Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Der Chemica Sinica, 2014, 5(1): 157-160

ISSN: 0976-8505
CODEN (USA) CSHIA5

Studies on metal complexes of some novel hydrazones

Ushma Joshi and *Sunil I. Marjadi

Shree Nutan Kelavani Mandal, Valsad, India

ABSTRACT

Ethyl-3-(2-(4-nitrophenyl)hydrazono)butanoate (NEP) was prepared from ethyl aceto acetate and 4-nitrophenyl hydrazine in the presence of acid. Ethyl-3-(2-(4-nitrophenyl)hydrazono)butanoate (NEP) was characterized by elemental analysis and spectral studies. The transition metal chelates viz. Cu(II), Ni(II), Co(II),Mn(II) and Zn(II) of NEP were prepared and characterized by metal-ligand (M:L) ratio, IR and reflectance spectroscopic and magnetic properties. The antifungal activity of NEP and its metal chelates was screened against various fungi. The results show that all these samples are good antifungal agents.

Keywords: Ethyl-3-(2-(4-nitrophenyl)hydrazono)butanoate, Spectroscopies study, Magnetic moment, Antifungal properties.

INTRODUCTION

Hydrazides containing compounds have not found wide application in organic synthesis, but several of these molecules display significant biological activity [1,2]. In recent years, extensive study of hydrazides and their derivatives has shown diverse biological activities like antibacterial, antifungicidal, analgesic, chemotherapeutic and anti-inflammatory properties [3-9]. Hydrazides play an important role in inorganic chemistry, as they easily form stable complexes with most transition metal ions. The development of the field of bioinorganic chemistry has increased the interest in hydrazide complexes, since it has been recognized that many of these complexes may serve as models for biologically important species [10,11]. Coordination compounds derived from aryl hydrazones have been reported to act as enzyme inhibitors and are useful due to their pharmacological applications [12-14]. In view of the importance of such hydrazones, we describe here the synthesis and characterization of Cu^{+2}, Ni^{+2}, Co^{+2}, Mn^{+2} and Zn^{+2} complexes of ethyl-3-(2-(4-nitrophenyl)hydrazono)butanoate (NEP) (Scheme-1).

MATERIALS AND METHODS

All the chemicals used were of laboratory grade.

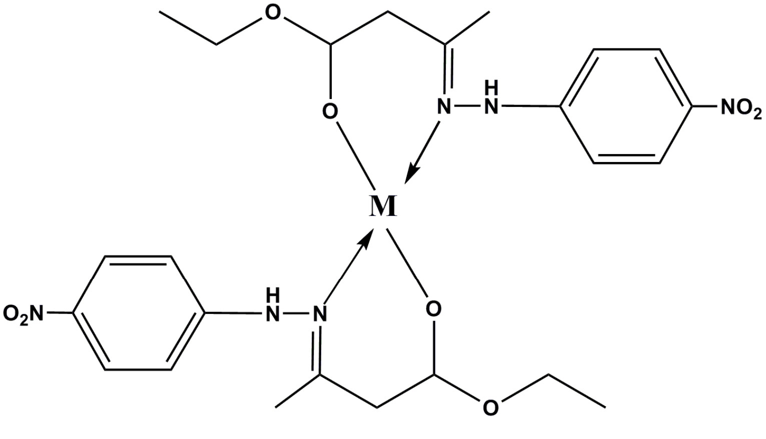
Synthesis of ethyl-3-(2-(4-nitrophenyl)hydrazono)butanoate (NEP): In a Erlenmeyer flask, Ethyl acetoacetate (0.1 mol) and 4-nitrophenyl hydrazine(0.12mol) was mixed in presence of conc.HCl(0.5ml) and allowed to stand overnight. The resulting mass was added to 50ml dry ether and washed with water. Then evaporation of ether gave product which was crystallized by Ethanol. It melts at 134°C.

