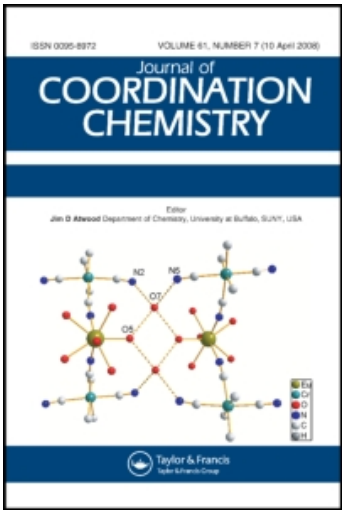

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Synthesis, spectroscopic studies, and antibacterial activities of 14-membered tetraazamacrocyclic complexes of divalent transition metal ions

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Synthesis, spectroscopic studies, and antibacterial activities of 14-membered tetraazamacrocyclic complexes of divalent transition metal ions

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A new series of macrocyclic complexes, $[M(C_{48}H_{32}N_4)X_2]$, where M = Co(II), Ni(II), Cu(II), and Zn(II); $X = Cl^-, NO_3^-, CH_3COO^-$, have been synthesized by condensation of 1,8-diaminonaphthalene and benzil, in the presence of divalent metal salts in methanolic medium. The complexes have been characterized by elemental analyses, conductance measurements, magnetic measurements, and electronic, NMR, IR, and MS spectral studies. The low value of molar conductance indicates the presence of non-electrolytes. A distorted octahedral geometry is proposed for the complexes. The metal complexes were also tested for their *in vitro* antibacterial activities against some bacterial strains and compared with the standard antibiotic Ciprofloxacin. Some tested complexes show good antibacterial activities against some bacterial strains.

Keywords: Antibacterial activity; Benzil; Macrocyclic complexes; MIC

1. Introduction

Metal-containing macrocycles is an interesting field of chemistry [1] with many synthetic and natural macrocyclic compounds investigated [2]. The chemistry of macrocyclic complexes has attracted the interest of both inorganic and bioinorganic chemists [3] and is developing very rapidly [4]. Macrocyclic compounds and their derivatives are good hosts for metal anions, neutral molecules, and organic cation guests [5]. 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 [6]. Aza-macrocyclic ligands have remained a focus for many decades [7]. *In situ* one-pot template condensation reactions lie at the heart of macrocyclic chemistry [8], widely used for the synthesis of macrocyclic complexes [9], where the transition metal ions are templating agents [10]. Metal ions direct the reaction preferentially towards cyclic rather than oligomeric or polymeric products [11]. Synthetic macrocyclic complexes mimic some naturally occurring macrocycles because of their resemblance to natural macrocycles like metalloproteins, porphyrins, and cobalamine [12, 13]. Transition metal

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macrocyclic complexes have biological activities, including antiviral, anticarcinogenic [13], antifertile [14], antibacterial, and antifungal [15] properties. Macrocyclic metal complexes of lanthanides, e.g., Gd^{3+}, are used as magnetic resonance imaging (MRI) contrast agents [16]. Macrocyclic metal chelating agents (tetra-azacyclododecanete-traacetic-acid (DOTA)) are useful for detecting tumor lesions [17]. Macrocyclic complexes are also used as NMR shift reagents [18]. In our previous paper, we reported the synthesis and characterization of macrocyclic complexes of cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) derived from 1,8-diaminonaphthalene and glyoxal [19]. This article reports template synthesis and characterization of macrocyclic complexes of cobalt(II), nickel(II), copper(II), and zinc(II) derived from 1,8-diamino-naphthalene and benzil. Complexes are characterized by IR, NMR, MS, elemental analyses, magnetic susceptibility and conductance measurements. All the synthesized complexes have been examined for their *in vitro* antibacterial activities against some bacterial strains *Staphylococcus aureus* (microbial-type culture collection (MTCC) 96), *Bacillus subtilis* (MTCC 121) (Gram-positive), *Escherichia coli* (MTCC 1652), and *Pseudomonas aeruginosa* (MTCC 741) (Gram-negative). The results are compared with Ciprofloxacin.

