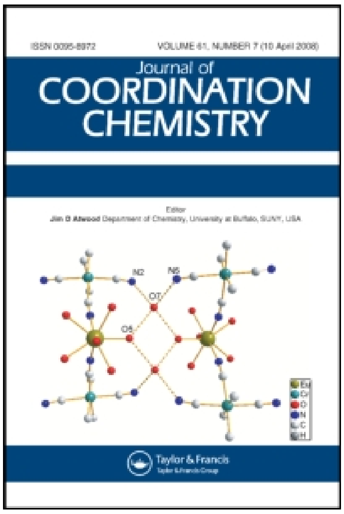

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and spectroscopic characterization of metal complexes with naphthofuran-2-carbohydrazide Schiff 's base

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To cite this Article Shashidhar, Shivakumar, K. , Reddy, P. Vithal and Halli, M. B.(2007) 'Synthesis and spectroscopic characterization of metal complexes with naphthofuran-2-carbohydrazide Schiff 's base', Journal of Coordination Chemistry, 60: 3, 243 — 256

To link to this Article: DOI: 10.1080/00958970601112051

URL: http://dx.doi.org/10.1080/00958970601112051

Journal of Coordination Chemistry
Vol. 60, No. 3, 10 February 2007, 243–256

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Synthesis and spectroscopic characterization of metal complexes with naphthofuran-2-carbohydrazide Schiff's base

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(*Received 19 January 2006; in final form 22 June 2006*)

Two Schiff-base ligands (**I**) naphthofuro-[phenylmethine]carbohydrazone [NPMC] and (**II**) naphthofruo-[3,4-dimethoxyphenylmethine]carbohydrazone [NDMeOPMC] were prepared by reaction between naphthofuran-2-carbohydrazone and benzaldehyde or 3,4-dihydroxybenzaldehyde, respectively. Both ligands are bidentate by coordinating through carboxy oxygen and azomethine nitrogen atoms. Complexes of the type MLX_n were obtained. where M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), UO_2(II) and Th(IV), L = [NPMC] or [NDMeOPMC] and $X = Cl_2$ for Co(II), Cu(II), Ni(II), Zn(II), Cd(II) and Hg(II) complexes, $X = NO_3$, $n = 2$ for UO_2(II) complexes and $X = NO_3$, $n = 4$ for Th(IV) complexes. All the complexes and ligands were characterized IR, electronic, ^{1}H NMR, ESR, conductance data and magnetic susceptibility measurements.

1. Introduction

Transition and non-transition metal complexes with Schiff-base ligands played a vital role in the development of coordination chemistry. Schiff-base ligands have been studied extensively because of their use in biological system [1a, b], analytical chemistry [2] and in non-linear optics [3]. Interest in Schiff bases and their metal complexes is enhanced by proteins and enzymes requiring metal ions for activity, catalytic activity in the hydrogenation of olefins [4], complexing ability towards toxic metals [5] and so on. Compounds with benzofuran/naphthofuran occur in natural products and are biologically important compounds. Some benzofuran derivatives viz., 2-acetylbenzofurans [6], and 2-nitrobenzofurans [7] are used as antimicrobial, anti-inflammatory and diuretic agents [8] particularly with amiodarone hydrochloride found to be a highly active antiarrhythamic drug [9, 10]. In the present investigation, the biological importance of naphthofuran derivatives and Schiff bases led to study of complexes of Schiff bases naphthofuro-[phenylmethine]carbohydrazone [NPMC] and naphthofuro-[3,4-dimethoxyphenylmethine]carobhydrazone [NDMeOPMC] derived from reaction

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970601112051

between naphthofuran-2-carbohydrazide and benzalaldehyde/3,4-dimethoxybenzaldehyde, with metal ions viz., Co(II), Cu(II), Ni(II), Zn(II), Cd(II), Hg(II), UO_2(II) and Th(IV).

2. Experimental

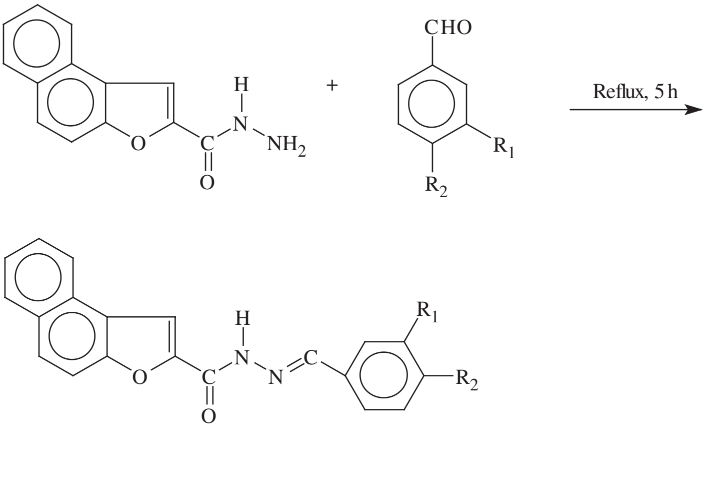
All chemicals used were of analytical reagent or equivalent grade. Naphthofuran-2-carboydrazide was prepared by the known method [11]. The metal and chloride contents were determined by Vogel's method [12]. Nitrogen content was estimated by Kjeldahl's method/microanalytically.

