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Synthesis and characterization of divalent metal complexes of the macrocyclic ligand derived from isatin and 1,2-diaminobenzene

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Abstract: A novel series of complexes of the type $[M(C_{28}H_{18}N_6)X_2]$, where M=Co(II), Ni(II), Cu(II) or Zn(II) and X = Cl^-, NO_3^- or CH_3COO^-, were synthesized by template condensation of isatin and 1,2-diaminobenzene in methanolic medium. The complexes were characterized with the help of various physico–chemical techniques, such as elemental analyses, molar conductance measurements, magnetic measurements, and NMR, infrared and far infrared spectral studies. The low value of molar conductance indicates them to be non-electrolytes. Based on various studies, a distorted octahedral geometry may be proposed for all the complexes. All the synthesized macrocyclic complexes were also tested for their *in vitro* antibacterial activity against some pathogenic bacterial strains. The *MIC* values shown by the complexes against these bacterial strains were compared with those of the standard antibiotics linezolid and cefaclor. Some of the complexes showed good antibacterial activities.

Keywords: macrocyclic ligands; infrared; magnetic measurements; divalent metal complexes; antibacterial.

INTRODUCTION

The chemistry of macrocyclic complexes has received much attention in recent years[1] due to their potential applications and importance in the area of coordination chemistry.[2,3] Thus, the study of macrocyclic complexes is becoming a growing class of research.[4] Macrocycles are best prepared by the aid of metal ions as templates to direct the condensation reaction towards ring closure.[5] Transition metal complexes of nitrogen donor ligands have been studied in detail on account of their stereochemistry and wide practical utility.[6] A number of nit-

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rogen donor macrocyclic derivatives have long been used in analytical, industrial and medical applications.[7] Nitrogen-containing macrocycles have a strong tendency to form stable complexes with transition metals.[8] Some macrocyclic complexes have been reported to exhibit potent antibacterial, antifungal and anti-HIV activities.[9–11] Macrocyclic nickel complexes find use in DNA recognition and oxidation[12] while macrocyclic copper complexes are employed in DNA binding and cleavage.[13] Schiff bases obtained by the condensation of aromatic amines with isatin are powerful anticonvulsant, antiviral, antibacterial and antifungal agents.[14,15] Cu(II) complexes with isatin Schiff base ligands are potential antitumour agents.[16] In a previous work, macrocyclic complexes derived from isatin and ethylenediamine were reported.[17] Based on the above-mentioned studies, in the present paper, macrocyclic complexes of Co(II), Ni(II), Cu(II) and Zn(II) derived from isatin and 1,2-diaminobenzene (*o*-phenylenediamine) are reported. The complexes were characterized by various physico-chemical techniques, such as IR and NMR spectroscopy, magnetic susceptibilities, elemental analyses, and conductance.

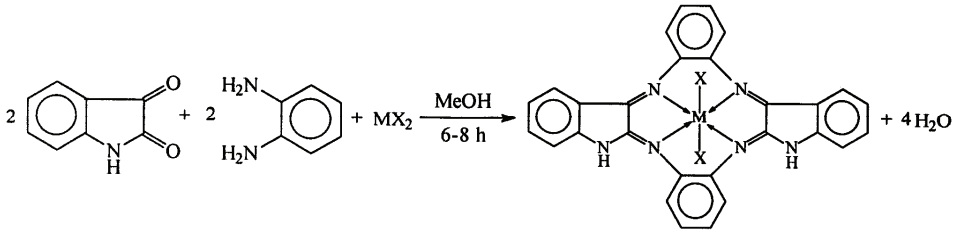
EXPERIMENTAL

Isolation of the complexes

All the chemicals used were of AnalR Grade. All the employed solvents were of high purity. Moisture was excluded from the glass apparatus using $CaCl_2$ tubes.