2. Experimental

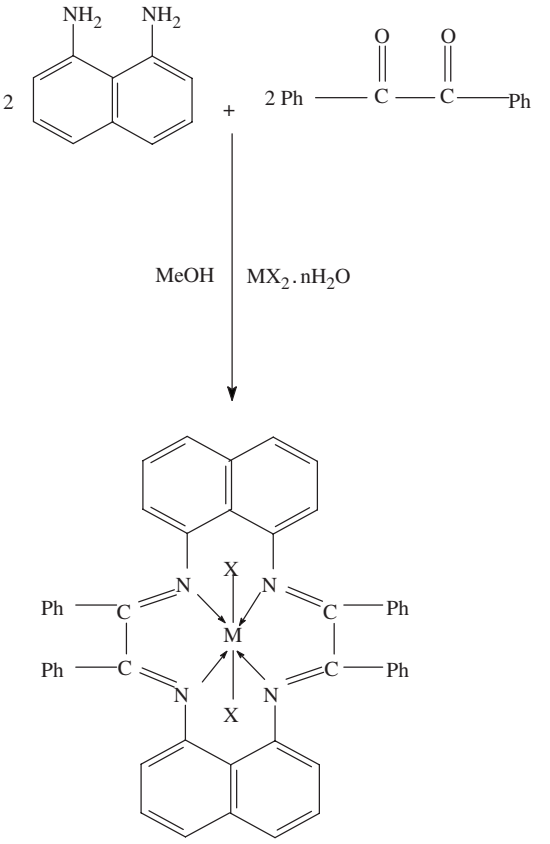
2.1. *Reagents*

All chemicals were of AnalaR grade. 1,8-Diaminonaphthalene and benzil were procured from Acros; metal salts were purchased from s.d.-fine, Merck, Ranbaxy and used as received.

2.2. *Isolation of complexes*

All the complexes were synthesized by template method, i.e., by condensation of 1,8-diaminonaphthalene and benzil in the presence of the respective divalent metal salt. To a hot stirring methanolic solution ($\sim$50 cm^3) of 1,8-diaminonaphthalene (10 mmol, 1.58 g), cobalt, nickel, copper, and zinc salts (Cl^-, NO_3^-, CH_3COO^-) (5 mmol) dissolved in the minimum of methanol ($\sim$20 cm^3) were added. The resulting solution was refluxed for 0.5 h. After that, benzil (10 mmol, 2.10 g) was added in the refluxing mixture and refluxing continued for 8–10 h. The mixture was concentrated to half of its volume, cooled to room temperature, and kept in a desiccator overnight. Dark precipitates were filtered, washed with methanol, acetone, and diethylether, and dried *in vacuo*. The purity of all the complexes was checked by thin-layer chromatography (TLC) which results in a single spot corresponding to the final product. The yields are $\sim$65–70%. The complexes are soluble in DMF and DMSO and thermally stable in the range $\sim$260–350°C, after which decomposition occurred.

The template condensation of 1,8-diaminonaphthalene and benzil in the presence of divalent metal salts in the molar ratio 2 : 2 : 1 is shown in figure 1.



where M = Co(II), Ni(II), Cu(II), Zn(II);
X = Cl^-, NO_3^-, CH_3COO^-
n = 2,3,4,6

Figure 1. Scheme for the synthesis of macrocyclic complexes and proposed structures. M = Co(II), Ni(II), Cu(II), Zn(II); X = Cl^-, NO_3^-, CH_3COO^-; n = 2,3,4,6.

2.3. *Analytical and physical measurements*

Microanalyses (C, H, and N) were estimated by an elemental analyzer (Perkin Elmer 2400) at SAIF, Punjab University, Chandigarh. Magnetic susceptibility measurements were carried out at SAIF, IIT Roorkee, on a Vibrating Sample Magnetometer (Model PAR 155). IR spectra were recorded on a FT-IR spectrophotometer (Perkin Elmer) from 4000 to 200 cm^{-1} using Nujol mull/KBr pellets. ^{1}H-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. Electronic spectra (in DMSO) were recorded on a Hitachi 330 spectrophotometer (850–200 nm) at room temperature. The EI mass spectra (at room temperature) were recorded on TOF MS ES + mass spectrometer. The metal content in the complexes was determined by literature methods. Molar conductivities were measured on a digital conductivity meter (HPG system, G-3001). Melting points were determined using capillaries in an electrical melting point apparatus.

