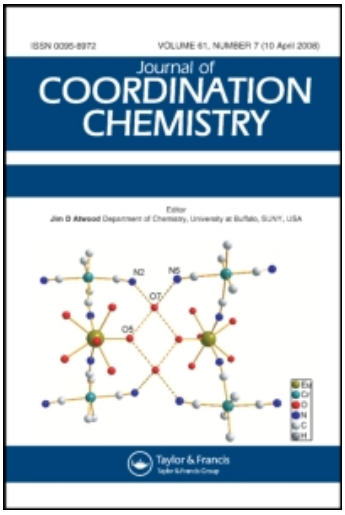

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Macrocyclic complexes of divalent transition metal ions derived from succinyldihydrazide and diacetyl with their antibacterial studies

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Macrocyclic complexes of divalent transition metal ions derived from succinyldihydrazide and diacetyl with their antibacterial studies

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Condensation of succinyldihydrazide with diacetyl in the presence of divalent metal ions in the molar ratio of 1:1:1 resulted in the formation of $[M(C_8H_{12}N_4O_2)X_2]$, where M = Co(II), Ni(II), Cu(II), Zn(II), and X = Cl^-, NO_3^-, CH_3COO^-. The complexes have been characterized with the aid of various physicochemical techniques, such as elemental analyses, conductance measurements, electronic, NMR, EPR, and IR spectral studies. On the basis of these studies, a distorted octahedral geometry in which two nitrogens and two carbonyl oxygens were coordinated have been proposed for all the complexes. The complexes were also tested for their *in vitro* antibacterial activities against some bacterial strains and compared with standard antibiotic *Ciprofloxacin*. Some of the complexes showed good antibacterial activities against selected bacterial strains.

Keywords: Antibacterial; Diacetyl; Macrocyclic Schiff base; EPR spectra

1. Introduction

The chemistry of macrocyclic complexes has attracted the interest of both inorganic and bioinorganic chemists [1, 2] as good hosts for metal ions, neutral molecules, and organic cation guests [3]. Metal-ion and host–guest chemistry of macrocyclic compounds are very useful 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]. Template reactions have been widely used for the syntheses of macrocyclic complexes where the transition metal ion is used as templating agent [7]. Macrocyclic metal complexes have close relationship with natural products, such as vitamin B_{12} and chlorophyll [8]. Some macrocyclic complexes have been reported to show antibacterial, antifungal, and anti-inflammatory activities [9–11]. Macrocyclic metal chelating agents are useful in detecting tumor lesions [12]. Macrocyclic metal complexes of lanthanides, e.g., Gd^{3+}, are used as MRI contrast agents [13]. Several amide macrocyclic complexes having redox properties were also

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reported [14, 15]. In a previous research, we reported macrocyclic complexes of divalent transition metal ions derived from succinyldihydrazide and benzil/glyoxal [16]. Prompted by these, a new series of macrocyclic complexes of Co(II), Ni(II), Cu(II), and Zn(II) obtained by template condensation reaction of succinyldihydrazide and diacetyl is now reported. The complexes are characterized with various physicochemical techniques, such as molar conductance, elemental analyses, magnetic susceptibilities measurements, infrared (IR), NMR, and electronic spectra and are screened for their *in vitro* antibacterial activities against some bacterial strains. Some complexes showed good antibacterial activities against some selected bacterial strains.

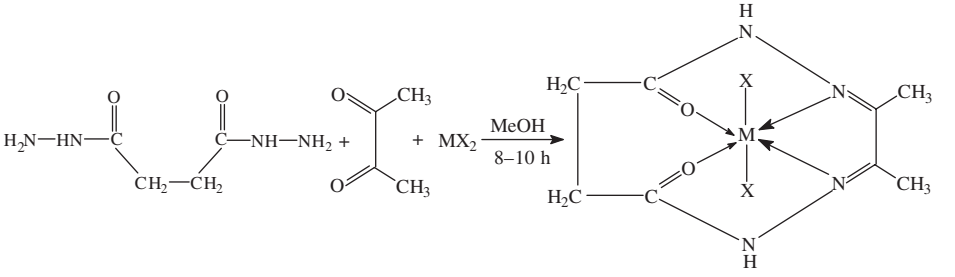
2. Experimental

2.1. *Materials*

All chemicals and solvents used in this study were of AnalaR grade. Diacetyl was procured from Acros, New Jersey, USA. Metal salts were purchased from S.D.-Fine, Mumbai, India, or Merck, Ranbaxy, India, and used as received.

