(C=N) of the five membered ring

Table 4

^{1}H and ^{13}C NMR signals (ppm) of HINH; DINH and their complexes

Compound	NH	CH_{py}	CH_2	CH_3	^{13}C signals
HINH	11.631(d, 2H)	8.694 (t, 4H); 7.350 (t, 4H)	2.616 (t, 4H)	2.011-1.927 (d, 6H)	164.44 (C=O); 151.53 $(C=N)_{hy}$; 139.18 $(C=N)_{py}$; 123.25 (CH); 104.63 (CH_2); 12.50 (CH_3)
$[Hg_2(HINH\text{-}2H)Cl_2]$	-	8.658 (s, 4H); 7.711 (s, 4H)	2.510 (s, 4H)		
$[Zn_2(HINH)Cl_4].6H_2O$	10.360 (s, 2H)	8.693 (d, 4H); 7.727 (d, 4H)	2.509 (s, 4H)		164.44; 151.53; 139.18; 123.25; 104.63; 12.50
$[Pd_2(HINH)(H_2O)_2Cl_4].5H_2O$	11.914 (s, 1H); 11.676 (s, 1H)	8.992 (t, 4H); 7.969 (t, 4H)	2.509 (s, 4H)	2.067 (t, 6H)	
DINH	11.593 (s, 1H)	8.840 (q, 2H); 7.883 (q, 2H)	5.741(s, 2H)*	2.062(s, 6H)	164.92; 151.08; 139.38; 127.42; 121.80; 103.88; 11.40
$[Hg(DINH)_2Cl_2]$	11.595 (s, 1H)	8.830 (d, 2H) 7.805 (d, 2H)	5.727 (s, 2H)*	2.062 (s, 6H)	164.84; 150.90; 140.58;127.41; 122.07; 103.91;

*****For the CH protons of the five membered ring

Table 5
Magnetic moments and electronic spectral bands of the compounds

Compound	μ_{eff} (BM)	Intraligand and charge transfer (cm^{-1})	d-d transition (cm^{-1})	Proposed structure	Ligand Field Parameters		
					Dq	B	β
HINH	-	37595	-				
$[Ni_2(HINH)(H_2O)_4Cl_2]\ Cl_2.2H_2O$	2.83*	27025	21140	trigonal bipyramid			
$[Cu(HINH)(H_2O)_2]Cl_2.H_2O$	1.97	-	20080	Square-planar			
$[Co_2(HINH)(H_2O)_4Cl_4]$	4.05*		22200; 16260; 14730	Octahedral	1033	789	0.81
$[Zn_2(HINH)Cl_4].6H_2O$	-	26350; 21730		Tetrahedral			
$[Cr_2(HINH)(H_2O)_2Cl_6].2H_2O$	4.10*	38460	22170; 20410; 15700; 14245	Octahedral	1834	657	0.729
$[Hg_2(HINH\text{-}2H)Cl_2]$	-	39060; 28650	-	Tetrahedral			
$[Pd_2(HINH)(H_2O)_2Cl_4].5H_2O$	0.00	33670; 24570		Square-planar			
$[Fe(HINH\text{-}2H)(H_2O)_2]Cl.3H_2O$	6.39	38460; 29960	21830	Octahedral			
$[Zn(DINH)_2Cl_2]$	-	39370; 37735	-	Tetrahedral			
$[Hg(DINH)_2Cl_2]$	-	39680;	-	Tetrahedral			
$[Co(DINH)_2(H_2O)Cl_2]$	3.59	37590	20530; 16920	Square pyramid			
$[Cu(DINH)_2]Cl_2.5H_2O$		39525; 34965	20920; 13810	Square-planar			

*For one atom only

Table 6

Decomposition steps of the complexes based on TG data

Complex	Middle Temp. ºC	Removed species	Weight loss % Found (Calcd)
HINH	264	- $C_{15}H_{20}N_4O_2$	92.34
	415	- 2C	5.49
	-800	- 1C	2.17
$[Ni_2(HINH)(H_2O)_4Cl_2]$ $Cl_2.2H_2O$	62	- $2H_2O$+Cl	12.76 (10.01)
	372	- $4H_2O$ + 3Cl + C_6H_{10}	32.91 (33.66)
	586	- $2C_5H_4N$	22.33 (21.70)
	> 700	- $C_2H_2N_4$	11.35 (11.41)
		2NiO (residue)	21.65 (20.89)
$[Cu(HINH)(H_2O)_2]Cl_2.H_2O$	50	- H_2O+Cl	8.94 (9.99)
	196	- Cl+$2H_2O$	13.2 (13.11)
	284	- $2C_5H_4N$	30.23 (28.87)
	630	- ($C_7H_{22}N_2$)	22.83 (24.81)
	> 650	CuN_2O_2 (Residue)	24.8 (22.8)
$[Co_2(HINH)(H_2O)_4Cl_4]$	46	- H_2O	2.03 (2.78)
	220	- H_2O	3.05 (2.70)
	334	- $2Cl_2$ +$2H_2O$	23.03 (23.32)
	402	- C_6H_{10}	12.59 (12.31)
	669	- $2C_5H_4N$	23.67(23.42)
	800	- N_4H_2	8.99 (8.70)
	> 800	2 CoO (Residue)	25.79 (22.52)
$[Cr_2(HINH)(H_2O)_2Cl_6].2H_2O$	61	- $2H_2O$ + Cl_2	14.40 (14.42)
	368	- $2H_2O$ + $2Cl_2$ + C_6H_{10}	35.19 (34.54)
	600	- $2C_5H_5N_2$	25.60 (25.09)
	> 600	$Cr_2N_2O_3$ (Residue)	24.75 (24.28)
$[Cu(DINH)_2]Cl_2.5H_2O$	556	- $5H_2O$	12.64 (13.71)