All the complexes were obtained by template synthesis since any attempt to isolate the free macrocyclic ligand was unsuccessful. To a hot, well-stirred methanolic solution (≈40 cm^3) of 1,2-diaminobenzene (10 mmol), divalent cobalt, nickel, copper or zinc salts (hydrated) (5 mmol) (Cl^-, NO_3^-, CH_3COO^-) dissolved in the minimum quantity of methanol were added. The resulting solution was refluxed for 0.5 h. Subsequently, isatin (10 mmol) dissolved in ≈20 cm^3 methanol was added to the refluxing mixture and refluxing was continued for 6–8 h. The mixture was concentrated to half its volume, cooled to room temperature and kept in a 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 41–48 %.

The template condensation of isatin and 1,2-diaminobenzene in the presence of divalent metal salts, in the molar ratio 2:2:1 is shown in Scheme I.



Scheme 1. Proposed structure of the synthesized complexes, where M = Co(II), Ni(II), Cu(II) or Zn(II) and X = Cl^-, NO_3^- or CH_3COO^-.

Analytical and physical measurements

The microanalyses of C, H and N were performed at the Sophisticated Analytical Instrument Facility (SAIF), CDRI, Lucknow. The melting points were determined using capillaries in an electrical M.P. apparatus. The metal contents were determined by standard EDTA methods. The electronic spectra (DMF) were recorded on a Cary 14 spectrophotometer. The magnetic susceptibility measurements were performed on a vibrating sample magnetometer at the SAIF, IIT Roorkee. The IR spectra were recorded on an FTIR spectrophotometer, Parkin Elmer, in the range 4000–200 cm^{-1} using Nujol Mull/KBr pellets. The NMR spectra were recorded on Bruker NMR spectrometer (300 MHz). The conductivity was measured on a digital conductivity meter (HPG System, G-3001).

Antibacterial activity

All synthesized macrocyclic complexes were tested for their *in vitro* antibacterial activity against some bacterial strains using the spot-on-lawn method on Muller Hinton Agar (MHA) medium.[18]

Five test pathogenic bacterial strains, *viz. Staphylococcus aureus*, *Bacillus pumilus*, *Bacillus megaterium* and *Staphylococcus epidermidis* (Gram-positive), *Pseudomonas aeruginosa* (Gram-negative) were considered for the determination of the minimum inhibitory concentration (*MIC*) value of selected complexes. The *MIC* is the lowest concentration of an antimicrobial agent that prevents viable growth of microorganisms after overnight incubation. The turbidity of all the bacterial cultures was adjusted to 0.5 McFarland by preparing bacterial suspension of 4–6 well-isolated colonies of the same morphological type selected from a soybean casein digest agar (SCDA) plate. In this method, the test concentrations of the synthesized complexes were made from 128 to 0.25 μg cm^{-3} (4 mg cm^{-3} of DMSO) in sterile tubes No. 1––10. SCDA medium was prepared and 100 μl of the sterile SCDA was poured into each sterile tube followed by the addition of 200 μl of the complex in tube 1. Two-fold serial dilutions were performed from tube 1–10 and the excess SCDA (100 μl) was discarded from the last tube No. 10. To each tube, 100 μl of standard inoculum was added. All the tubes were incubated for 24 h at 37 °C. Dilutions of standard antibiotics (linelozid and cefaclor) were prepared in the same manner for comparison. DMSO, the solvent, was used as a negative control.

RESULTS AND DISCUSSION

The complexes were soluble in DMF and DMSO but were insoluble in common organic solvents and water. All complexes were thermally stable up to 255 °C. Conductivity measurements in DMSO indicated them to be non-electrolyte (10 S cm^2 mol^{-1}).[19] The tests for the anions were positive only after decomposition of the complexes, indicating their presence inside the coordination sphere. The analytical data of the reported complexes are as follows:

$Co(C_{28}H_{18}N_6)Cl_2$ ***(1)***. Yield: 48.70 %; F.W.: 567.9; Anal. Calcd.: C, 59.16; H, 3.16; N, 14.79; Co, 10.37 %. Found: C, 59.09; H, 3.10; N, 14.71; Co, 10.21 %.

