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Synthesis, Spectral and Theoretical Studies of Macrocyclic Cu(II), Ni(II) and Co(II) Complexes by Template Reaction of Malonic Acid with Metal (II) Chloride and Urea or Thiourea

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Research Article

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ABSTRACT

Six new macrocyclic complexes were synthesized by template reaction of urea or thiourea with malonic acid and metal (II) chloride. The metal to ligand ratio of the complexes was found to be (1:1). The Co(II) and the Ni(II) complexes are proposed to be square planar and Cu(II) complexes are proposed to be octahedral geometry. Macrocyclic complexes are (1:2) electrolytes for Cu(II) and Ni(II) complexes while Co(II) complexes are non-electrolytic nature as shown by their molar conductivities (Λ_M) in DMSO (Dimethyl sulphoxide) of 10⁻³ M solution. The structure of metal complexes from FTIR, UV-Vis., magnetic susceptibility measurements, molar conductivity measurements, atomic absorption and melting points. A theoretical treatment of the formation of complexes in the gas phase was studied, this was done using the HYPERCHEM-6 program for the Molecular mechanics and Semi-empirical calculations. The complexes have been tested for their antibacterial activities against Two type of human pathogenic bacteria (*Staphylococcus aureus* and *Escherichia coli*). The first are

human pathogenic bacteria (*Staphylococcus aureus* and *Escherichia coli*). The first are Gram positive while the second are Gram negative (by using agar well diffusion method). Finally, it was found that compounds show different activity of inhibition on growth of the bacteria.

Keywords: Macrocyclic; complex; template; malonic acid; urea; thiourea.

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1. INTRODUCTION

The synthesis and characterization of coordination compounds with macrocyclic ligands has evolved during the last years as one of the main research areas in coordination chemistry (Singh and Srivastava, 2000; Fry et al., 1997; Rosignoli et al., 1997; Xu et al., 1997; Blake et al., 1996). The preparation of macrocyclic polyamine ligands bearing functional pendant donor groups and their subsequent ligation to various metal ions has been an active area of research in recent year (Khanmohammad et al., 2007; Wainwright, 1997; Lihan et al., 2007). Macrocyclic ligands containing a heteroatom are important complexes agent for cations. anions and molecules (Izatt et al., 1995; Khandar et al., 2007). The stability of macrocyclic metal complexes depend upon a number of factors, including the number and type of donor atom present in the ligand and their relative positions within the macrocyclic skeleton, as well as the number and size of the chelate rings formed on complexation. For transition metal ions, features such as the nature and magnitude of crystal - field effects play also an important role (Vance et al., 1997). Synthetic macrocycles are a growing class of compounds with varying chemistry a wide range different molecular topologies and sets of donor atoms (Choi et al., 2001; Chandra and Gupta, 2002). The chemical properties of macrocyclic complexes can be turned to force metal ions to adopt unusual coordination geometry. Transition metal macrocyclic complexes have received much attention as an active part of metalloenzymes (Chaudhary et al., 2002) as bio mimic model compounds (Chandra and Gupta, 2005) due to their resemblance with natural proteins like hemerythrin and enzymes. Synthesis of these Schiff base complexes is achieved through the template reaction (Lindoy, 1971; Lodeiro et al., 2003) or transition reactions (Khalil and Bashir, 2002), which are used when the transition metal cations are ineffective as templates.

In the present work, we have synthesized six macrocyclic Schiff base complexes by template effect by reaction of metal (II) chloride with malonic acid and urea or thiourea. Spectral, magnetic properties of the new complexes were studied in detail.

2. EXPERIMENTAL DETAILS

2.1 Physical Measurements

A Fisher-100 infrared spectrophotometer was used to record the IR spectra as KBr and Csl disc, UV/VIS spectra were measured by a HITACHI U-2000 spectrophotometer. Determination of all metals percentage was done by atomic absorption spectrophotometry on AA-680G (Shimadzu). Electrical conductance was measured on conductivity CDC304 (Jenway4070). Melting points determined by an electric heated block apparatus (Gallen Kamp), and were uncorrected. Room temperature magnetic susceptibility measurements were carried out on a B.M 6 BRUKER type magnets, balance, Diamagnetic correction was done using Pascal constants.

2.2 Materials

All the chemicals and solvents were of analytical grade, and used as received.