2.1. *Preparation of naphthofuro-[phenylmethine]carbohydrazone [NPMC] and naphthofuro-[3,4-dimethoxy phenylmethine]carbohydrazone [NDMeOPMC]*

The benzaldehyde/3,4-dimethoxybenzaldehyde (0.1 mol, 0.212 g and 0.1 mol, 0.332 g) in ethyl alcohol 20 mL was added to an ethanolic solution (20 mL) of naphthofuran-2-carbohydrazide (0.1 mol, 0.452 g). The reaction mixture was heated under reflux on a water bath for about 3 h. On partial evaporation of the solvent and cooling the reaction mixture to room temperature, the light yellowish colored Schiff base separated out. The product was filtered, washed with ethyl alcohol several times and recrystallized from ethyl alcohol and dried in vacuum over fused $CaCl_2$.

The reaction is as shown below on figure 1:

Mol .formula [NPMC], $C_{20}H_{14}O_2N_2$, m.p. 226°C yield = 80%
[NDMeOPMC], $C_{22}H_{18}O_4N_2$, m.p. 218°C yield = 80%



where, $R_1 = R_2 = H$ [NPMC]
$R_1 = R_2 = OCH_3$ [NDMeOPMC]

Figure 1. Structure of ligand.

2.2. *Preparation of metal complexes*

The metal complexes were prepared by reaction between Schiff base ligand (0.636 g [NPMC]; 0.756 g [NDMeOPMC]; 0.1 mol) in ethyl alcohol (20 mL) with the corresponding metal chlorides/nitrates (0.1 mol) in ethyl alcohol (10 mL). The reaction mixture was heated under reflux for 3–4 h on a water bath. In the case of Zn(II), Cd(II) and Co(II) complexes, the pH of the solution was adjusted to 5–6 by adding 50% (2–3 mL) aqueous ethanolic solution of sodium acetate. The light colored complexes separated on cooling to room temperature, were filtered, washed with alcohol and water, then dried in open air and kept in vacuum desiccators. The formation of complexes may be represented by the following equations.

$$\underset{(\mathrm{L=NPMC/NDMeOPMC})}{n\mathrm{NiCl_2 \cdot 6H_2O} + n\mathrm{L}} \xrightarrow[\text{Reflux, 3 h}]{\text{Ethanol}} [\mathrm{NiLCl_2}]_n + 6\mathrm{H_2O} \tag{1}$$

$$\underset{(\mathrm{L=NPMC/NDMeOPMC})}{n\mathrm{CoCl_2 \cdot 6H_2O} + n\mathrm{L}} \xrightarrow[\text{Reflux, 3 h}]{\text{Ethanol}} [\mathrm{CoLCl_2}]_n + 6\mathrm{H_2O} \tag{2}$$

$$\underset{(\mathrm{L=NPMC/NDMeOPMC})}{n\mathrm{CuCl_2 \cdot 2H_2O} + n\mathrm{L}} \xrightarrow[\text{Reflux, 3 h}]{\text{Ethanol}} [\mathrm{CuLCl_2}]_n + 2\mathrm{H_2O} \tag{3}$$

$$\underset{\substack{(\mathrm{L=NPMC/NDMeOPMC} \\ \mathrm{M=Cd,\ Zn\ or\ Hg})}}{\mathrm{MCl_2} + n\mathrm{L}} \xrightarrow[\text{Reflux, 3 h}]{\text{Ethanol}} [\mathrm{MLCl_2}] \tag{4}$$

$$\underset{\substack{(\mathrm{L=NPMC/NDMeOPMC,} \\ \mathrm{M=UO_2(II)},\ x{=}2\quad \mathrm{Th(IV)},\ x=4)}}{\mathrm{M(NO_3)}_x \cdot 6\mathrm{H_2O} + n\mathrm{L}} \xrightarrow[\text{Reflux, 3 h}]{\text{Ethanol}} [\mathrm{ML(NO_3)}_x] + 6\mathrm{H_2O} \tag{5}$$

2.3. *Physico-chemical studies*

The complexes were analyzed for their metal, chloride and nitrogen contents following standard methods [12]. Magnetic susceptibility measurements were made on a Gouy balance at room temperature using $\mathrm{Hg[Co(SCN)_4]}$ as the calibrant. Electronic spectra were recorded on a Hitachi 150-20 model spectrophotometer in the range 200–1100 nm in DMF (10^{-3} M) solution. IR spectra were recorded on Impact 410 Nicolet FTIR and Perkin-Elmer 783 model spectrophotometers in the region 4000–250 $\mathrm{cm^{-1}}$ in KBr discs. ^{1}H NMR spectra were obtained in $\mathrm{CDCl_3}$/DMSO-$\mathrm{d_6}$ on a Brucker 300 MHz spectrometer using TMS as an internal reference. The CHN analyses were carried out on a Perkin–Elmer 240 model micro analyzer at CDRI Lucknow. ESR spectra of Cu(II) complexes in polycrystalline state (solid) were recorded on Varian E-4 X-band using TCNE as a '*g*' marker at room temperature. Mass spectra of ligands [NPMC] and [NDMeOPMC] were recorded on a JL2518X LRP spectrophotometer from RSIC-IIT Madras. The conductivity measurements were made on an Elico CM-82 conductivity bridge using DMF (10^{-3} M) solution.