$Co(C_{28}H_{18}N_6)(CH_3COO)_2$ ***(2)***. Yield: 42.15 %: F.W.: 614.9; Anal. Calcd.: C, 62.45; H 3.90; 13.66; Co, 9.58 %. Found: C, 62.36; H, 3.81; N, 13.58; Co, 9.43 %.

$Ni(C_{28}H_{18}N_6)Cl_2$ ***(3)***. Yield: 43.12 %; F.W.: 567.7; Anal. Calcd.: C, 59.19; H, 3.17; N, 14.79; Ni, 10.34 %. Found: C, 59.11; H, 3.09; N, 14.66; Ni, 10.23 %.

Ni($C_{28}H_{18}N_6$)(NO_3)$_2$ ***(4)***. Yield: 43.89 %; F.W.: 620.7; Anal. Calcd.: C, 54.13; H, 2.93; %: N, 18.04; Ni, 9.46 %. Found: C, 54.02; H, 2.87; N, 17.98; Ni, 9.29.

Ni($C_{28}H_{18}N_6$)(CH_3COO)$_2$ ***(5)***. Yield: 41.50 %; F.W.: 614.7; Anal. Calcd.: C, 62.47; H, 3.90; N, 13.67; Ni, 9.55 %. Found: C, 62.35; H, 3.81; N, 13.59; Ni, 9.34 %.

Cu($C_{28}H_{18}N_6$)Cl_2 ***(6)***. Yield: 46.95 %; F.W.: 572.5; Anal. Calcd.: C, 58.69; H, 3.14; N, 14.67; Cu, 11.09 %. Found: C, 58.54; H, 3.07; N, 14.58; Cu, 10.89 %.

Cu($C_{28}H_{18}N_6$)(NO_3)$_2$ ***(7)***. Yield: 42.46 %; F.W.: 625.5; Anal. Calcd.: C, 53.72; H, 2.88; N, 17.91; Cu, 10.15 %. Found: C, 53.63; H, 2.82; N, 17.85; Cu, 9.92 %.

Cu($C_{28}H_{18}N_6$)(CH_3COO)$_2$ ***(8)***. Yield: 45.59 %; F.W.: 619.5; Anal. Calcd.: C, 61.99; H, 3.87; N, 13.56; Cu, 10.25 %. Found: C, 61.82; H, 3.80; N, 13.46; Cu, 10.12 %.

Zn($C_{28}H_{18}N_6$)(CH_3COO)$_2$ ***(9)***. Yield: 42.64 %; F.W.: 621.0; Anal. Calcd.: C, 61.84; H, 3.86; N, 13.53; Zn, 10.47 %. Found: C, 61.79; H, 3.76; N, 13.44; Zn, 10.27 %.

IR spectra

The presence of a single medium band in the region ≈3265–3350 cm^{-1} in all the complexes may be assigned to N–H stretching vibrations (Table I).[20] It was noted that a pair of bands corresponding to ν(NH_2) stretching vibrations appeared at 3210–3435 cm^{-1} in the IR spectrum of 1,2-diaminobenzene but was absent in the IR spectra of all the metal complexes. Furthermore, no strong absorption band was observed in the spectra of the complexes near 1700 cm^{-1}, indicating the absence of the >C=O group of isatin and thus confirming the condensation of the carbonyl group of isatin and the amino group of 1,2-diaminobenzene.[21,22] A strong absorption band in the region 1595–1625 cm^{-1} may be assigned to C=N stretching vibrations.[5,23] These results provide strong evidence for the formation of the macrocyclic frame.[24] The lower values of ν(C=N) may be explained based on a drift of the lone pair electron density of the azomethine nitrogen towards the central metal atom.[22,25] Another set of medium intensity bands in the region 1500–1585 cm^{-1} were attributed to ν(C=C) aromatic stretching vibrations of the phenyl groups and the bands around 845–875 cm^{-1} may be assigned to C–H out--of-plane bending vibrations of the phenyl groups. The C–N stretching vibrations may occur in the range 1015–1355 cm^{-1}.

