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Spectroscopic and antibacterial studies of new octaazamacrocyclic complexes derived from carbohydrazide and isatin



Krishan Kumar^{a,*}, Monika Kamboj^b, Kiran Jain^c, D.P. Singh^b

^a Catalysis and Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Pune 411 008, India

^b Department of Chemistry, National Institute of Technology, Kurukshetra 136 119, India

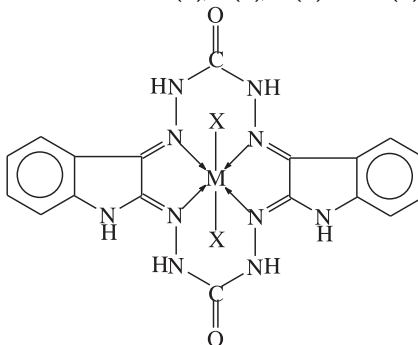
^c Department of Chemistry, M.L.N. College, Yamunanagar 135 001, India

HIGHLIGHTS

- We synthesized the macrocyclic complexes by template method in presence of divalent transition metal ions.
- Complexes were characterized by various spectral techniques, such as IR, NMR, EPR, and electronic.
- Distorted octahedral geometry has been proposed for the complexes.
- *In vitro* antibacterial activities were reported.

GRAPHICAL ABSTRACT

A novel series of macrocyclic complexes have been synthesized by template method followed by their characterization by various physicochemical techniques. These metal complexes were tested for their *in vitro* antibacterial activities against some pathogenic bacterial strains to assess their inhibiting potential. Where M = Co(II), Ni(II), Cu(II) and Zn(II); X = Cl⁻, NO₃⁻ and CH₃COO⁻.



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ABSTRACT

A novel series of the macrocyclic complexes of the type: $[M(C_{18}H_{14}N_{10}O_2)X_2]$, where M = Co(II), Ni(II), Cu(II) and Zn(II); X = Cl⁻, NO₃⁻ and CH₃COO⁻, has been synthesized by template condensation of carbohydrazide and isatin in methanolic medium. The complexes were characterized by various physico-chemical techniques, such as elemental analyses, molar conductance measurements, magnetic measurements, and electronic, NMR, IR and EPR spectral studies. The low value of molar conductance indicates them to be non-electrolytes. Based on various studies, a distorted octahedral geometry was proposed for all the metal complexes. Metal complexes were tested for their *in vitro* antibacterial activities against some pathogenic bacterial strains and compared with standard antibiotic, Ciprofloxacin. Some of the tested complexes was found effective against Gram-positive bacterial strains.

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Abbreviations: B.M., Bohr magneton; DMF-N, N-dimethylformamide; DMSO, dimethylsulphoxide; CFU, colony forming unit; MIC, minimum inhibitory concentration; MTCC, microbial type culture collection; MHA, Mueller Hinton agar; DNA, deoxyribonucleic acid; MHB, Mueller Hinton broth; NMR, nuclear magnetic resonance; MRI, magnetic resonance imaging; IR, infrared; NCCLS, National Committee for Clinical Laboratory Standards; EPR, electron paramagnetic resonance; EDTA, ethylenediaminetetraacetic acid; DOTA, tetra-azacyclododecanetetra-acetic acid.

* Corresponding author. Tel.: +91 1744 233512; fax: +91 1744 238050.

E-mail address: krishandhaka2005@gmail.com (K. Kumar).

Introduction

The design and study of well-arranged metal-containing macrocycles is an interesting field of chemistry [1]. The chemistry of macrocyclic complexes has attracted the interest of both inorganic and bioinorganic chemists in recent years [2]. Macrocyclic compounds and their derivatives are interesting ligand-system because

they are good hosts for metal ions, neutral molecules and organic cation guests [3]. The metal–ion and host–guest chemistry of macrocyclic compounds are very useful in fundamental studies *e.g.* in phase transfer catalysis and biological studies [4]. Macrocyclic nickel complexes find use in DNA recognition and oxidation [5]; while macrocyclic copper complexes find use in DNA binding and cleavage [6]. *In situ*, one pot template condensation reactions lie at the heart of macrocyclic chemistry. Therefore, template reactions have been widely used for the synthesis of macrocyclic complexes; where, transition metal ions are used as the templating agent [7]. Macrocyclic metal complexes have been useful because of their close relationship with natural products such as vitamin B₁₂ and chlorophyll [8]. Some macrocyclic complexes have been reported to show antibacterial, antifungal and anti-inflammatory activities [9–11]. Macrocyclic metal chelating agents; DOTA are useful for detecting tumor lesions [12] as well as have DNA nuclease activity [13]. Macrocyclic metal complexes of lanthanides *e.g.* Gd³⁺ are used as MRI contrast agents [14]. Prompted by these applications, in the present study, template synthesis and characterization of macrocyclic complexes of cobalt(II), nickel(II) copper(II), and zinc(II) derived from isatin and carbohydrazide has been reported. The complexes were characterized by IR, NMR, EPR, and electronic spectroscopy, elemental analyses, magnetic susceptibility and conductance measurements. The biological activity of the synthesized complexes was examined against some bacterial strains, *Staphylococcus aureus* (MTCC 96), *Bacillus subtilis* (MTCC 121) (Gram-positive), *Escherichia coli* (MTCC 1652) and *Pseudomonas aeruginosa* (MTCC 741) (Gram-negative). The results obtained were compared with standard antibiotics, Ciprofloxacin.

Experimental

Reagents

All the chemicals used were of AnalaR grade. Carbohydrazide and isatin procured from Sigma Aldrich, metal salts were purchased from s.d.-fine, Merck, Ranbaxy and were used as received.