2.4. *Biological activity*

2.4.1. Antibacterial screening using the agar cup-plate method: peptone 10 g, NaCl 5 g, Beef extract 3 g, Nutrient agar 15 g, was used as the medium. The sterile molten medium held at 55°C was poured aseptically into sterile petri dishes and allowed to solidify. After solidification 24 h culture (incubated at 37°C) of each of the bacterial cultures was spread on the agar medium with the help of a glass spreader. Then with the help of the sterile cork borer (8 mm) cups were punched and scooped out from the agar at suitable distances from each other. The cups were filled with 0.1 mL of the test solutions ($10\,\mathrm{mg\,mL^{-1}}$ in DMF) streptomycin ($10\,\mathrm{mg\,mL^{-1}}$) was used as the standard antibiotic and DMF as the control. The plates were incubated upright at 37°C for 24 h before reading the inhibition zones around each cup.

2.4.2. Antifungal screening using cup-plate method. Sabouraud Dextrose Agar (SDA) was used for the screening of test compounds for their antifungal activity.

The test compounds were screened for their antifungal activity with the agar cup diffusion method using SDA ($10\,\mathrm{mg\,mL^{-1}}$) as the medium against *Aspergillus niger*, *Aspergillus flavous* and *Aspergillus fumigatus*. The fungal inoculate was prepared in SDA broth and incubated at room temperature for 3 days; the fungal spores were harvested in sterile DW and used as inoculate.

The sterile molten medium held at 55°C was poured aseptically into sterile petri dishes and allowed to solidify. After solidification 3 days, culture (incubated at 37°C) of each of the bacterial cultures was spread on the agar medium with the help of a glass spreader. Then with the help of the sterile crock borer (4 mm) cups were punched and scooped out from the agar at suitable distances from each other. The cups were filled with 0.1 mL of the test solutions ($10\,\mathrm{mg\,mL^{-1}}$ in DMF) streptomycin ($10\,\mathrm{mg\,mL^{-1}}$) was used as the standard antibiotic and DMF as the control. The plates were incubated upright at 37°C for 3 days before reading the inhibition zones around each cup [13, 14].

3. Results and discussion

The analytical data for the complexes indicate MLX_n stiochiometry for all the complexes, where L = NPMC/NDMeOPMC, M = metal ions, X = Cl/NO_3 and $n = 2/4$ (table 1). The melting points of all complexes are above 280°C; the complexes are stable in air. All the complexes are partially or insoluble in common organic solvents and soluble in DMF, DMSO and pyridine. The molar conductances in DMF (10^{-3} M) solution fall in the range of $8.90–19.40\,\mathrm{Ohm^{-1}\,cm^{2}\,mol^{-1}}$, indicating the non-electrolytic nature of the complexes [15].

3.1. *Magnetic susceptibility of Schiff-base metal complexes*

The magnetic susceptibility values for Co(II), Cu(II) and Ni(II) paramagnetic complexes are given in table 1. The observed μ_{eff} values for Co(II) complexes (4.84 BM and 5.10 BM) are helpful in determining the geometry around Co(II), suggesting octahedral geometry for both Co(II) complexes [16]. The measured

Table 1. Analytical, molar conductance and magnetic susceptibility data of the complexes.

