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ORIGINAL ARTICLE

Synthesis, spectral and antifungal studies of some coordination compounds of cobalt(II) and copper(II) of a novel 18-membered octaaza [N_8] tetradentate macrocyclic ligand

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Abstract The stereochemistry and coordination behavior of Co(II) and Cu(II) complexes of a novel 18-membered quadridentate macrocyclic ligand (3,4,12,13-tetraphenyl-1,2,5,6,10,11,14,15-octaazacyclooctadecane-7,9,16,18-tetraone-2,4,11,13-tetraene) have been investigated after their template synthesis. The synthesized macrocycles have been characterized by means of various physicochemical techniques viz. elemental analyses, magnetic, conductivity measurements,and spectral (IR, electronic, mass and EPR) techniques. The structure of complexes has been determined with the help of spectroscopic as well as conductivity values and found to be six coordinated octahedral and tetragonal for Co(II) and Cu(II), respectively. The ligand was coordinated to the metal ion via the malonylhydrazide moiety's imine nitrogen in a tetradentate fashion. Molar conductance measurements revealed that reported macrocyclic complexes were non-ionic in nature. All the complexes have been screened for their *in vitro* antifungal activity against a number of fungi isolated from plants. The compounds exhibit significant antifungal activity.

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1. Introduction

Metal complexes with macrocyclic ligands have gained accelerated research interest in recent years and attracted the attention of both inorganic and bioinorganic chemists (Bayri and Karakaplan, 2007; Singh et al., 2009). Aza macrocyclic ligands as well as their coordination compounds play important roles in catalytically activating small molecules in electrochemically-assisted reactions with several substrates (Chandra and Sharma, 2002). The formation of macrocyclic complexes mainly depends on the size of the internal cavity and the rigidity

of the macrocycle formed (Raman, 2009). The importance of macrocyclic complexes in coordination chemistry is because of various applications in biological processes such as photosynthesis and dioxygen transport (Singh et al., 2008a,b). The chemistry of macrocyclic complexes is also important due to its use as dyes and pigments as well as NMR shift reagents (Singh et al., 2008a,b). In the light of above applications the present paper reports the syntheses, spectral characterization and antifungal activity of cobalt(II) and copper(II) complexes of 3,4,12,13-tetraphenyl-1,2,5,6,10,11,14,15-octaazacyclooctadecane-7,9,16,18-tetraone-2,4,11,13-tetraene ligand.

2. Materials and methods

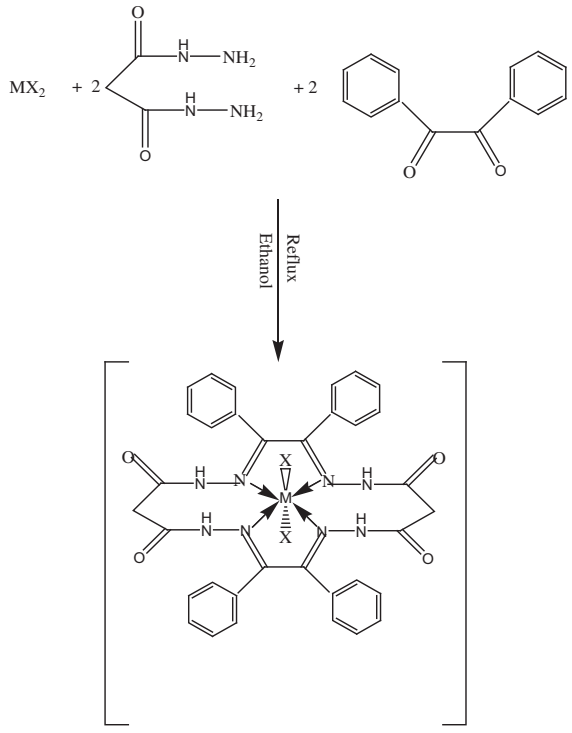
Reagent grade commercially available chemicals (Sigma–Aldrich) were used to perform all experimental work.

2.1. Elemental analysis and physical measurements

The C and H were analyzed on the Carlo – Erba 1106 elemental analyzer. The nitrogen content of the complexes was determined using Kjeldahl method. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. Magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility Gouy balance (Model no. MK1) at room temperature using copper sulphato as calibrant. Electronic spectra (UV–Vis) in the range of 200–1100 nm in DMSO were recorded on Shimadzu UV-1601 spectrophotometer. IR spectra were recorded as KBr pellets and CsI pellets in the region 4000−200 cm^{-1} on a FT-IR spectrum BX-II spectrophotometer. The X band EPR spectra of complexes were recorded at 77 K (LNT) by using frozen DMSO glass as the matrix on E_4-EPR spectrometer using DPPH as the *g* marker. Electronic impact mass spectrum was recorded on Jeol, JMS-DX-303 mass spectrometer.

2.2. General procedure: synthesis of complexes

A template reaction was carried out to synthesize the complexes. A hot EtOH solution (20 mL) of the respective divalent metal salt (10 mmol) was mixed with a hot solution (20 mL) of malonyldihydrazide (20 mmol, 2.88 g) in the same solvent. Then an EtOH solution (20 mL) of benzil (20 mmol, 4.20 g) in the presence of a few drops of conc. HCl (to adjust the pH) was added to the resultant solution and the reaction mixture was left under reflux for about 3–4 h as appropriate. The complexes precipitated out (yields and m.p. are given in Table 1) on cooling the solution. They were collected by filtration, washed and recrystallized with ethanol and dried in vacuum over anhydrous calcium chloride. The purity of complexes was checked by TLC. The general reaction for the syntheses of complexes is given below.



3. Results and discussion

The general composition for all the complexes was found to be MLX_2 (where M = Co(II), Cu(II), L = $C_{34}H_{24}N_8O_4$ and X = Cl^-, NO_3^-, NCS^-). All the complexes provide proper C,

Table 1 Physical properties and analytical data of Co(II) and Cu(II) complexes.

Complexes	Color	M.P. (°C)	Molar conductance (Ω^{-1} cm^2 mol^{-1})	Yield (%)	Elemental analysis found (calculated) (%)			
					M	C	H	N
$[CoLCl_2]$ $CoC_{34}H_{24}N_8O_4Cl_2$	Brown	246–248	17	59	7.82 (7.98)	55.32 (55.30)	3.19 (3.27)	15.24 (15.17)
$[CoL(NO_3)_2]$ $CoC_{34}H_{24}N_{10}O_{10}$	Light pink	265–268	14	62	7.52 (7.44)	51.65 (51.59)	3.13 (3.05)	17.76 (17.69)
$[CoL(NCS)_2]$ $CoC_{36}H_{24}N_{10}O_4S_2$	Brown	260–262	12	65	7.62 (7.51)	55.12 (55.17)	3.14 (3.08)	17.78 (17.87)
$[CuLCl_2]$ $CuC_{34}H_{24}N_8O_4Cl_2$	Light blue	255-257	17	59	8.58 (7.93)	54.85 (54.95)	3.15 (3.25)	15.04 (15.07)
$[CuL(NO_3)_2]$ $CuC_{34}H_{24}N_{10}O_{10}$	Light green	255–258	16	65	7.99 (7.40)	51.25 (51.29)	3.10 (3.03)	17.72 (17.59)
$[CuL(NCS)_2]$ $CuC_{36}H_{24}N_{10}O_4S_2$	Green	265–268	18	64	8.06 (7.47)	54.95 (54.84)	3.07 (3.06)	17.85 (17.76)