2.2. *Synthesis of metal complexes*

Several attempts to isolate the free macrocyclic ligand were unsuccessful. Hence, all complexes were synthesized by the template method. To a hot stirring methanolic solution (~50 cm^3) of succinyldihydrazide (10 mmol) divalent cobalt, nickel, copper, and zinc salts (10 mmol) (Cl^-, NO_3^-, or CH_3COO^- anions) dissolved in 20 cm^3 methanol were added. The resulting solution was refluxed for 0.5 h. After that, diacetyl (10 mmol) dissolved in ~20 cm^3 methanol was added to the refluxing mixture and again refluxed for 6–8 h. On overnight cooling, light colored complexes formed, which were filtered, washed with methanol, acetone, and ether, and dried *in vacuo* (yield 60–75%). The purities of the complexes were checked by TLC with the single spot corresponding to the final product. The complexes were soluble in DMF and DMSO and thermally stable to ~250–280°C. The template syntheses of the complexes are shown in scheme 1.



Scheme 1. Scheme for synthesis of macrocyclic complexes, where M = Co(II), Ni(II), Cu(II), Zn(II), and X = Cl^-, NO_3^-, and CH_3COO^-.

2.3. *Analytical and physical measurements*

Microanalyses of C, H, and N were carried out by elemental analyzer (Perkin Elmer 2400) at SAIF, Punjab University, Chandigarh, and the metal contents were determined by standard EDTA methods. Electronic spectra (DMF) were recorded on a Cary 14 spectrophotometer. Magnetic susceptibility measurements were carried out at SAIF, IIT Roorkee. IR spectra were recorded using KBr pellets at SAIF, Punjab University, Chandigarh. Far IR spectra were recorded using Nujol mulls at IIC, IIT Roorkee. NMR spectra (at room temperature) (in DMSO-d_6) were recorded on a Bruker AVANCE II 400 NMR spectrometer (400 MHz) with Me_4Si reference (0.0 ppm) at SAIF, Punjab University, Chandigarh. EPR spectra were recorded at room temperature on a Varian E-112 ESR spectrometer at SAIF, IIT Bombay. Conductivities were measured on a digital conductivity meter (HPG System, G-3001).

3. Biological assay

All the synthesized macrocyclic complexes were tested for their *in vitro* antibacterial activities against some bacterial strains using the agar well diffusion method [17].

3.1. *Test microorganisms*

Four bacterial strains, namely *Staphylococcus aureus* (MTCC 96), *Bacillus subtilis* (MTCC 121) (Gram-positive), *Escherichia coli* (MTCC 1652), and *Pseudomonas aeruginosa* (MTCC 741) (Gram-negative) were selected for the evaluation of antibacterial activities of the synthesized macrocyclic complexes.

3.2. *Primary screening*

The antibacterial activities of all the newly synthesized macrocyclic metal complexes were evaluated by the agar well diffusion method. All the microbial cultures were adjusted to 0.5 McFarland standards, which is visually comparable to a microbial suspension of approximately 1.5×10^8 cfu mL^{-1}. A 20 mL of Mueller Hinton agar medium was poured into each Petri plate and the plates were swabbed with 100 µL inocula of the test microorganisms and kept for 15 min for adsorption. Using a sterile cork borer of 8 mm diameter, wells were bored into the seeded agar plates and these were loaded with a 100 µL volume of 4 mg mL^{-1} of each complex in DMSO. All the plates were incubated at 37°C for 24 h. Antibacterial activities of all the synthesized complexes were evaluated by measuring the zone of growth inhibition against the test microorganisms with zone reader (Hi Antibiotic Zone Scale). The medium with DMSO as solvent was used as a negative control, whereas media with *Ciprofloxacin* was used as positive control. The experiments were performed in triplicate.

3.3. *Determination of minimum inhibitory concentration of the synthesized complexes*

Minimum inhibitory concentration (MIC) is the lowest concentration of an antimicrobial compound that will inhibit the visible growth of microorganisms after overnight incubation. The MIC of the complexes was tested against bacterial strains through a macrodilution tube method. In this method, the test concentrations of the synthesized complexes were made from 128 to 0.25 $\mu g\,mL^{-1}$ in the sterile tubes no. 1–10 and in the case of antibiotic dilutions were made from 20 to 0.039 $\mu g\,mL^{-1}$. Mueller Hinton Broth (MHB) medium was prepared and 100 µL sterile MHB medium was poured in each sterile tube followed by the addition of 200 µL of the complex in tube 1. Twofold serial dilutions were carried out in tubes no. 1–10 and excess broth (100 µL) was discarded from the last tube no. 10. To each tube, 100 µL of standard inoculum was added. *Ciprofloxacin* (standard antibiotic) were used as control. All the tubes were incubated for 24 h at 37°C and growth was observed on each plate.