The far IR spectra of the complexes showed bands in the region 422–435 cm^{-1} corresponding to ν(M–N) stretching vibrations,[26,27] which give insight into the coordination of the azomethine nitrogen to the central metal atom.[28] The bands present at 315–330 cm^{-1} in the chloro compounds were assigned to ν(M–Cl)

stretching vibrations.[3,26] The bands present at 210–245 cm^{-1} in all nitrate and acetate complexes may be assigned to ν(M–O) stretching vibrations (Table I).[26]

Table I. Infrared spectral data, ν / cm^{-1}, of the divalent Co, Ni, Cu and Zn complexes derived from isatin and 1,2-diaminobenzene

Cmpd.	Complex	N–H	C=N	C=C	C–N	M–N	M–Cl	M–O
1	$[Co(C_{28}H_{18}N_6)Cl_2]$	3270	1605	1500–1580	1230	425	320	–
2	$[Co(C_{28}H_{18}N_6)(CH_3COO)_2]$	3265	1599	1502–1580	1245	422	–	238
3	$[Ni\ (C_{28}H_{18}N_6)Cl_2]$	3320	1623	1500–1585	1268	455	330	–
4	$[Ni(C_{28}H_{18}N_6)(NO3)_2]$	3345	1625	1502–1584	1136	456	–	210
5	$[Ni(C_{28}H_{18}N_6)(CH_3COO)_2]$	3318	1598	1502–1575	1015	460	–	245
6	$[Cu(C_{28}H_{18}N_6)Cl_2]$	3299	1595	1510–1570	1333	453	311	–
7	$[Cu(C_{28}H_{18}N_6)(NO_3)_2]$	3289	1625	1502–1580	1299	428	–	220
8	$[Cu(C_{28}H_{18}N_6)(CH_3COO)_2]$	3336	1610	1502–1575	1355	432	–	235
9	$[Zn(C_{28}H_{18}N_6)(CH_3COO)_2]$	3350	1622	1502–1575	1256	445	–	228

NMR Spectra

The ^{1}H-NMR spectrum of the zinc(II) complex showed a broad signal at 10.8 ppm, which may be assigned to the NH protons of the isatin moiety.[29,30] The multiplets observed in the region 6.65–7.88 ppm may be assigned to the aromatic ring protons of isatin and the *o*-phenylene moiety.[31]

Magnetic measurements and electronic spectra

Cobalt complexes. The magnetic moments of the cobalt(II) complexes were measured at room temperature and were found in the range 4.92–4.96 μ_B, which is consistent with three unpaired electrons. The solution spectra of the cobalt(II) complexes exhibited absorptions in the regions 8185–9100cm^{-1} (ν_1), ≈12650–15750 cm^{-1}(ν_2) and 18,720–20,250 cm^{-1}(ν_3). The spectra resemble to those reported for distorted octahedral cobalt(II) complexes.[32] The various bands may be assigned to $^4T_{1g} \rightarrow {}^4T_{2g}$(F), ($\nu_1$); $^4T_{1g} \rightarrow {}^4A_{2g}$(F) ($\nu_2$) and $^4T_{1g} \rightarrow {}^4T_{1g}$(P) ($\nu_3$). The assignment of the first spin-allowed band seems plausible since the first band appears at approximately half the energy of the visible band.[33]

Nickel complexes. The magnetic moments of nickel(II) complexes were measured at room temperature and were found in the range 2.96–2.99 μ_B, consistent with two unpaired electrons in the nickel(II) ion. The solution spectra of the Ni(II) complexes exhibit a well discernable band with a shoulder on the low energy side. Two other bands, generally observed in the region 16650–17020 cm^{-1} (ν_2), and 27800–28260 cm^{-1} (ν_3), were assigned to $^3A_{2g} \rightarrow {}^3T_{1g}$(F), and $^3A_{2g} \rightarrow {}^3T_{1g}$(P), respectively. The first two bands, resulting from the splitting of the ν_1 band, were in the range 9700–10280 and 11750–12280 cm^{-1} and may be assigned to $^3B_{1g} \rightarrow {}^3E_g$ and $^3B_{1g} \rightarrow {}^3B_{2g}$.[33] The intense higher energy band at 34480 cm^{-1} may be due to a π–π* transition of the (C=N) group. The various

bands do not follow any regular pattern and seem to be anion independent. The spectra suggest a distorted octahedral nature for these complexes.