Analysis:

		C%	H%	N%
Elemental Analysis	Calculated:	54.33	5.70	15.84
$C_{12}H_{15}N_3O_4$ (265)	Found :	54.30	5.68	15.81

IR Spectral Features (cm^{-1}): 3310 (NH), 1615(C=O), 1589(C=N), 1061(N-N), 1545, 1350(NO_2).

NMR Signals: δ ppm 8.24-7.29 (m, 4H, Ar-H), 6.85 (s, NH, 1H), 4.18(q, O-CH_2, 2H), 2.71(s, CH_2, 2H), 1.33(t, 3H, CH_3, 3H), 1.96(s, 3H, CH_3, 3H).



Metal Ccomplex of ethyl 3-(2-(4-nitrophenyl)hydrazono)butanoate
Where M=Cu^{+2},Co^{+2},Ni^{+2},Mn^{+2},Zn^{+2}

Scheme-I

Synthesis of metal chelates of NEP:
The metal chelates of NEP with Cu^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, and Ni^{2+} metal ions were prepared in two steps. All the metal chelates were prepared in an identical procedure.

Preparation of NEP solution:
NEP (0.05 mol) was taken in 500 ml beaker and formic acid (85% v/v) was added up to slurry formation. To this slurry, distilled water was added till the complete dissolution of NEP. It was then diluted to 100 ml with distilled water.

Synthesis of NEP-metal-chelates:
In an ethanolic solution of metal chloride (0.005 mol) and 20 ml of above mentioned NEP solution (i.e. containing 0.01 M NEP) was added with vigorous stirring at room temperature. The appropriate pH was adjusted by addition of sodium acetate for complete precipitation of metal chelate. The precipitates were digested on a boiling water bath. The precipitates of chelate were filtered off, washed by water and air-dried.

Measurements
The elemental contents were determined by Thermo Finigen Flash1101 EA (Itally), the metals were determined volumetrically by Vogel's method [15]. To a 100 mg chelate sample, each 1 ml of HCl, H_2SO_4 and $HClO_4$ were added and then 1 g of $NaClO_4$ was added. The mixture was evaporated to dryness and the resulting salt was dissolved in double distilled water and diluted to the mark. From this solution the metal content was determined by titration with standard EDTA solution. Infrared spectra of the synthesized compounds were recorded on Nicolet 760 FT-IR spectrometer. NMR spectrum of NEP was recorded on 60 MHz NMR spectrophotometer. Magnetic susceptibility measurement of the synthesized complexes was carried out on Gouy Balance at room temperature. Mercury tetrathio cynatocobalate (II) Hg [$Co(NCS)_4$] was used as a calibrant. The electronic spectra of complexes in solid were recorded on at room temperature. MgO was used as reference. Antifungal activity of all the samples was monitored against various fungi, following the method reported in literature [16].

RESULTS AND DISCUSSION

The synthesis of ethyl-3-(2-(4-nitrophenyl)hydrazono)butanoate (NEP) was made by a simple condensation reaction of ethyl acetoacetate and 4-nitrophenyl hydrazine. The resulted NEP ligand was white crystalline powder. The C,H,N contents of NEP (Table-1) are consistent with the structure predicted (Scheme-1). The IR spectrum of NEP comprises the important bands of C=N at 1592 cm^{-1}.

Table-1: Analysis of NEP ligand and its metal chelates

Empirical Formula	**Mol. Wt. gm/mole**	**Yield (%)**	**Elemental Analysis**							
			C%		**H%**		**N%**		**M%**	
			Found	**Cald**	**Found**	**Cald**	**Found**	**Cald**	**Found**	**Cald**
$C_{12}H_{15}N_3O_4$	265	74	54.28	54.33	5.66	5.70	15.80	15.84	-	-
$C_{24}H_{30}N_6O_4Cu^{2+}$	529.54	70	54.38	54.39	5.65	5.67	15.84	15.86	11.98	12.00
$C_{24}H_{30}N_6O_4Co^{2+}$	524.94	68	54.84	54.86	5.70	5.71	15.97	16.00	11.19	11.21
$C_{24}H_{30}N_6O_4Ni^{2+}$	524.71	70	54.87	54.89	5.70	5.72	16.00	16.01	11.17	11.19
$C_{24}H_{30}N_6O_4Mn^{2+}$	520.94	72	55.26	55.28	5.73	5.76	16.10	16.12	10.53	10.55
$C_{24}H_{30}N_6O_4Zn^{2+}$	531.38	69	54.18	54.20	5.64	5.65	15.79	15.81	12.28	12.30