4. Results and discussion

4.1. *Chemistry*

The analytical data shown in table 1 suggest $[M(C_8H_{12}N_4O_2)X_2]$, where M = Co(II), Ni(II), Cu(II), and Zn(II) and X = Cl^-, NO_3^-, and CH_3COO^-. The test for anions was positive only after decomposing the complexes, indicating their presence inside the coordination sphere. Molar conductance measured in DMSO indicates them to be non-electrolytes (10–20 $Ohm^{-1}\,cm^2\,mol^{-1}$) [18]. Several attempts failed to obtain a single crystal suitable for X-ray crystallography. However, the analytical, spectroscopic, and magnetic data enable us to predict the structures of the complexes.

4.2. *IR spectra*

A pair of medium intensity bands at ~3200 and ~3250 cm^{-1} corresponding to $\nu(NH_2)$ was present in succinyldihydrazide, but absent in IR spectra of all the metal complexes [19]. A broad peak at ~3350–3400 cm^{-1} was observed in all the metal complexes which

Table 1. Analytical data of divalent cobalt, nickel, copper, and zinc complexes derived from succinyldihydrazide and diacetyl.

Complexes	Found (Calcd %)				Color	Yield (%)
	M	C	H	N		
$[Co(C_8H_{12}N_4O_2)Cl_2]$ (**1**)	18.00(18.07)	29.43(29.44)	3.66(3.68)	17.14(17.17)	Dark brown	60
$[Co(C_8H_{12}N_4O_2)(NO_3)_2]$ (**2**)	15.49(15.54)	25.33(25.32)	3.14(3.16)	22.16(22.16)	Gray	63
$[Co(C_8H_{12}N_4O_2)(OAc)_2]$ (**3**)	15.69(15.79)	38.58(38.60)	4.83(4.82)	14.99(15.01)	Dark gray	64
$[Ni(C_8H_{12}N_4O_2)Cl_2]$ (**4**)	18.01(18.05)	29.43(29.53)	3.67(3.69)	17.19(17.23)	Light gray	67
$[Ni(C_8H_{12}N_4O_2)(NO_3)_2]$ (**5**)	15.48(15.52)	25.38(25.39)	3.15(3.17)	22.19(22.22)	Light brown	70
$[Ni(C_8H_{12}N_4O_2)(OAc)_2]$ (**6**)	15.70(15.77)	38.70(38.71)	4.81(4.84)	15.05(15.05)	Dark brown	74
$[Cu(C_8H_{12}N_4O_2)Cl_2]$ (**7**)	19.17(19.25)	29.02(29.09)	3.63(3.63)	16.94(16.96)	Yellowish brown	71
$[Cu(C_8H_{12}N_4O_2)(NO_3)_2]$ (**8**)	16.34(16.59)	25.05(25.06)	3.12(3.13)	21.94(21.93)	Light yellow	75
$[Cu(C_8H_{12}N_4O_2)(OAc)_2]$ (**9**)	16.69(16.85)	38.00(38.19)	4.76(4.77)	14.81(14.85)	Brown	61
$[Zn(C_8H_{12}N_4O_2)(OAc)_2]$ (**10**)	17.19(17.25)	37.91(37.99)	4.72(4.75)	14.76(14.77)	Yellowish white	69

may be assigned to the ν(NH) stretching vibrations [20, 21]. A strong absorption at $\sim$1660 cm^{-1} in succinyldihydrazide was attributed to >C=O group of the −CONH. This peak shifted to lower frequency ($\sim$1625–1640 cm^{-1}) in IR spectra of the metal complexes [22], suggesting coordination of oxygen of amide group. No strong absorption was observed near $\sim$1716 cm^{-1} as observed in the spectrum of diacetyl indicating the absence of >C=O of diacetyl, indicating condensation of carbonyl of diacetyl and amino of succinyldihydrazide [23, 24]. This is supported by the appearance of a new strong absorption at $\sim$1595–1620 cm^{-1} which may be assigned to ν(C=N) [25, 26]. These results provide strong evidence for the formation of the macrocycle [27]. The lower values of ν(C=N) indicate coordination of azomethine nitrogen to metal [28]. The presence of absorption bands in the regions $\sim$1410–1440, $\sim$1285–1320, and $\sim$1000–1030 cm^{-1} in the nitrate complexes suggests that the nitrates were unidentate coordinated to the metal [29]. IR spectra of the acetate complexes showed absorptions at 1665–1680 cm^{-1}, assigned to ν(COO$^-$) asymmetric stretching of acetate and another at 1270–1290 cm^{-1}, assigned to ν(COO$^-$) symmetric. A difference between ν_{as} and ν_s was 395–390 cm^{-1}, greater than 144 cm^{-1}, indicating unidentate acetate [30].