Copper complexes. The magnetic moments of copper complexes were found in the range 1.76–1.82 μ_B, corresponding to one unpaired electron in the copper(II) ion. The absorption spectra of the copper complexes exhibited bands in the region 17700–19630 cm^{-1} with a shoulder on the low energy side at 14550––16320 cm^{-1}, which showed that these complexes were distorted octahedral.[32,33] Assuming tetragonal distortion in the molecule, the d-orbital energy level sequence for these complexes may be represented as: $x^2–y^2 > z^2 > xy > xz > yz$ and the shoulder may be assigned to: $z^2 \rightarrow x^2–y^2$ ($^2B_{1g} \rightarrow {}^2B_{2g}$) and the broad band contains both the $xy \rightarrow x^2–y^2$ ($^2B_{1g} \rightarrow {}^2E_g$) and $xz, yz \rightarrow x^2–y^2$ ($^2B_{1g} \rightarrow {}^2A_{2g}$) transitions.[34] The band separation of the spectra of the complexes was of the order of 2500 cm^{-1}, which is consistent with the proposed geometry of these complexes.[34] Therefore, it may be concluded that all the complexes of copper(II) have a distorted octahedral geometry.

Biological results

All the synthesized macrocyclic metal complexes were tested for their *in vitro* antibacterial activities against five test bacterial strains, *viz. S. aureus*, *B. pumilus*, *B. megaterium*, *P. aeruginosa* and *S. epidermidis*. It has been suggested that chelation/coordination reduces the polarity of the metal ion mainly because of the partial sharing of its positive charge with donor groups within the whole chelate ring system.[35] Thus, the process of chelation increases the lipophilic nature of the central metal atom, which, in turn, favours its permeation through the lipoid layer of the bacterial membrane, thereby allowing the metal complex to cross the membrane more effectively, thus increasing the activity of the complexes. In addition to this, many other factors, such as solubility, dipole moment and conductivity, are influenced by the metal ion, which may be possible reasons for the antibacterial activities of these metal complexes.[36] It was also observed that some moieties, such as an azomethine linkage or a heteroaromatic nucleus, introduced into such compounds exhibit extensive biological activities that may be responsible for the increase in the hydrophobic character and liposolubility of the molecules in crossing the cell membrane of the microorganism, thereby enhancing the biological utilization ratio and activity of such complexes.[37]

All the complexes of the tested series possessed good antibacterial activities against all the tested bacterial strains. The *MIC* (minimum inhibitory concentration) shown by the metal complexes against these bacterial strains was compared with the *MIC* values shown by the standard antibiotics linezolid and cefaclor (Table II). In the whole series, complex **7** showed the highest activity, with *MIC* of 2 μg cm^{-3} against the bacterial strains *P. aeruginosa* and *S. epidermidis*. Complex **7** also showed a *MIC* of 8 μg cm^{-3} against the bacterial strain *B. pumilus*,

which was equal to the *MIC* shown by the standard antibiotic cefaclor against the same bacterial strain. Complex **5** showed an *MIC* of 8 μg cm^{-3} against the bacterial strain *P. aeruginosa*, which was equal to the *MIC* values shown by the standard antibiotics cefaclor and linezolid against the same bacterial strain. Complexes **6** and **8** showed an *MIC* of 8 μg cm^{-3} against the bacterial strain *B. megaterium*, which was equal to the *MIC* shown by the standard antibiotic cefaclor against the same bacterial strain. Similarly, complex **9** also showed an *MIC* of 8 μg cm^{-3} against the bacterial strain *B. pumilus*, which was equal to *MIC* shown by standard antibiotic cefaclor against the same bacterial strain (Table II).