Ligand/Complex	Colour	Mol. wt.	M.p. (°C)	Yield (%)	Elemental analysis % found/(calculated)					Λ_M (Ohm^{-1} cm^2 mol^{-1})	μ_{eff} (BM)
					C	H	N	M	Cl		
NPMC											
[$C_{20}H_{14}O_2N_2$]	–	314	226	85	76.00 (76.43)	4.50 (4.46)	4.45 (4.458)	–	–	–	
[$Co(C_{20}H_{14}O_2N_2)Cl_2]_n$	Dark brown	443.93	280	75	54.00 (54.06)	3.00 (3.15)	6.09 (6.30)	13.04 (13.27)	15.87 (15.99)	10.55	4.84
[$Ni(C_{20}H_{14}O_2N_2)Cl_2]_n$	Brownish green	443.69	290	80	53.82 (54.09)	3.00 (3.15)	6.11 (6.31)	13.20 (13.23)	16.12 (16.00)	15.05	2.90
[$Cu(C_{20}H_{14}O_2N_2)Cl_2]_n$	Brown	448.5	>300	70	53.40 (53.51)	3.20 (3.12)	6.42 (6.24)	14.23 (14.16)	16.01 (15.83)	8.90	1.85
[$Zn(C_{20}H_{14}O_2N_2)Cl_2$]	Orange	450.38	>300	75	53.10 (53.29)	3.00 (3.11)	6.50 (6.22)	14.10 (14.52)	15.28 (15.76)	11.25	–
[$Cd(C_{20}H_{14}O_2N_2)Cl_2$]	Yellow	497.41	>300	75	48.40 (43.25)	3.00 (2.81)	5.12 (5.63)	22.80 (22.60)	14.65 (14.27)	11.40	–
[$Hg(C_{20}H_{14}O_2N_2)Cl_2$]	Light brown	585.59	290	80	40.88 (40.98)	2.50 (2.39)	4.20 (4.78)	34.03 (34.25)	13.02 (12.13)	10.00	–
[$Th(C_{20}H_{14}O_2N_2)(NO_3)_4$]	Yellowish	794.04	>300	80	30.10 (30.23)	1.60 (1.76)	10.16 (10.58)	29.60 (29.22)	–	18.80	–
[$UO_2(C_{20}H_{14}O_2N_2)(NO_3)_2$]	Yellowish	708.03	>300	75	34.00 (33.89)	2.00 (1.98)	7.69 (7.91)	33.13 (33.62)	–	12.25	–
NDMeOPMC											
[$C_{22}H_{18}O_4N_2$]		374	218	80	70.40 (70.59)	5.00 (4.81)	3.70 (3.74)	–	–	–	–
[$Co(C_{22}H_{18}O_4N_2)Cl_2]_n$	Dark brown	503.93	290	80	52.40 (52.39)	3.50 (3.57)	5.05 (5.56)	11.17 (11.69)	14.37 (14.09)	17.05	5.10
[$Ni(C_{22}H_{18}O_4N_2)Cl_2]_n$	Brownish green	503.69	>300	75	52.50 (52.41)	3.60 (3.57)	5.52 (5.55)	11.26 (11.65)	14.46 (14.09)	14.8	3.05
[$Cu(C_{22}H_{18}O_4N_2)Cl_2]_n$	Brown	508.5	>300	80	51.80 (51.92)	3.40 (3.34)	5.83 (5.50)	12.67 (12.49)	14.28 (13.96)	9.05	2.05
[$Zn(C_{22}H_{18}O_4N_2)Cl_2$]	Orange	510.38	>300	75	51.80 (51.73)	3.60 (3.53)	5.87 (5.49)	12.79 (12.81)	14.30 (13.91)	12.00	–
[$Cd(C_{22}H_{18}O_4N_2)Cl_2$]	Yellow	557.41	295	75	47.50 (47.36)	3.00 (3.23)	4.85 (5.02)	20.05 (20.17)	13.10 (12.74)	18.74	–
[$Hg(C_{22}H_{18}O_4N_2)Cl_2$]	Light brown	645.59	>300	75	41.00 (40.89)	3.80 (2.79)	4.61 (4.34)	31.48 (31.07)	11.38 (10.99)	10.20	–
[$Th(C_{22}H_{18}O_4N_2)(NO_3)_4$]	Light yellowish	854.04	>300	70	31.00 (30.91)	2.20 (2.11)	10.21 (9.84)	27.45 (27.17)	–	19.40	–
[$UO_2(C_{22}H_{18}O_4N_2)(NO_3)_2$]	Light yellowish	768.03	>300	80	34.40 (34.37	2.40 (2.34)	7.77 (7.29)	31.17 (30.99)	–	13.85	–

μ_{eff} values for Ni(II) complexes (2.90 BM and 3.05 BM) correspond to two unpaired electrons for Ni(II) complex. These values suggests six coordination for Ni(II) ion [17]. The Cu(II) complexes have magnetic moment values of 1.85 BM for Cu[NPMC] and 2.05 BM for Cu[NDMeOPMC] at room temperature, which fall in the range associated with d^9 systems with one unpaired electron. The slightly higher values over 1.73 BM may be due to a small orbital contribution [18]. These values suggest distorted octahedral geometry for Cu(II) complexes.

3.2. *Electronic spectra*

The electronic spectral data of Co(II), Ni(II) and Cu(II) complexes taken in DMF (10^{-3} M) solutions are presented in table 2.

The electronic spectra of Co(II) complexes show two absorption bands at 16280 $\mathrm{cm^{-1}}$, 15740 $\mathrm{cm^{-1}}$ and at 20790 $\mathrm{cm^{-1}}$, 20570 $\mathrm{cm^{-1}}$ for [NPMC] and [NDMeOPMC], respectively, assignable to $^4T_{1g}$ (F) $\rightarrow$ $^4A_{2g}$ (F) (ν_2) and $^4T_{1g}$ (F) $\rightarrow$ $^4T_{2g}$ (F) (ν_3) transitions, respectively, in an octahedral environment [19, 20]. The band ν_1 could be calculated using band-fitting method [21]. The octahedral geometry is further supported by values of ligand field parameters such as Dq, B^1, β, β%, ν_2/ν_1 ratio and LFSE. The reduction in Racah parameter value from free ion value of (971 $\mathrm{cm^{-1}}$) to 957 $\mathrm{cm^{-1}}$ and 958 $\mathrm{cm^{-1}}$ suggests covalent character of the metal-ligand bond.