2.2.1 General procedure for preparation of complexes

Stirred solution of urea or thiourea (0.002 mole) and $M(CI)_2.nH_2O$ (0.002 mole) in methanol (10 mL) was added drop wise to Malonic acid (0.002 mole) in methanol (40 mL). After the

addition was completed, the stirring was continued for 12 h. The precipitate was filtered and washed with methanol, then dried in air (M= Cu, n=2 or M=Co, Ni, n=6).

Nickel chloride (II) (0.002 mole, 0.47 g), dissolved in ethanol (25 mL), was added to refluxing solution of malonic acid (0.004, 0.28 g) and urea (0.004 mole, 0.24 g) or thiourea (0.004 mole, 0.30 g) in ethanol (25 mL). The mixture was refluxed for 11 h. when color of the solution turned green. The complexes were filtered and solvent was removed under vacuum at room temperature and the green product was obtained. The complexes purified by washing with 10 ml of ethanol, with yield of 60%.

The same procedure was adopted for the synthesis of other metal chloride Co(II) (0.002 mole, 0.47 g) and Cu(II) (0.002 mole, 0.34 g).

2.2.2 Study of biological activity for complexes

The biological activity of the ligands and their metal complexes were studied against two selected type of bacteria which included *Escherichia coli*, as gram negative (-Ve) and *Staphylococcus aureus* as gram positive (+Ve) to be cultivated and as control for the disc sensitivity test (Chohan, 1999), this method involves the exposure of the zone of inhibition toward the diffusion of micro–organism on agar plat. The plates were incubated for (48 h), at 37 °C, the zone of inhibition of bacteria growth around the disc was observed.

3. RESULTS AND DISCUSION

In this work, the reaction between urea or thiourea with metal (II) chloride and Malonic acid in ethanol, gave (1+1) macrocyclic Schiff base complexes as the product, the macrocyclic complexes were characterized by, FT-IR, UV.-VIS., conductivity measurement and Magnetic susceptibility (table 1).

3.1 FT-IR Spectra

Infrared spectra of the complexes were recorded in KBr pellet from 4000 to 400 cm⁻¹. IR spectrum of the prepared complexes does not exhibit any band corresponding for the free primary amine (urea or thiourea) and carboxylic group (malonic acid) (Chandra and Gupta, 2005). Four new bands appear in the spectrum of the complexes in the regions 1630, 1585, 1240, and 790 cm⁻¹ assigned to amide I[ν (C=O)], amide II [ν (C-N) + \overline{o} (N-H)], amide III [\overline{o} (N-H)] and IV [\overline{o} (C=O)] bands, respectively (Chaudhary et al., 2002; Chandra and Gupta, 2005). On complexes formation the shifting toward lower side of [ν (N-H)] band and the band of amides II and III, suggest the coordination through nitrogen of –NH group [N4], which is further supported by the appearance of a medium intensity band in the range 550-500 cm⁻¹ attributed to [ν (M-N)] (Temel et al., 2002).

3.2 Electronic Absorption Spectroscopy

Electronic absorption spectral data of the complexes in Dimethyl sulfoxide (DMSO) at room temperature are presented in table 1. The electronic spectra of complexes in DMSO show four bands in the visible – ultraviolet region. The absorption bands below 300 nm are practically identical and can be attributed to π - π * transitions in the azomethine (-C=N) group (Llhan et al., 2007). The proposed molecular structures of the complexes are shown in fig. (1). The Ni(II) and Co(II) complexes possess square-planar geometry and Cu(II) complexes possess show octahedral geometry around the central metal ions.

No.	Complexes	Colour	$\Delta M (\Omega^{-1})$	M.P (°C)	Yield	μ _{eff.}	UV/VIS		Elementa	l analysis
			cm²mol⁻')		(%)	BM			(% found)% Cal.	
			In DMSO				λmax	ε l.mol ⁻¹ . Cm ⁻¹	M%	CI%
							(nm)			
1	[Cu(L1)]Cl ₂	blue	160	165-167	71	2.02	220,240,	780,156,89,75	16.26	18.18
							300,660		(16.22)	(18.14)
2	[Cu(L2)]Cl ₂	blue	170	138-140	70	2.17	220,245,	880,189,115,87	15.02	16.80
							330,695		(15.00)	(16.75)
3	[Ni(L1)]Cl ₂	Orange	190	180-182	75	Dia.	220,240,	175,120,95,80	15.21	18.40
							315,565		(15.18)	(18.35)
4	[Ni(L2)]Cl ₂	Orange	185	188-190	78	Dia.	240,260,	195,130,90,80	14.05	16.99
							320,660		(14.0)	(16.96)
5	$[Co(L1)Cl_2]$	Pink	12	> 240	66	4.98	220,270,	975,260,150,85	15.26	18.39
							310,595		(15.23)	(18.35)
6	$[Co(L2)Cl_2]$	Pink	10	> 240	65	5.02	230,280,	935,190,135,65	14.09	16.98
							300,650		(14.05)	(16.94)