Table II Minimum inhibitory concentration (*MIC* / μg cm^{-3}) of the complexes determined using the macro dilution method

Cmpd.	Complex	*MIC* / μg cm^{-3}				
		S. aureus	*B. pumilus*	*B. megaterium*	*P. aeruginosa*	*S. epidermidis*
1	$[Co(C_{28}H_{18}N_6)Cl_2]$	64	128	>128	32	64
2	$[Co(C_{28}H_{18}N_6)(CH_3COO)_2]$	64	32	64	32	16
3	$[Ni(C_{28}H_{18}N_6)Cl_2]$	128	64	32	16	32
4	$[Ni(C_{28}H_{18}N_6)(NO_3)_2]$	8	16	32	64	16
5	$[Ni(C_{28}H_{18}N_6)(CH_3COO)_2]$	32	64	16	8	32
6	$[Cu(C_{28}H_{18}N_6)Cl_2]$	16	32	8	16	16
7	$[Cu(C_{28}H_{18}N_6)(NO_3)_2]$	32	8	16	2	2
8	$[Cu(C_{28}H_{18}N_6)(CH_3COO)_2]$	64	32	8	6	32
9	$[Zn(C_{28}H_{18}N_6)(CH_3COO)_2]$	16	8	32	4	16
Linezolid		4	4	4	8	8
Cefaclor		2	8	8	8	2

Some complexes, *i.e.*, **7**–**9**, showing *MIC* values of 2, 6 and 4 μg cm^{-3}, respectively, were found to be even better than the standard antibiotics against some bacterial strains (Table II). The *MIC* values of complex **2** were found to be in the range 16–64 μg cm^{-3} and complex **4** registered *MIC* values in the range 8–––64 μg/cm^{-3} (Table II).

ABBREVIATIONS

MIC – Minimum inhibitory concentration
MTCC – Microbial type culture collection
MHA – Muller Hinton agar
CFU – Colony forming unit
DMF – *N*,*N*-Dimethylformamide
DMSO – Dimethyl sulphoxide
NMR – Nuclear Magnetic Resonance
IR – Infrared
SCDA – Soybean casein digest agar
EDTA – Ethylenediaminetetraacetic acid

DNA – Deoxyribonucleic acid
HIV – Human immunodeficiency virus.

CONCLUSIONS

Based on elemental analyses, conductivity and magnetic measurements, and electronic, IR and NMR spectral studies, the structure as shown in Scheme I may be proposed for all of the synthesized complexes.

However, not all the synthesized macrocyclic metal complexes showed good antibacterial activities against all the bacterial strains, but some of the complexes of copper and zinc, *viz*., **7**–**9** that showed *MIC* values of 2, 6 and 4 μg cm^{-3}, respectively, were even better than the standard antibiotics linezolid and cefaclor against some bacterial strains.

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И З В О Д

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА НЕКИХ МЕТАЛ(II) КОМПЛЕКСА СА МАКРОЦИКЛИЧНИМ ТИПОМ ЛИГАНДА КОЈИ ЈЕ ДОБИВЕН У РЕАКЦИЈИ ИЗАТИНА СА 1,2-ДИАМИНОБЕНЗЕНОМ

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Темплатном кондензационом синтезом, полазећи из изатина и 1,2-диаминобензена, синтетизована је серија новик комплекса опште формуле $[M(C_{28}H_{18}N_6)X_2]$, где је M = Co(II), Ni(II), Cu(II), Zn(II); X = Cl^-, NO_3^-, CH_3COO^-. За карактеризацију ових комплекса употребљене су различите физичкохемијске методе, као што се елементална микроанализа, кондуктометријска и магнетна мерења, нуклеарна магнетно-резонанциона, инфрацрвена и далека инфрацрвена спектроскопска мерења. Ниске вредности за моларну проводљивост указују да су изоловани комплекси неелектролити, а на бази спектроскопских мерења закључено је да ови комплекси имају дисторговану октаедарску геомтерију. Сви изоловани макроциклични комплекси су тестирани *in vitro* на антибактеријску активност за неколико патогених бактеријских линија. Добивене MIC вредности ових комплекса су поређене са одговарајућим вредностима за стандардне антибиотике линезолид и цефаклор. Нађено је да неки испитивани комплекси имају завидну антибактеријску активност.

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