The broad band due to –NH group appeared at 3310 cm^{-1}. The band is observed at 1589 vibration of C=N of NEP. The NMR spectrum of NEP in DMSO indicates that the singlet of 2 H at 2.74 for N-CH_2 and 4.16 O-CH_2 group. While the singlet at 6.89 δ ppm due to –NH group. The aromatic protons are appeared in multiplicity at 8.24-7.29 δ. It is m.p. is 134°C. Thus the structure of NEP is confirmed as shown in Scheme-I.

The metal and C, H, N contents of metal chelates of NEP (Table-I) are also consistent with the predicted structure. The results show that the metal: ligand (M:L) ratio for all divalent metal chelate is 1:2.

TABLE-2: Spectral features and magnetic moment of NEP metal chelates

Metal Chelates	**Electronic spectral data (cm^{-1})**	**Transition**	**μ_{eff} (BM)**
NEP-Cu^{2+}	23449 13211	Charge transfer $^2B_{1g}\rightarrow{}^2A_{1g}$	1.86
NEP-Ni^{2+}	22594 15368	$^3A_{1g}\rightarrow{}^3T_{1g}(P)$ $^3A_{1g}\rightarrow{}^3T_{1g}(F)$	3.71
NEP-Co^{2+}	23731 19100 8920	$^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$ $^4T_{1g}(F)\rightarrow{}^4T_{2g}$ $^4T_{1g}(F)\rightarrow{}^4T_{2g}(P)$	4.74
NEP-Mn^{2+}	23231 19040 16838	$^6A_{1g}\rightarrow{}^6A_{2g}\ {}^4E_g$ $^6A_{1g}\rightarrow{}^4T_{2g}$ (4G) $^6A_{1g}\rightarrow{}^4T_{1g}$(PG)	5.54
NEP-Zn^{2+}	-----	---------	Diamag.

The infrared spectra of all the chelates are identical and suggest the formation of all the metalocyclic compound by the absence of band characteristic of free –OH group of parent NEP. The other bands are almost at their respectable positions as appeared in the spectrum of parent-NEP ligand. However, the band due to (M-O) band could not be detected as it may appear below the range of instrument used. The important IR Spectral data are shown in Table-2.

Magnetic moments of metal chelates are given in Table-2. The diffuse electronic spectrum of Cu^{2+} chelates shows two broad bands around 13211 and 23449 cm^{-1}. The first band may be due to a $^2B_{1g}\rightarrow{}^1A_{1g}$ transition. While the second band may be due to charge transfer. The first band shows structures suggesting a distorted octahedral structure for the Cu^{2+} metal chelates. The higher value of the magnetic moment of the Cu^{2+} chelate supports the same. The Co^{2+} metal chelate gives rise to two absorption bands at 23731 and 19100 cm^{-1}, which can be assigned $^4T_{1g}\rightarrow{}^2T_{2g}$, $^4T_{1g}\rightarrow{}^4T_{1g}$(P)transitions, respectively. These absorption bands and the µeff value indicate an octahedral configuration of the Co^{2+} metal chelate [17]. The spectrum of Mn^{2+} polymeric chelate comprised two bands at 19040 cm^{-1} and 23231 cm^{-1}. The latter does not have a very long tail. These bands may be assigned to $^6A_{1g}\rightarrow{}^4T_{2g(G)}$ and $^6A_{1g}\rightarrow{}^4A_{2g(G)}$ transitions, respectively. The high intensity of the bands suggests that they may have some charge transfer character. The magnetic moment is found to be lower than normal range. In the absence of low temperature measurement of magnetic moment it is difficult to attach any significance to this. As the spectrum of the metal chelate of Ni^{2+} show two distinct bands at 22594 and 15368 cm^{-1} are assigned as $^3A_{1g}(F)\rightarrow{}^3T_{1g}(P)$ and $^3A_{1g}(F)\rightarrow{}^3T_{1g}(F)$ transition, respectively suggested the octahedral environment for Ni^{2+} ion. The observed µeff values in the range 1.87-5.56 B.M are consistent with the above moiety [17].

