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Synthesis, spectroscopic and antifungal studies of Ni(II) complexes with macrocyclic ligands

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Abstract

Nickel(II) complexes have been synthesized with macrocyclic ligands 2, 7, 9, 14-tetrahydroxy phenyl-1, 3, 6, 8, 13-hexaazacycloocta decane (L^1), 2, 7, 9, 14-tetracyclohexane-1, 3, 6, 8, 13-hexaazacyclo-octadecane(L^2) by template method. The complexes were characterized on the basis of elemental analysis, molar conductance measurements, magnetic susceptibility measurements, IR and electronic spectral studies. The complexes were found to have general compositions, $[Ni(L)X_2]$ (where L = L^1 and L^2 ligands, X = Cl^-, NO_3^- and CH_3COO^-). The ligands coordinate to metal ion via four donor sites to give six coordinate complexes having octahedral geometry. The complexes were also examined for antifungal studies against pathogenic strains like *Alternaria brassicae*, *Alternaria porri* and *Fusarium oxysporum.* Food Poison Technique was employed for screening the *in vitro* antifungal studies of the complexes

Keywords: Macrocyclic ligands; nitrogen; synthesis; transition elements; antifungal studies.

Introduction

The rich and lively topic of coordination chemistry of synthetic macrocycles originated during the 1960s, in which the Ni(II) ion was employed as a templating agent [1]. Condensation between carbonyl group with primary amine has played an important role in the development of synthetic macrocyclic ligands [2-7]. Template synthesis of one pot lies at the centre of macrocyclic chemistry. The design and synthesis of polyaza macrocycles have attracted increasing interest in recent years because of importance in bioinorganic chemistry, catalyst extraction of metal ions from solution [8-14].

In view these expects, we report here the synthesis, spectral characterization and antifungal studies of nickel(II) complexes with macrocyclic ligands, 2, 7, 9, 14-tetrahydroxy phenyl-1, 3, 6, 8, 13-hexaazacyclooctadecane (L^1) and 2, 7, 9, 14-tetracyclo-hexane-1,3,6,8,13-hexaazacyclo-octadecane (L^2).

Materials and methods

All chemicals used were of AR grade and procured from Sigma-Aldrich and Fluka. Metal salts were purchased from E. Merck and were used as received. Other solvents and chemicals were of commercial product (Fluka, S.D. Fine, E. Merck and Thomas Backer).

2.2. Synthesis of complexes

2.2.1. Preparation of Ni(II) complexes with 2,7,9,14-Tetrahydroxyphenyl-1,3,6,8,13-hexaazacyclooctadecane (L^1)

An ethanolic solution (20 mL) of diethylene triammine (2.0 mmol) was heated for 10 min. in the presence of one or two drop of dilute HCl. To this solution a hot ethanolic solution (20 mL) of the corresponding metal salt like nitrate, chloride or acetate (1.0 mmol) and a hot ethanolic solution (20 mL) of salicyldehyde (2.0 mmol) were added with constant stirring. The resulting mixture was refluxed for 8-12 h at 80-85°C and then allowed to cool overnight at 0°C. The precipitated complex was filtered, washed with ethnol and dried under *vacuum* over P_4O_{10}.

2.2.2. Preparation of of Ni(II) complexes with 2,7,9,14-Tetracyclohexane-1,3,6,8,13-hexaazacyclooctadecane(L^2)

An ethanolic solution (20 mL) of diethylene triammine (2.0 mmol) was heated for 10 min. in the presence of one or two drop of dilute HCl. To this solution a hot ethanolic solution (20 mL) of the corresponding metal salt like nitrate, chloride or acetate (1.0 mmol) and a hot ethanolic solution (20 mL) of cyclohexanone (2.0 mmol) were added with constant stirring. The resulting mixture was refluxed for 10-18 h at 80°C and then allowed to cool overnight at 0°C. The precipitated complex was filtered, washed with ethnol and dried under *vacuum* over P_4O_{10}.