Table 1. Some physical and chemical properties of the prepared complexes

The absorption bands observed within 300-330 nm range are most probably due to the transitions of n- π^* of imine group (Llhan et al., 2002). The electronic spectra of the Cu(II) complexes shown an absorption band at 666 - 695 nm attributed to the ${}^2\text{Eg} \rightarrow {}^2\text{T}_2\text{g}$ transition, characteristic for square planar geometry (Llhan et al., 2007; Llhan et al., 2002; Llhan et al., 2007). The energy of the band assigned to d-d transitions can provide a rough estimate of the ligand field strength, since one of the electronic transition is 10Dq-C (Llhan et al., 2007; Llhan et al., 2002; Llhan et al., 2007; Llhan et al., 2002; Llhan et al., 2007; Llhan et al., 2002; Llhan et al., 2007). The electronic spectra of the Ni(II) and Co(II) complexes show an absorption band at 565-660 nm attributed to the ${}^2\text{Eg} \rightarrow {}^2\text{T}_2\text{g}$ transition , characteristic for tetragonally elongated octahedral or square planar geometry (Llhan et al., 2007; Llhan et al., 2007). The electronic absorption bands of the presented Ni(II) and Co(II) complexes in the visible region exhibit solvent dependence behavior. The observed red shifts in the low- energy d-d band of Ni(II) and Co(II) complexes in DMSO can be interpreted in terms of weak ligand field strength (Llhan et al., 2007; Llhan et al., 2007).

3.3 Magnetic Studies

The magnetic moment measurements of the Cu(II) complexes at room temperature are in the range 2.02 - 2.17 B.M,(table 1), which are typical for Cu(II) complexes having one unpaired electron at this temperature. Magnetic susceptibility measurements provide sufficient data to characterize the structure of the Ni(II) and Co(II) complexes. the magnetic moment measurements of compounds were carried out at 25 °C, the magnetic moments of the Ni(II) complexes carried out at room temperature these complexes show the diamagnetic behavior, indicating the square-planar environment around the Ni(II) ion (Llhan et al., 2007; Llhan et al., 2007).

The room temperature magnetic moment (4.98- 5.02 B.M) determined for Co(II) metal complexes, are close to the spin-only magnetic moment (μ =5.00 B.M) for three unpaired electrons. This result and the absorption bands observed for the electronic spectra of Ni(II) and Co(II) complexes also support the square- planar geometry for Ni(II) and octahedral geometry for Co(II) complexes (Massino et al., 2009; Fabbrizzi et al., 2010).

3.4 Conductivity Measurements

The Co(II) and Ni(II) complexes are (1:2) electrolytes as shown by their molar conductivities (Λ_M) in DMSO at 10⁻³ M, which are in the range 160-190 Ω^{-1} cm mol⁻¹. The conductivities of the complexes in DMSO are in range reported for (1:2) electrolytes (35-38) (Table 1). (Yasemine et al., 2009; Mitu et al., 2010), while non-electrolyte nature for Cu(II). Thus, these complexes may be formulated as [Co (L1)X₂] or [Co (L2)X₂] and [M(L1)]X₂ or [M(L2)]X₂ [where M= Ni (II), Cu (II) and X=Cl⁻].

3.5 The Proposed Structure

The novel six Schiff base macrocyclic complexes were prepared and characterized by metal analysis, FT-IR and UV-VIS Spectra, conductivity measurements and magnetic susceptibility.

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Fig. 1. The proposed structure of complexes

3.6 Theoretical Study

The ball and cylinders and some of selected structural parameters (bond length and angles) of the optimized geometries are shown in fig. (2) and table 2.