Isolation of complexes

All the complexes were synthesized by template method since any attempt to isolate the free macrocyclic ligand was unsuccessful. To a hot, well-stirred methanolic solution (~50 cm³) of carbohydrazide (10 mmol), divalent cobalt, nickel, copper and zinc salts (hydrated) (Cl⁻, NO₃⁻, CH₃COO⁻) (5 mmol) dissolved in minimum quantity of methanol were added. The resulting solution was refluxed for 0.5 h. Subsequently, isatin (10 mmol) dissolved in ~20 cm³ methanol was added in the refluxing mixture and refluxing was continued for 8–10 h. The mixture was concentrated to half its volume, cooled to room temperature and kept in desiccator overnight. After overnight standing, dark coloured precipitates separate out, which were filtered, then washed with methanol, acetone, and ether and dried *in vacuo*. The obtained yields were ~60–75%.

The template condensation of thiocarbohydrazide and isatin in the presence of divalent metal salts, in the molar ratio 2:2:1 is shown in Fig. S1 1.

Analytical and physical measurements

The microanalyses of C, H, and N were performed on elemental analyzer (Perkin Elmer 2400) at Sophisticated Analytical Instrumentation Facility (SAIF), Punjab University, Chandigarh. Magnetic susceptibility measurements were performed at room temperature on a Vibrating Sample Magnetometer (Model PAR 155) at Indian Institute of Technology (IIT) Roorkee, The metal contents were

determined by EDTA methods [15]. IR spectra were recorded on a Fourier transform (FT)-IR spectrophotometer (Perkin Elmer) in the range 4000–200 cm⁻¹ using Nujol Mull/KBr pellets. ¹H NMR spectra (at room temperature, in DMSO d₆) were recorded on a Bruker AVANCE II 400 NMR spectrometer (400 MHz) with reference to Me₄Si (0.0 ppm), at SAIF, Punjab University, Chandigarh. Electronic spectra (in DMSO) were recorded at room temperature on a Hitachi 330 spectrophotometer (850–200 nm). The EPR spectra were recorded at room temperature on a Varian E-112 ESR spectrometer, at SAIF, IIT Bombay. The conductivity was measured on digital conductivity meter (HPG system, G-3001). Melting points were determined by using capillaries in electrical melting point apparatus.

Results and discussion

Chemistry

Analytical data (Table 1) showed the formulae for macrocyclic complexes as: [M(C₁₈H₁₄N₁₀O₂)X₂]; where M = Co(II), Ni(II), Cu(II), and Zn(II); X = Cl⁻, NO₃⁻, and CH₃COO⁻. The complexes were soluble in DMF and DMSO but insoluble in water. They are thermally stable to ~270 °C and decomposed without melting. Conductivity in DMSO indicated them to be non-electrolyte (15–20 Ω⁻¹ cm² mol⁻¹) [16]. Attempts at crystallization using mixtures of solvents, slow diffusion or low-temperature crystallization were unsuccessful. However, analytical, spectroscopic, and magnetic data enable us to predict the structures of the complexes. All the complexes give satisfactory elemental analyses, as given in Table 1.

IR spectra

IR spectral data of all the metal complexes are given in Table 2. A medium intensity band appeared at ~3245 cm⁻¹, which was assigned to the ν(N–H) stretching vibrations (Fig. S1 2) of carbohydrazide and isatin moieties [17]. A pair of bands corresponding to ν(NH₂) appeared at ~3250–3340 cm⁻¹ in the IR spectrum of carbohydrazide but are absent in IR spectra of the metal complexes. Further, no strong absorption band was observed near 1733 cm⁻¹, indicating the absence of >C=O of isatin, confirming condensation of carbonyl group of acetonylacetone and amino group of carbohydrazide [18]. A strong absorption band in the region ~1595–1640 cm⁻¹ were assigned to ν(C=N) stretching vibrations [19,20]. These results provide strong evidence for the formation of macrocyclic frame [18–20]. The value of ν(C=N) stretching vibration was found lower (1595–1640 cm⁻¹) than the expected value (1650–1690 cm⁻¹), which may be explained on the basis of a drift of lone pair density of azomethine nitrogen towards the metal atom, [21] indicate the coordination through nitrogen atom. IR bands at ~2893–2995 cm⁻¹ were assigned to ν(C–H) stretching vibrations [21]. Another set of medium intensity bands in the region 1400–1600 cm⁻¹ were attributed to ν(C=C) aromatic stretching vibrations of isatin and the bands around 845–875 cm⁻¹ may be attributed to C–H out-of-plane bending vibrations of the aromatic group [20,22]. Four amide bands appeared in the region 1645–1660, 1510–1530, 1230–1250, 750–785 cm⁻¹ were assigned to amide I [ν(C=O)], amide II [ν[(C–N) + δ(N–H)]], amide III [δ(N–H)] and amide IV [φ(C–O)] bands, respectively [23]. The presence of absorption bands in the region 1410–1430, 1280–1325 and 1010–1040 cm⁻¹, in all the nitrate complexes suggest that the nitrates were unidentate coordinated to metal atom [24]. IR spectra of the acetate complexes showed absorption bands in the region 1650–1680 cm⁻¹ and 1258–1290 cm⁻¹ which were assigned to ν(COO⁻)_{as} and ν(COO⁻)_s stretching vibrations, respectively. The difference between ν_{as} and ν_s was 392–380 cm⁻¹, greater than 144 cm⁻¹, indicating unidentate

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