2.3. Biological Screening

The compounds were screened against the opportunistic pathogens like *Alternaria brassicae*, *Alternaria porri* and *Fusarium oxysporum.* Food Poison Technique was employed for screening the *in vitro* antifungal studies of the complexes [15-17]. The stock solution of the compound was directly mixed to the PDA (Potato Dextrose Agar) medium according to the tested concentration. A disc of 5 mm of test fungal culture of a specific age growing on solid medium is then cut with a sterile cork borer and was placed at the center of the solid PDA plate with the help of inoculums' needle. The plates were sealed by parafilm and incubated at 29 ± 2°C for 7 days. DMSO was used as a control and Captan as a standard fungicide. The inhibition of the fungal growth expressed in percentage terms was determined from the growth in the test plate to the respective control plate as given below:

$$\text{Inhibition (\%)} = (C-T)\ 100 / C$$

Where C = diameter of fungal growth in the control plate, T = diameter of fungal growth in the test plate

Physical Measurements

Elemental analyses were performed in carlo-Erba 1106 elemental analyzer. Infra-red spectra were recorded on a Perkin Elmer 137 instrument as KBr pellets. The magnetic susceptibility was measured at room temperature on a Gouy balance using $CuSO_4.5H_2O$ as callibrant. Molar conductance was measured on an ELICO (CM82T) conductivity bridge. The electronic spectra were recorded in DMF/DMSO on a Shimadzu UV mini-1240 spectrophotometer.

Results and Discussion

4.1. Physical Properties

The elemental analytical data of the complexes are listed in Table 1. The magnetic moments of the complexes accounts for their nature. The molar conductance values of complexes were found to be 14-18 $\Omega^{-1}cm^2mol^{-1}$ corresponding to their non electrolytic nature [18].

Table 1: Analytical data of the complexes

S. No.	Complex	Yield (%)	Color	Molar Conductance ($\Omega^{-1}cm^2mol^{-1}$)	Analytical data (%) Calculated (Found)			
					C	H	N	M
1	$[Ni(L^1)(Cl)_2]$	70	Orange	11.2	56.26 (56.10)	7.85 (7.79)	10.96 (10.90)	7.68 (7.66)
2	$[Ni(L^1)(NO_3)_2]$	67	Brown	11.6	52.64 (52.55)	7.35 (7.29)	13.76 (13.62)	7.24 (7.17)
3	$[Ni(L^1)(CH_3COO)_2]$	61	Orange	11.7	58.81 (58.75)	8.15 (8.07)	10.33 (10.28)	7.24 (7.18)
4	$[Ni(L^2)(Cl)_2]$	67	Light Brown	11.3	58.61 (58.53)	8.89 (8.84)	12.88 (12.80)	9.01 (8.97)
5	$[Ni(L^2)(NO_3)_2]$	69	Dark Brown	18.5	54.21 (54.16)	8.25 (8.18)	15.84 (15.79)	8.36 (8.32)
6	$[Ni(L^2)(CH_3COO)_2]$	71	Light Brown	18.7	61.52 (61.45)	9.19 (9.10)	11.98 (11.94)	8.48 (8.39)

Table 2: IR spectral bands of the complexes

S. No.	Complex	ν(C=N)	ν(N–H)	Anion bands	Δν
1	$[Ni(L^1)(Cl)_2]$	1624	3221	327	-
2	$[Ni(L^1)(NO_3)_2]$	1630	2942	1413, 1355, 1122	58
3	$[Ni(L^1)(CH_3COO)_2]$	1601	2958	1453, 1291	162
4	$[Ni(L^2)(Cl)_2]$	1637	3224	322	-
5	$[Ni(L^2)(NO_3)_2]$	1631	2951	1434, 1311, 1096	123
6	$[Ni(L^2)(CH_3COO)_2]$	1625	3000	1440, 1256	184

4.2. *Infrared spectra*

The IR data of the complexes are given in Table 2. IR spectra of the complexes do not show any band corresponding to aldehyde and primary amine which suggests the condensation between aldehyde and primary amine groups. IR spectra give the bands in the range 1624-1640 cm^{-1} due to coordinated azomethine group [19]. Additionally, the spectra also give the bands at 380-440 cm^{-1} due to ν(Ni–N) which supports the coordination through nitrogen atom [20]. The nitrato complexes show the IR bands in the range 1413-1434 (ν_5), 1311-1355 (ν_1) and 1096-1122 cm^{-1}

(ν_2) due to NO stretching vibrations of NO_3 groups. The value of $\Delta(\nu_5-\nu_1)$, i.e., 58-123 cm^{-1} suggests the monodentate coordination of NO_3^- ion [21,22]. The acetato complexes show the IR bands in the region 1440-1453 and 1256-1291 cm^{-1} due to ν_{as}(OAc) and ν_s(OAc) stretching vibrations. The $\Delta\nu$ i.e. 162-184 cm^{-1} suggests the unidentate coordination of the OAc^- ion. The chloro complexes give IR bands at 322-327 cm^{-1} due to ν(M–Cl) [23].