Far IR spectra of the complexes showed bands at $\sim$425–445 cm^{-1} corresponding to ν(M–N) [31–33], consistent with the coordination of azomethine nitrogen [34]. Bands at $\sim$300–315 cm^{-1} may be assigned to ν(M–Cl) [31, 33]. Bands at $\sim$220–250 cm^{-1} in nitrate complexes were assigned due to ν(M–O) of nitrate [31].

4.3. *NMR spectra*

The ^{1}H-NMR spectrum of zinc(II) complex showed a broad singlet at 8.45 ppm due to −CONH [20, 35]. A singlet at 2.45 ppm may be due to $-CH_2$ [36]. The singlet at 2.12 ppm may be assigned to protons of diacetyl [37].

4.4. *Magnetic measurements and electronic spectra*

4.4.1. Cobalt complexes. The magnetic moments of cobalt complexes at room temperature were 4.85–4.92 B.M., corresponding to three unpaired electrons [38]. The electronic spectra of cobalt complexes showed bands at $\sim$8125–9045 (ν_1), 12,440–15,650 (ν_2), and 18,750–20,290 cm^{-1} (ν_3), similar to those reported for distorted octahedral cobalt complexes [39]. Thus, the bands may be assigned to $^4T_{1g} \rightarrow {}^4T_{2g}$ (F), (ν_1); $^4T_{1g} \rightarrow {}^4A_{2g}$ (F), (ν_2); and $^4T_{1g} \rightarrow {}^4T_{1g}$ (P), (ν_3), respectively. The assignment of the first spin-allowed band seems plausible since the first band appears at approximately half the energy of the visible band [39].

4.4.2. Nickel complexes. The nickel complexes showed magnetic moments of 2.83–2.87 B.M. at room temperature corresponding to two unpaired electrons [38]. Electronic spectra of nickel complexes exhibit a band with a shoulder on the low energy side. The other two bands observed at $\sim$16,760–17,040 cm^{-1} (ν_2) and 26,890–28,150 cm^{-1} (ν_3) were assigned to $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) (ν_3). The first two bands resulted from the splitting of one band ν_1 ($\sim$9730–1120 and 11,850–12,400 cm^{-1}), which may be assigned to $^3B_{1g} \rightarrow {}^3E_g$ and $^3B_{1g} \rightarrow {}^3B_{2g}$ transitions, assuming the effective symmetry to be D_{4h} (component of $^3T_{2g}$ in O_h symmetry) [39]. The intense higher energy

Table 2. EPR spectral data of the copper(II) complexes.

Complexes	$g_{\parallel}$	$g_{\perp}$	G
1	2.2195	2.1525	1.4393
2	2.2185	2.1605	1.3613
3	2.2208	2.1250	1.7664

band at ~34,120 cm^{-1} may be due to a π–π^* transition of (C=N). The spectra were consistent with distorted octahedral complexes.

4.4.3. Copper complexes. The magnetic moments of copper complexes were 1.75–1.79 B.M., corresponding to one unpaired electron. The electronic spectra of the copper complexes exhibit bands at ~17,650–19,540 cm^{-1} with a shoulder at ~14,460–16,150 cm^{-1}, and showed that these complexes have distorted octahedral geometry [39]. 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 $xy \rightarrow x^2-y^2$ ($^2B_{1g} \rightarrow {}^2E_g$) and xz, $yz \rightarrow x^2-y^2$ ($^2B_{1g} \rightarrow {}^2A_{2g}$) transitions [40]. Band separation in the spectra of these complexes was of the order of 2530 cm^{-1}, which was consistent with the proposed geometry [40]. Therefore, it may be concluded that all the copper complexes are distorted octahedral.