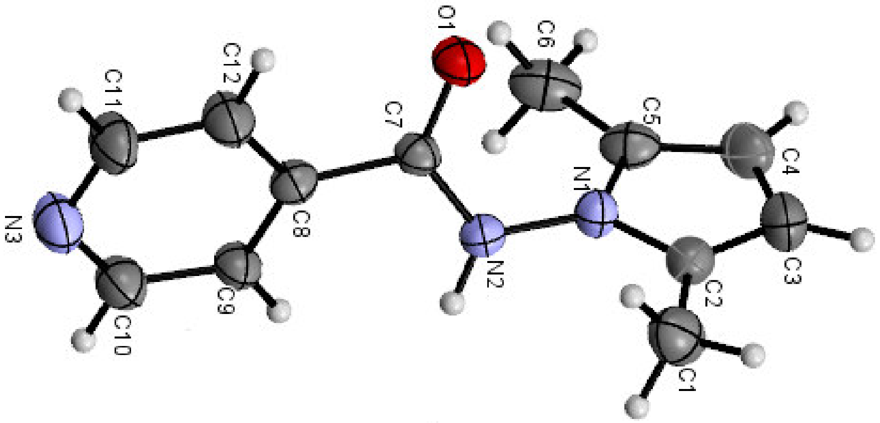
	191	- C_6H_8N	14.9 (14.33)
	290	- Cl_2+($C_6H_5N_2O$)	23.1 (23.8)
[Co(DINH)$_2$(H_2O)Cl_2]	262	- DINH + Cl_2 + H_2O	53.9 (52.4)
	> 300	- DINH + Co	46.1 (47.2)
[Zn(HINH)Cl_2]	303	- $C_{12}H_{13}N_2OCl$	40.54 (41.76)
	572	- C_6H_8N	15.79 (16.61)
	600	- C_6H_4O	15.00 (15.86)
	>800	ZnN_3Cl	29.26 (25.20)
[Hg(HINH-2H)Cl_2]	286	- $C_{24}H_{26}N_6O_2Cl_2$	71.71 (71.35)
	> 400	Hg	29.29 (28.57)

Table 7

Antimicrobial activity of HINH; DINA and some of their complexes (mm)

Serial	Tested microorganisms	HINH	DINA	Co- HINH	Ni- HINH	Pd -HINH	Cd-HINH	Ampicillin	Gentamicin
1	Bacillus sp. M3010	Nil	Nil	Nil	9±1	10±1	27±2		25
2	Bacillus sp. M3010	Nil	Nil	20±2	9±1	9±1	25±1		
3	Staphylococcus aureus PA128	Nil	Nil	14±2	9±1	9±1	21±1	29.5	
4	Staphylococcus aureus PA129	10±1	Nil	18±1	13±2	11±1	15±1		
5	Salmonella sp. PA393	Nil	Nil	12±1	Nil	7±1	14±1		
6	Salmonella sp. PA392	Nil	10±1	11±1	Nil	Nil	20±2		
7	E.coli PA149	Nil	Nil	13±1	Nil	Nil	20±1	27	20
8	E.coli PA151	Nil	Nil	Nil	Nil	Nil	7±1		
9	Pseudomonas aeruginosa Ps-8	Nil	Nil	12±2	Nil	Nil	Nil		
10	Pseudomonas aeruginosa Ps-15	Nil	Nil	12±2	11±1	10±1	24±2		
11	Candida albicans PA47	Nil	Nil	10±1	Nil	9±1	30±1		48
112	Candida albicans PA48	30±2	Nil	10±1	Nil	11±2	30±1		
13	Saccharomyces cereviciae	11±1	9±1	14±1	10±1	12±1	40±2		

Numbers represent the diameter of zone inhibition in mm with standard deviation of three independent experiments;
Nil denotes the absence of zone of inhibition.



(a)

Crystal structure of DINH

The reaction between 2,5-hexanedione and isonicotinic acid hydrazide gave two products. One is ethanolic insoluble named as 2,5-hexanedione bis(isonicotinylhydrazone). The soluble one is named as N-(2,5-dimethyl-1H-pyrrol-1-yl)iso-nicotinamide and isolated as crystals and analyzed as shown in the figure. New complexes were synthesized from the two ligands.

- X-ray crystallography of N-(2,5-dimethyl-1H-pyrrol-1-yl)isonicotinamide and its Zn(II) and Hg(II) complexes
- Cr(III), Fe(III), Co(II), Ni(II) Cu(II), Zn(II), Cd(II), Hg(II) and Pd(II) of 2,5-hexanedione bis(isonicotinylhydrazone) [HINH] and Co(II), Cu(II), Zn(II) and Hg(II) complexes of N-(2,5-dimethyl-1H-pyrrol-1-yl)isonicotinamide [DINH]
- Octahedral, tetrahedral and square-planar stereochemistries for the complexes
- The antimicrobial activity of the ligand and its complexes