The examination of antifungal activity of NEP ligand and its all chelates (Table-3) reveals that the ligand is moderately toxic against fungi, while all the chelates are more toxic than ligand. Among all the chelates the Cu^{2+} chelate is more toxic against fungi.

TABLE-3: Antifungal activity of NEP ligand and its metal chelates

Sample	Zone of inhibition of fungus at 1000 ppm (%)			
	Penicillum expansum	***Rhisopus Nigricans***	***Nigrospora Sp.***	***Botrydeplaia thiobromine***
NEP	55	66	62	68
NEP-Cu^{2+}	77	71	84	83
NEP-Zn^{2+}	67	84	83	82
NEP-Ni^{2+}	77	78	69	79
NEP-Co^{2+}	76	75	75	82
NEP-Mn^{2+}	69	74	79	79

Acknowledgement
We are thankful to the Management & Principal of B. K. M. Science College, Valsad for providing research facility.

REFERENCES

[1] Baleizno C, Gigante B, Garcia H and Corma A., *J.Catal.*, **2004,**221,77.
[2] Bandini M, Cozzi P. G.and Umani-Ronichi A., *Chem. comun.*,**2002**,919.
[3] Janin Y., *Bioorg. and Medi. Chem*. **2007,** 15, 2479.
[4] Gursoy E and Guzeldemirci–Ulusoy N., *Eur. J. of Medi. Chem.* **2007,** 42, 320.
[5] Rao M R, Hart K, Devanna N and Chandrasekhar K B, *Asian J. of Chem.*,**2008,** 20, 1402.
[6] Kalsi R, Shrimali M, Bhalla T N and Barthwal J P, *Ind. J. of Pharm. Sci*. **2006,** 41, 353.
[7] Nayyar A and Jain R, *Curr. Medi. Chem*. **2006,** 12, 1873.
[8] Shah P. J., Shah A. I. and Raj D. S., *Der Pharmacia Sinica,* **2010**, 1 (3), 165.
[9] Farghaly A R and El-Kashef H, *ARKIVOC*. **2006,** 11, 76.
[10] Shah P. J., Shah A. I. and Raj D. S., *Der Chemica Sinica***, 2010**,1(3), 70.
[11] Dave B.P., Patel B.C. and Shah P. J., *J. Chem.Pharm.Res.*,**2013**, 5(3),112.
[12] Gujarathi S C, Shah A R, Jagdale S C, Datar P A, Choudhari V P and Kuchekar B S, *Inter. J. of Phar. Sci.* **2010,** 3, 1.
[13] Qian R and Mingshe Z, *Chem. Res. Toxicol*. **2010,** 23 (5), 909.
[14] Shah P. J., Solanki Y.K., Shah A.R. and Raj D. S., *J. Chem.Pharm.Res.*,**2012**, 4(8),3950.
[15] Vogel A.I., *Textbook of Quantitative Chemical Analysis,* ELBS 5th Edn. London, **1996**.
[16] Baily W.R. and Scott E.G., *Diagnostic Microbiology*, The C. V. Moshy Co. St. Lovis,**1966**, 257.
[17] Patil B.R., *Oriental J.Chem*.,**2006**,18,547.