Table 3: Electronic spectral data, magnetic moments and ligand field parameters of the complexes

S. No.	Complex	λ_{max} (cm^{-1})	μ_{eff} (BM)	B (cm^{-1})	β	ν_2 / ν_1
1	$[Ni(L^1)(Cl)_2]$	10450, 14700, 26300	3.03	643	0.61	1.40
2	$[Ni(L^1)(NO_3)_2]$	11494, 18650, 25641	3.00	653	0.62	1.62
3	$[Ni(L^1)(CH_3COO)_2]$	13333, 18622, 31650	2.94	686	0.65	1.39
4	$[Ni(L^2)(Cl)_2]$	10532, 15600, 25906	3.04	660	0.63	1.48
5	$[Ni(L^2)(NO_3)_2]$	10350, 14650, 26250	3.02	656	0.63	1.41
6	$[Ni(L^2)(CH_3COO)_2]$	10300, 14600, 26200	3.01	660	0.63	1.41

4.3. Electronic spectra

The electronic spectral data of the complexes are given in Table 3. The electronic spectra of the complexes display three absorption bands in the range 10,300-13,333 cm^{-1}, 14,600-18650 cm^{-1} and 25,641-26,300 cm^{-1} . These bands may assigned to the $^3A_{2g}$ (F) $\rightarrow$ $^3T_{2g}$ (F) ν_1, $^3A_{2g}$ (F) $\rightarrow$ $^3T_{1g}$ (F) ν_2 and $^3A_{2g}$ (F) $\rightarrow$ $^3T_{1g}$ (P) ν_3 d-d transition, respectively. Complex **3** also give the high energy band at 31650 cm^{-1} due to charge-transfer transition. These bands indicate that the complexes have six-coordinated octahedral geometry [24-26]. The Nephelauxetic parameter β was readily obtained by using the relation β= B(complex)/B(free ion), where B(free ion) for Ni(II) is 1041 cm^{-1}.The value of β lie in the range of 0.61-0.65. These values indicate the covalent character in metal ligand sigma bond.

4.4. Antifungal studies

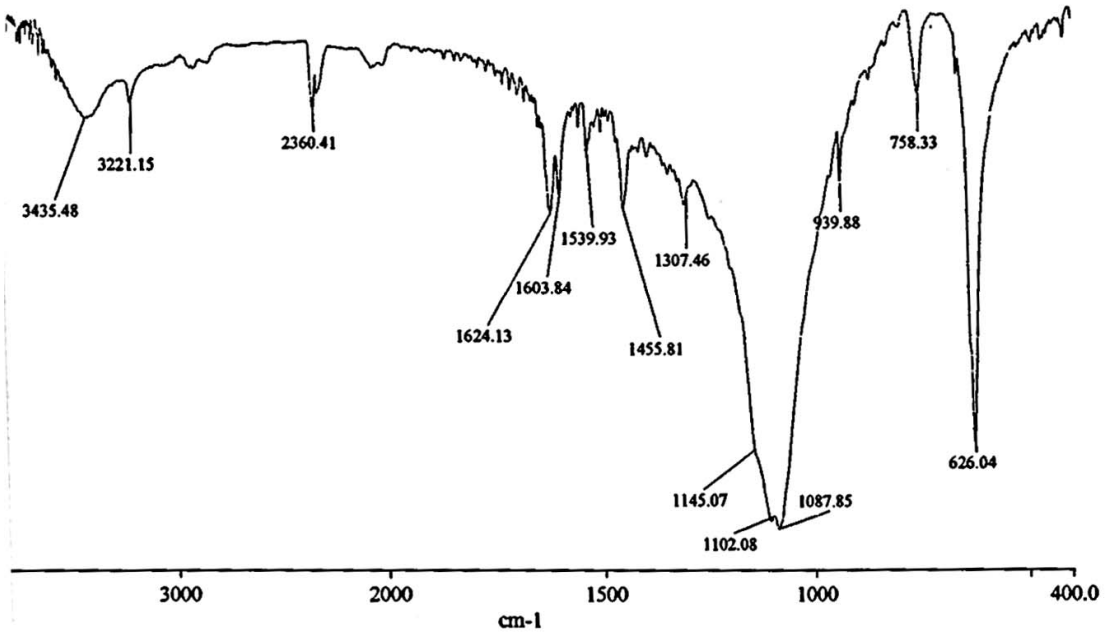
The data of the antifungal and antibacterial activities of ligand and complexes are given in Table 4. The observed finding led to the conclusion the complexes have the higher activities than the reactants. This modified activity of compounds on complexation can be explained by Overtone's Concept and Chelation Theory [27, 28]. The theory states that chelation reduces the polarity of the metal atom by the partial sharing of its positive charge with donor groups and possible π–electron delocalization over the whole ring.