The electronic spectra of Ni[NPMC] and Ni[NDMeOPMC] complexes show two absorption bands at 15040 $\mathrm{cm^{-1}}$, 15550 $\mathrm{cm^{-1}}$ and 26110 $\mathrm{cm^{-1}}$, 26040 $\mathrm{cm^{-1}}$, assignable to $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) (ν_3) transitions, respectively. The octahedral geometry is further supported by ligand field parameters like Dq, B^1, β, β%, ν_2/ν_1 ratio and LFSE values (table 2). The values of B^1 and β show covalent bonding.

The electronic spectra of Cu(II) complexes show single asymmetric bands in the region 12990–15500 $\mathrm{cm^{-1}}$ (asymmetry on the lower energy side). The broadness of the band may be due to dynamic Jahn–Teller distortion. The appearance of a high energy band may be assigned to charge transfer [22].

3.3. *Infrared spectra*

In the IR spectra of the complexes the coordination sites were determined by comparison of the spectra of both ligands [NPMC] and [NDMeOPMC] and their metal complexes. The IR spectra of both ligands show broad bands in the region 3439–3420 $\mathrm{cm^{-1}}$ and 3220–3170 $\mathrm{cm^{-1}}$ due to ν(NH) stretching vibrations of hydrazine. These bands are assigned to ν_{asy}(NH) and ν_{sy}(NH) stretching vibrations, respectively, of secondary amide. According to Marcotrigiano [23], coordination of NH through N should cause splitting or shifting of bands to lower frequency side or decrease in intensity. In the present study no such changes are observed and the ν(NH) band shifts to higher wave number indicating non-participation of N atom of NH in bonding with metal ions.

The amide I, ν(C=O) stretching band is observed at 1669 $\mathrm{cm^{-1}}$ and 1685 $\mathrm{cm^{-1}}$ in [NPMC] and [NDMeOPMC], respectively for free ligands (table 3). These bands shift to lower wave number in all complexes and appear in the region 1621–1653 $\mathrm{cm^{-1}}$,

Table 2. Electronic spectral data and ligand field parameters of the Co(II), Cu(II) and Ni(II) complexes with Schiff's bases [NPMC] and [NDMeOPMC].

Complex	Transitions (cm^{-1})			Dq (cm^{-1})	B (cm^{-1})	β	β (%)	ν_2/ν_1	LFSE (k Cal.)
	ν_1[a]	ν_2 (ε)[b]	ν_3 (ε)[b]						
$[Co(C_{20}H_{14}O_2N_2)Cl_2]_n$	7580	16,280 (28)	20,790 (52)	870	957	0.98	1.44	2.14	14.91
$[Co(C_{22}H_{18}O_4N_2)Cl_2]_n$	7320	15,740 (34)	20,570 (46)	842	958	0.99	1.34	2.15	14.43
$[Ni(C_{20}H_{14}O_2N_2)Cl_2]_n$	9110	15,040 (32)	26,110 (53)	911	921	0.88	11.44	1.65	31.23
$[Ni(C_{22}H_{18}O_4N_2)Cl_2]_n$	9550	15,550 (32)	26,040 (78)	955	862	0.83	17.12	1.63	32.74
$[Cu(C_{20}H_{14}O_2N_2)Cl_2]_n$		13,600–15,500 (40)		1420	–	–	–	–	24.34
$[Cu(C_{22}H_{18}O_4N_2)Cl_2]_3$		12,990–15,130 (42)		1380	–	–	–	–	24.72

[a] Calculated values.

[b] Molar extinction coefficient values are given in parentheses (in units of $L\,mol^{-1}\,cm^{-1}$).

Table 3. Important IR spectral bands (cm^{-1}) for ligands [NPMC] and [NDMeOPMC] and their metal complexes.

Compound	$\nu_{(C=O)}$	$\nu_{(C=N)}$	$\nu_{(N–N)}$	$\nu_{(M=O)}$	$\nu_{(M–N)}$
NPMC					
$[C_{20}H_{14}O_2N_2]$	1669	1609	935	–	–
$[Co(C_{20}H_{14}O_2N_2)Cl_2]_n$	1655	1590	948	502	450
$[Ni(C_{20}H_{14}O_2N_2)Cl_2]_n$	1640	1585	950	509	458
$[Cu(C_{20}H_{14}O_2N_2)Cl_{2n}$	1635	1592	945	530	460
$[Zn(C_{20}H_{14}O_2N_2)Cl_2]$	1636	1590	942	528	438
$[Cd(C_{20}H_{14}O_2N_2)Cl_2]$	1648	1588	950	530	445
$[Hg(C_{20}H_{14}O_2N_2)Cl_2]$	1642	1578	948	510	435
$[Th(C_{20}H_{14}O_2N_2)(NO_3)_4]$	1621	1590	945	518	448
$[UO_2(C_{20}H_{14}O_2N_2)(NO_3)_2]$	1638	1591	946	519	450
NDMeOPMC					
$[C_{22}H_{18}O_4N_2]$	1685	1603	890	–	–
$[Co(C_{22}H_{18}O_4N_2)Cl]_{2n}$	1653	1561	905	550	455
$[Ni(C_{22}H_{18}O_4N_2)Cl_2]_n$	1646	1570	903	548	453
$[Cu(C_{22}H_{18}O_4N_2)Cl_2]_n$	1638	1585	900	535	430
$[Zn(C_{22}H_{18}O_4N_2)Cl_2]$	1640	1590	901	510	425
$[Cd(C_{22}H_{18}O_4N_2)Cl_2]$	1635	1588	905	540	421
$[Hg(C_{22}H_{18}O_4N_2)Cl_2]$	1632	1580	902	535	429
$[Th(C_{22}H_{18}O_4N_2)(NO_3)_4]$	1625	1585	901	550	445
$[UO_2(C_{22}H_{18}O_4N_2)(NO_3)_2]$	1638	1578	900	528	428