4.5. *EPR spectra*

EPR spectra of the copper(II) complexes were recorded at room temperature in solid state, on X-band, at a frequency of 9.5 GHz under the magnetic field of 3000 G. The spectra of copper(II) complexes exhibit a single anisotropic broad signal. The analyses of the spectra give $g_{\parallel}$ values in the range 2.2185–2.2208 and $g_{\perp}$ values in the range 2.1250–2.1605 (table 2). The trend $g_{\parallel} > g_{\perp} > 2.0023$ (g_e) observed for these complexes indicate that the unpaired electron was localized in $d_{x^2-y^2}$ orbital of copper(II), with distortion in the copper(II) complexes from O_h symmetry to D_{4h} symmetry. The observed $g_{\parallel}$ value for the copper(II) complexes was less than 2.3, which was in agreement with the covalent character of the metal ligand bond [41].

$G = (g_{\parallel}-2)/(g_{\perp}-2)$, which measures the exchange interaction between the copper centers in a polycrystalline solid has been calculated. Values of "G" less than 4 indicate considerable exchange interaction in the solid complex [41]. In the copper(II) complexes reported in this article, the "G" values were less than 4 (table 2).

4.6. *Biological results and discussion*

The synthesized macrocyclic complexes were tested for their *in vitro* antibacterial activities against four test bacteria, namely *S. aureus* (MTCC 96), *B. subtilis* (MTCC 121) (Gram-positive), *E. coli* (MTCC 1652), and *P. aeruginosa* (MTCC 741). The MIC shown by the complexes against these bacterial strains was compared with MIC shown by a standard antibiotic *Ciprofloxacin* (table 3, figure 1). The complexes **5** and **8** showed

Table 3. MIC shown by complexes against test bacteria using agar dilution assay.

	MIC ($\mu g\ mL^{-1}$)[a]			
Complexes	a	b	c	d
1	64	128	32	>128
2	32	>128	128	64
3	64	32	>128	16
4	32	64	64	>128
5	16	8	16	32
6	32	64	64	>128
7	64	–	>128	128
8	16	8	16	32
9	8	64	64	>128
10	32	64	64	64
Ciprofloxacin	5	5	5	5

a – *S. aureus* (MTCC 96); b – *B. subtilis* (MTCC 121); c – *E. coli* (MTCC 1652); d – *P. aeruginosa* (MTCC 741); Ciprofloxacin – a standard antibiotic.
"–" Means no activity.
[a]Means of three replicates.

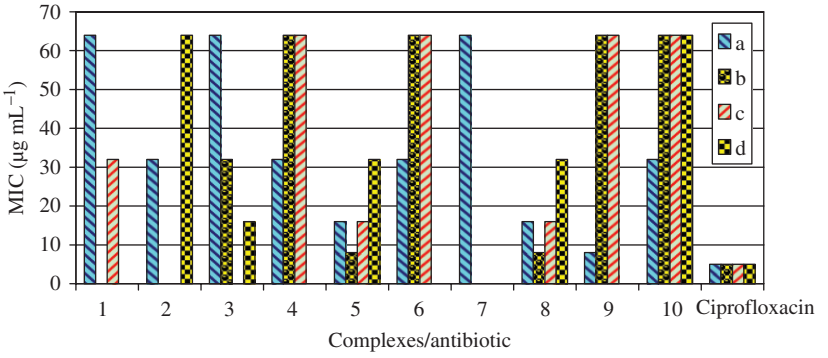


Figure 1. Comparison of MIC of complexes with Ciprofloxacin (a – *S. aureus* (MTCC 96); b – *B. subtilis* (MTCC 121); c – *E. coli* (MTCC 1652); d – *P. aeruginosa* (MTCC 741); and Ciprofloxacin – a standard antibiotic).

MIC of $8\,\mu g\,mL^{-1}$ against *B. subtilis* and a MIC of $16\,\mu g\,mL^{-1}$ against both the bacterial strains *S. aureus* and *E. coli*. The MIC of **2**, **4**, **6**, and **10** were $32\,\mu g\ mL^{-1}$ against bacterial strain *B. subtilis*.

5. Conclusions

Based on elemental analyses, conductivity, magnetic, electronic, IR, NMR, and EPR spectral studies, the structure shown in scheme 1 may be proposed for all complexes.

The synthesized macrocyclic metal complexes do not show good antibacterial activities against all the bacterial strains, but some of the copper complexes show good

antibacterial activities against *S. aureus* and *B. subtilis*, and some of the nickel complexes also show good activity against *B. subtilis*. It has been suggested that chelation/coordination reduces the polarity of the metal ion [42]. Other factors such as solubility, dipole moment, and conductivity influenced by metal ion may affect antibacterial activities of these metal complexes [43]. It also has been observed that azomethine linkage or heteroaromaticity in such compounds exhibit extensive biological activities [44].

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