Table 4: Antifungal activity data of the complexes

S. No.	Complex	Fungicidal activity (%) (conc. in μgmL^{-1})								
		A. brassicae			*A. porri*			*F. oxysporum*		
		200	300	400	200	300	400	200	300	400
1	$[Ni(L^1)(Cl)_2]$	60	72	80	48	56	62	50	61	68
2	$[Ni(L^1)(NO_3)_2]$	57	70	78	50	56	63	53	62	70
3	$[Ni(L^1)(CH_3COO)_2]$	60	70	77	46	55	64	50	60	71
4	$[Ni(L^2)(Cl)_2]$	55	70	82	52	60	70	55	66	76
5	$[Ni(L^2)(NO_3)_2]$	52	66	78	50	61	72	50	62	74
6	$[Ni(L^2)(CH_3COO)_2]$	50	63	75	48	58	68	50	60	72
7	Standard(Captan)	80	100	100	90	100	100	75	100	100

This results with increasing of the lipophilic character of the complex and favor the permeation of the complex through the lipid layer of cell membrane. The complex blocks the metal binding sites in the enzymes of microorganisms. Consequently, the complex disturbs the metabolism pathways in cell and as a result microorganisms die.

Figure 1: IR Spectrum of $[Ni(L^1)Cl_2]$



Conclusion

The Ni(II) complexes with macrocyclic ligands are successfully synthesized by template method. The synthesized macrocyclic complexes are characterized by elemental analysis, molar conductance measurements, magnetic susceptibility measurements, IR and electronic spectral analysis. The studies supports that the ligands have four donor sites and coordinate to metal ion in NNNN fashion to give octahedral complexes. The *in vitro* antifungal screening to the compounds shows that the compounds have the considerable therapeutic action and act as antifungal agents.

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References

[1] NF Curtis. *Coord. Chem. Rev.*, **1968**, 3, 3.
[2] HZ Kou; S Gao; BQ Ma; DZ Liao. *Chem. Commun.*, **2000,** 713.
[3] TB Lu; H Xiang; RL Luck; L Jiang; ZW Mao; LN Ji. *New J. Chem.*, **2002**, 26, 969.
[4] M Salavati.- Niasari; A Amiri. *J. Mol. Catal. A***, 2005,** 235, 114.
[5] M Salavati. Niasari; H. Najafian. *J. Chem. Rev***., 2003,** 9, 586.

[6] RW Hay; JM Armstrong; MM Hassan. *Trans. Metal Chem*., **1992**, 17, 270.
[7] SV Rosokha; YD Lampeka, IM Malostan. *J. Chem. Soc., Dalton Trans*.**, 1993**, 631.
[8] M Shakir; SP Varkey; OSM Nasman. *Polyhedron*, **1995**, 14, 1283.
[9] DE Fenton; PA Vigato. *Chem. Commun*.**, 1973**, 62.
[10] RW Hay; A Dandy; P Lightfoot; YD Lampeka. *Polyhedron*, **1997**, 16, 2777.
[11] H Bang; EJ Lee; EY Lee; J Suh; MP Suh. *Inorg. Chim. Acta*, **2000,** 308, 2633.
[12] S Chandra; D; Jain, AK Sharma; P Sharma. *Molecules*, **2009**, 14, 174.
[13] S Chandra; AK Sharma. *J. Coord. Chem.*, **2009**, 62, 3688.
[14] S Chandra; AK Sharma. Res. Lett. Inorg. Chem., **2009,** 2009 Article ID 945670, doi:10.1155/2009/945670.
[15] WG Geary; *Coord. Chem. Rev.*, **1971**, 7, 81.
[16] K Nakamoto. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd Edition. Wiley Intrescience, New York, **1978**.
[17] JR Ferraro. Low Frequency Vibrations of Inorganic and Coordination Compounds, Plenum Press, New York, **1971**.
[18] S Chandra; D Jain; AK Sharma. *Spectrochim. Acta A*, **2009**, 71, 1712.
[19] S Chandra; A.K. Sharma. *J. Indian Chem. Soc.*, **2009**, 86, 690.
[20] S Chandra; AK Sharma. *Spectrochim. Acta A*, **2009**, 74, 271.
[21] BP Lever. Inorganic Electronic Spectroscopy, 1st Edition., Elsevier, Amsterdam, **1968**.
[22] RS Drago. Physical Methods in Chemistry, Saunders College Publishing, Orlando, **1977**.
[23] S Chandra; AK Sharma. *Spectrochim. Acta A*, **2009**, 72, 851.
[24] PG Lawrence; PL Harold; OG Francis. *Antibiotic Chemother.*, **1980**, 5, 1597.
[25] BG Tweedy. *Phytopathology*, **1964**, 55, 910.