indicating bonding of oxygen of ν(C=O) to metal ions. In some complexes the band becomes weak and splits [24].

The medium strong intensity band at 1609 cm^{-1} and 1603 cm^{-1} in free ligands is attributed ν(C=N) stretching vibrations [25]. Comparison of ν(C=N) stretch of the Schiff base with that found in the complexes, shows shift towards lower wave number in the region 1561–1592 cm^{-1}. These shifts suggest 'N' of C=N group is a coordination site. The coordination of 'N' to metal ions would reduce the electron density in the azomethine and shift the ν(C=N) stretching frequency to lower side.

The bands at 935 and 890 cm^{-1} in free ligands due to ν(N–N), shift to higher wave number by about 10–15 cm^{-1} in all the complexes, additional evidence for coordination of azomethine [26].

Many workers [26, 27] have reported medium intensity bands for ν(C–O–C) of furan ring vibrations in the region 1020–1250 cm^{-1}. In the present case we observed the ν(C–O–C) stretch at 1110–1230 cm^{-1} in [NPMC] and [NDMeOPMC]. This band remains un-altered in all the metal complexes indicating non-participation of the furan O-atom in bonding with metal ions.

In the IR spectra of uranyl nitrate and thorium nitrate there are additional bands not present in the spectra of ligands. The medium bands around 1035 cm^{-1} and 1040 cm^{-1} are assignable to ν_2 vibrations to coordinated nitrate; strong bands at 1490–1470 cm^{-1} and 1290–1250 cm^{-1} are assignable to ν_4 and ν_1 modes, respectively, of unidentate coordinated NO_3 [27]. The characteristic bands at 920 cm^{-1} and 970 cm^{-1} indicate the linear character of O=U=O group [28].

The assignment of bands to various ν(M–O) and ν(M–N) stretching vibrations in the region 600–200 cm^{-1} are much more complicated as ligand vibrations interfere in this region. However, we have made tentative assignments for ν(M–O) and ν(M–N) bands in the region 500–550 cm^{-1} and 421–460 cm^{-1}, respectively [29].

Table 4. ^{1}H NMR spectral data of [NPMC] and [NDMeOMPC] and their Zn(II) and Cd(II) complexes [chemical shifts in δ (ppm)].

Ligand/complexes	–CONH–	–N=CH–	Aromatic protons	Methoxy protons (–OCH_3)
[NPMC]	12.30 (s, 1H)	8.58 (s, 1H)	6.5–8.2 (m, 12H)	–
Zn(II)	12.42 (s, 1H)	8.82 (s, 1H)	6.6–8.3 (m, 12H)	–
Cd(II)	12.48 (s, 1H)	8.80 (s, 1H)	6.6–8.3 (m, 12H)	–
[NDMeOPMC]	12.10 (s, 1H)	8.50 (s, 1H)	6.9–8.50 (m, 10H)	3.80 (s, 6H)
Zn(II)	12.18 (s, 1H)	8.70 (s, 1H)	6.92–8.52 (m, 10H)	3.82 (s, 6H)
Cd(II)	12.20 (s, 1H)	8.64 (s, 1H)	6.92–8.52 (m, 10H)	3.85 (s, 6H)

Table 5. ESR spectral data of Cu(II) complexes.

Complex	$g_\parallel$	$g_\perp$	g_{av}	$A_\parallel \times 10^{-4}\,cm^{-1}$	$g_\parallel/A_\parallel$	α^2	G
$[Cu(C_{20}H_{14}O_2N_2)Cl_2]_n$	2.285	2.127	2.179	192.02	119	0.8715	2.248
$[Cu(C_{22}H_{18}O_4N_2)Cl_2]_n$	2.256	2.148	2.184	189.58	119	0.8809	1.733

In the case of polymeric complexes ν(M–Cl) stretch for terminal halogen is observed at higher frequencies compared to that for the bridging halogen [30]. We have assigned broad and medium intensity bands to ν(M–Cl) terminal and ν(M–Cl) bridging, stretching vibrations, in the region 370–347 cm^{-1} and 285–305 cm^{-1}, respectively, for Co(II), Ni(II) and Cu(II) complexes of both ligands. The bands in the region 300–358 cm^{-1} are assigned to ν(M–Cl) stretching vibrations, for Zn(II), Cd(II) and Hg(II) complexes [31].