Table 2.Structural parameters, bond length (°A) and angles (°) of the [Cu(L1)Cl₂] complex

Parameters		Parameters	
Bond angles(^o)		Bond lengths (^e A)	
Cl(21)-Cu(19)-Cl(20)	177.0914	Cl(21)-Cu(19)	2.1576
Cl(21)-Cu(19)-N(7)	98.5315	Cl(20)-Cu(19)	2.1601
Cl(21)-Cu(19)-N(3)	83.0636	N(7)-Cu(19)	1.8384
Cl(21)-Cu(19)-N(1)	85.3065	N(3)-Cu(19)	1.8405
CI(21)-Cu(19)-N(9)	97.0780	N(1)-Cu(19)	1.8363
CI(20)-Cu(19)-N(7)	82.1400	N(9)-Cu(19)	1.8407
CI(20)-Cu(19)-N(3)	94.0332	C(12) - O(18)	1.2093
CI(20)-Cu(19)-N(1)	94.0591	C(10) - O(17)	1.2030
CI(20)-Cu(19)-N(9)	85.8298	C(8) - O(16)	1.2061
N(7)-Cu(19)-N(3)	107.3720	C(6) - O(15)	1.2087
N(7)-Cu(19)-N(1)	176.1072	C(2) O(12)	1.2000
N(7)-Cu(19)-N(9)	74.6989	N(1)-C(12)	1.2059
N(3)-Cu(19)-N(1)	73.6285	C(11) - C(12)	1.5790
N(3)-Cu(19)-N(9)	177.8923	C(10)-C(11)	1 5412
N(1)-Cu(19)-N(9)	104.2786	N(9)-C(10)	1 4401
Cu(19)-N(9)-C(10)	109.6373	C(8)-N(9)	1.4207
Cu(19)-N(9)-C(8)	89.3597	N(7)-C(8)	1.3992
C(10)-N(9)-C(8)	133.2848	C(6)-N(7)	1.3818
O(16)-C(8)-N(9)	121.2182	C(5)-C(6)	1.5411
O(16)-C(8)-N(7)	120.9732	C(4)-C(5)	1.5419
N(9)-C(8)-N(7)	104.6525	N(3)-C(4)	1.3840
H(26)-N(7)-Cu(19)	113.0731	C(2)-N(3)	1.4047
H(23)-N(3)-Cu(19)	112.6310	N(1)-C(2)	1.4046
H(23)-N(3)-C(4)	105.3588		
H(23)-N(3)-C(2)	106.9311		
Cu(19)-N(3)-C(4)	104.9447		
Cu(19)-N(3)-C(2)	90.3357		
C(4)-N(3)-C(2)	135.1745		
O(13)-C(2)-N(3)	122.0620		
O(13)-C(2)-N(1)	122.0734		
N(3)-C(2)-N(1)	103.3025		
H(22)-N(1)-Cu(19)	113.4924		



[Cu(L1)Cl₂]

[Ni(L1)]Cl₂

Fig. 2. The optimized structural geometry of complexes

As shown in this figure, there is no obvious trend for the variation of these parameters. The values of the bond length and angles of the optimized geometries are quite similar to the experimental results of the corresponding compounds.

3.7 Biological Activity

The antibacterial action of the complexes of Ni(II), Co(II) and Cu(II) was checked by the disc diffusion technique. This was done on *Staphylococcus aureus* (gram - positive) and *Escherichia coli* (gram - negative) bacteria at 25 °C. The disc of Whatman no.4 filter paper having the diameter 6.00 mm were soaked in the solution of compounds in DMSO (1.0 mg cm⁻¹). After drying it was placed on nutrient agar plates. The inhibition area was observed after 48 h. DMSO used as control.

The bacterial growth inhibition capacity of the complexes follow the order Cu(II)>Ni(II)> Co(II) given in fig. (3).

The moderate effect was observed with Cu(II) complexes against *Staphylococcus aureus*; which known as a resistant to most commercial antibiotic. The complexes had more antibacterial activity than other ligands used this effect may be due to the presence of C=O and -NH groups which are electron-releasing. The antibacterial results evidently showed that the activity of the compounds became more pronounced when coordination to the metal ions (Ohlan et al., 2008; Singh et al., 2009).



Fig. 3. The effect complexes toward bacteria

4. CONCLUSION

Six new macrocyclic complexes were synthesized by template reaction of urea or thiourea with malonic acid and metal (II) chloride were prepared and characterized by elemental analysis, FTIR and UV-Vis. Spectra, conductivity measurements and magnetic susceptibilities. General structures of the complexes were shown in fig. (1). The Co(II) and the Ni(II) complexes are proposed to be square planar and Cu(II) complexes are proposed to be octahedral geometry around the central metal ion. The complexes have been tested for their antibacterial activities against two types of human pathogenic bacteria. It was found that compounds show different activity of inhibition on growth of the bacteria.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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