3.4. *1H NMR spectra*

The ^{1}H NMR spectra of [NPMC] and [NDMeOPMC] show signals at δ 12.30 and δ 12.10 (s, 1H) due to (CONH) amide proton and δ 8.58 and δ 8.50 due to (–H–C=N–) azomethine proton. The aromatic protons of naphthofuran and benzene are in the region δ 6.5–8.5 and the signals at δ 3.80 (s, 6H) show methoxy protons at the 3,4-positions of benzene ring. In the ^{1}H NMR spectra of Zn(II) and Cd(II) complexes the signals due to –CONH– and –N=CH– protons show a downfield shift of δ (0.08–0.18) and δ (0.14–0.24), respectively, thereby suggesting the involvement of oxygen and nitrogen atoms in bonding with metal table 4.

3.5. *ESR spectra of Cu(II) complexes*

The room temperature ESR spectra of powdered samples of $[Cu(NPMC)Cl_2]$ and $[Cu(NDMeOPMC)Cl_2]$ shows the spectra having asymmetric bands with two '*g*' values i.e. $g_\parallel > g_\perp$. The trend $g_\parallel > g_\perp > g_{av}$ (2.0036) indicates that the Cu site has a $d_{x^2-y^2}$ ground state, characteristic for distorted octahedral geometry [29]. The exchange interaction parameter G, is calculated using $G = (g_\parallel - 2)/(g_\perp - 2)$. The value of G is less than 4, indicates considerable exchange interaction between the metal ions. The values of A_{11}, nuclear hyperfine constant and α^2 degree of covalency support the structures [32, 33] table 5.

Table 6. Mass fragmentation pattern of [NPMC] and [NDMeOPMC].

Ligands	*m*/*z*	Weight loss	Assignments
[NPMC]	314	–	[$C_{20}H_{14}O_2N_2$] Molecular ion peak (M^+)
	211	103 (C_7H_5N)	$[C_{13}H_9O_2N]^+$
	195	16 (NH_2)	$[C_{13}H_7O_2]^+$
	167	28 (CO)	$[C_{12}H_7O]^+$
	139	28 (CO)	$[C_{11}H_7]^+$
[NDMeOPMC]	374	–	[$C_{22}H_{18}O_4N_2$] Molecular ion peak (M^+)
	211	163 ($C_9H_9NO_2$)	$[C_{13}H_9O_2N]^+$
	195	16 (NH_2)	$[C_{13}H_7O_2]^+$
	167	28 (CO)	$[C_{12}H_7O]^+$
	139	28 (CO)	$[C_{11}H_7]^+$

3.6. *Mass spectra*

The mass spectra of [NPMC] and [NDMeOPMC] were performed to determine their molecular weight and fragmentation pattern. The mass spectrum of [NPMC]/[NDMeOPMC] showed molecular ion peaks M^+ at *m*/*z* 314/374, corresponding to their molecular weights. Both ligands gave a fragmentation peak at *m*/*z* 211 ($M^+ - 103/163$) from explusion of $C_7H_5N/C_9H_9NO_2$ species. This fragment ion underwent fragmentation with loss of NH_2 and gave a fragment ion at *m*/*z* 195 ($M^+ - 16$). Further fragmentation with loss of CO gave a peak at *m*/*z* 167 ($M^+ - 28$) due to $[C_{12}H_7O]^+$ and further a peak at *m*/*z* 139 ($M^+ - 28$) due to $[C_{11}H_7]^+$. The fragmentation pattern is given in table 6.

4. Biological activity

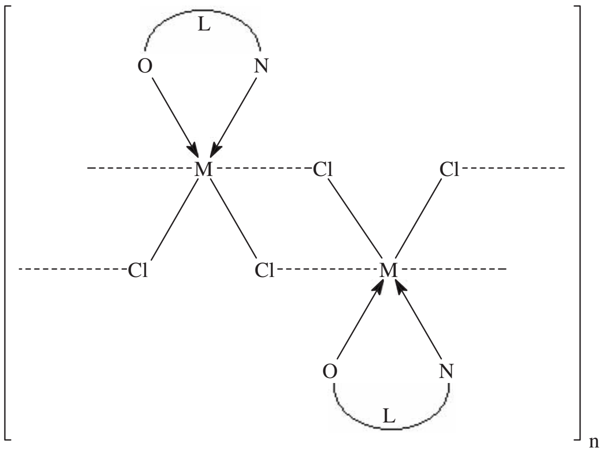
Both ligands, [NPMC] and [NDMeOPMC], and metal complexes were tested for their antimicrobial activity against *Escherichia coli*, *Pseudomonas* and *Bacillus substilis* and antifungal activity against *A. niger*, *A. flavous*, and *A. fumigatus*. The bacterial and fungal species were obtained from the Department of Microbiology and Botany, Gulbarga University, Gulbarga. DMF was used as solvent with negligible biological activity. The tests were carried out by the cup-plate zone inhibition technique.

The [Cu(NPMC)Cl_2,], [Cd(NPMC)Cl_2], [Cu(NDMeOPMC)Cl_2] and [Cd(NDMeOPMC)Cl_2] complexes are more active against all the three bacteria, tested, compared with the [NPMC] and [NDMeOPMC] and the metal salts. Co(II), Ni(II), Zn(II) complexes of [NPMC] and [NDMeOPMC] are moderately active. All other complexes are less active against the three bacteria. However, compared to the antibacterial activity of the standard antibiotic streptomycin, the activity exhibited by ligands and metal complexes were lower.

The [Cd(NPMC)Cl_2] and [Cd(NDMeOPMC)Cl_2] complexes showed higher fungicidal activity than the parent ligands [NPMC] and [NDMeOPMC] against all the three fungal species.

Table 7. Antimicrobial activity results of ligands and their metal complexes.

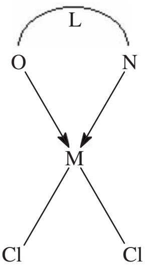
	Zone of inhibition (mm)					
	Bacteria			Fungi		
Ligands/complexes	*E. coli*	*Pseudomonas*	*B. substilis*	*A. niger*	*A. flavous*	*A. fumigatus*
[NPMC]	13	16	12	11	13	10
Co(II)	12	09	12	10	07	12
Ni(II)	11	10	11	09	06	13
Cu(II)	15	17	13	09	08	13
Zn(II)	12	13	12	10	13	10
Cd(II)	14	18	16	15	14	18
Hg(II)	10	12	10	10	08	10
[NDMeOPMC]	14	17	13	13	11	13
Co(II)	10	14	11	07	06	06
Ni(II)	12	15	10	06	06	10
Cu(II)	14	17	13	09	08	09
Zn(II)	12	12	12	10	08	10
Cd(II)	15	17	14	14	13	16
Hg(II)	11	12	10	09	10	12
Standard: Streptomycine	22	23	20	–	–	–
: Nystatin	–	–	–	21	19	20
Control DMF	8	8	8	4	4	4



where, M = Co(II), Ni(II) or Cu(II)
L = [NPMC] or [NDMeOPMC]

Figure 2. Suggested structures of Co(II), Ni(II) or Cu(II) complexes with [NPMC] and [NDMeOPMC] ligands.

The Cu(II), Co(II), Ni(II) and Cd(II) complexes of [NPMC] ligand showed more activity against *A. fumigatus* than the ligand itself. All other complexes are less active than the ligands against all the fungal species. However, compared to the standard antifugnal agent Nystatin, the fungicidal activity of ligands and their metal complexes were lower. Results are summarized in table 7.



M = Zn(II), Cd(II) or Hg(II)

Figure 3. Suggested structures of Zn(II), Cd(II) or Hg(II) complexes with [NPMC] or [NDMeOPMC] ligands.

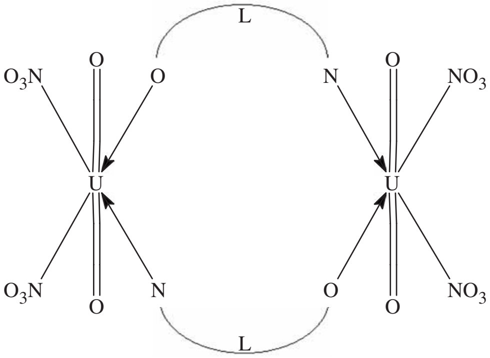


Figure 4. Suggested structure of $[UO_2L(NO_3)_2]$ complexes.

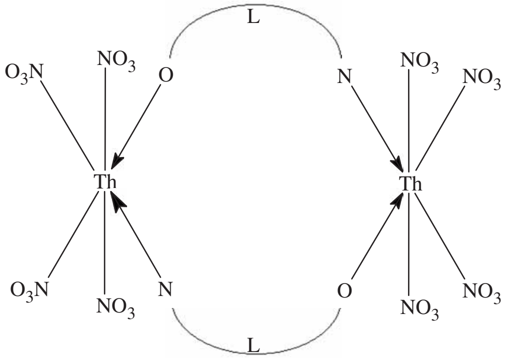


Figure 5. Suggested structure of $[ThL(NO_3)_4]$ complexes.

5. Conclusion

Based on the elemental analysis, spectral studies, conductance data and magnetic susceptibility data, these ligands coordinate bidentate to a metal ion via the carboxy oxygen and azomethmine nitrogen donor atoms. Hence the following tentative structures have been proposed for all the complexes.

(1) Chloride bridged polymeric octahedral structures of Co(II), Cu(II) and Ni(II) complexes (figure 2).
(2) Tetrahedral structures of Zn(II), Cd(II) and Hg(II) complexes (figure 3).
(3) Dimeric structure for UO_2(II) and Th(IV) complexes (figures 4 and 5).

Acknowledgements

One of the authors (MBH) is thankful to University Grants Commission (UGC), New Delhi for financial assistance in the form of a major research project and we are thankful to the Chairman, Department of Chemistry, Gulbarga University, Gulbarga for encouragement and providing the facilities. We also thank the Chairman, Department, Microbiology and Botany, Gulbarga University, Gulbarga for providing facilities to carry out biological activity.

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