3. Biological assay

3.1. *Test microorganisms*

Four bacterial strains were selected on the basis of their clinical importance in causing diseases in humans. *S. aureus* (MTCC 96), *B. subtilis* (MTCC 121) (Gram-positive), *E. coli* (MTCC 1652), and *P. aeruginosa* (MTCC 741) (Gram-negative) were screened for antibacterial activity of the compounds.

3.2. In vitro *antibacterial activity*

3.2.1. Primary screening. The bacterial activities were evaluated by agar well diffusion method [20]. 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} [21]. Twenty milliliters of Mueller Hinton agar media were poured into each petri plate and plates were swabbed with 100 µL inocula of the test microorganisms and kept for 15 min for adsorption. Using 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 compound reconstituted in DMSO. All the plates were incubated at 37°C for 24 h. Antimicrobial activity was evaluated by measuring the zone of growth inhibition against the test organisms with a zone reader (Hi Antibiotic zone scale). The medium with DMSO as solvent was used as a negative control, whereas Ciprofloxacin was used as positive control. The experiments were performed in triplicate.

3.2.2. Determination of minimum inhibitory concentration of the 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 MICs of the macrocyclic complexes were tested against bacterial strains through a macrodilution tube method [21]. In this method, the test concentrations of complexes were made from 128 to 0.25 µg mL^{-1} in the sterile tubes No. 1–10. Mueller Hinton Broth (MHB) medium was prepared and 100 µL sterile MHB medium was poured in each sterile tube, followed by addition of 200 µL of the complex in tube 1. Two-fold serial dilutions were carried out from tubes 1–10 and excess broth (100 µL) was discarded from tube No. 10. To each tube, 100 µL of standard inoculum was added. Ciprofloxacin (antibacterial drug) was used as control. All the tubes were incubated for 24 h at 37°C.

4. Results and discussion

4.1. *Chemistry*

The analytical data show the suggested formula for macrocyclic complexes, $[M(C_{48}H_{32}N_4)X_2]$, where $M = Co(II), Ni(II), Cu(II), Zn(II)$, and $X = Cl^-, NO_3^-$, CH_3COO^-. The low molar conductance values (10–17 Ohm^{-1} cm^2 mol^{-1}) in DMSO indicate the presence of non-electrolytes [22]. Various attempts such as crystallization

Table 1. Analytical data of divalent cobalt, nickel, copper, and zinc complexes derived from 1,8-diaminonaphthalene and benzil.

	Complexes	Found (Calcd) % M	C	H	N	Color	Molecular weight
1	$[Co(C_{48}H_{32}N_4)Cl_2]$	7.40 (7.42)	72.50 (72.54)	3.92 (4.03)	6.98 (7.05)	Dark grey	793.9
2	$[Co(C_{48}H_{32}N_4)(NO_3)_2]$	6.83 (6.95)	67.88 (68.00)	3.76 (3.78)	9.91 (9.92)	Black	846.9
3	$[Co(C_{48}H_{32}N_4)(OAc)_2]$	6.98 (7.00)	74.13 (74.19)	4.38 (4.51)	6.59 (6.66)	Black	840.9
4	$[Ni(C_{48}H_{32}N_4)Cl_2]$	7.32 (7.40)	72.63 (72.63)	3.99 (4.04)	7.00 (7.06)	Shiny green	793.7
5	$[Ni(C_{48}H_{32}N_4)(NO_3)_2]$	6.88 (6.93)	68.00 (68.08)	3.73 (3.78)	9.68 (9.93)	Reddish brown	846.6
6	$[Ni(C_{48}H_{32}N_4)(OAc)_2]$	6.89 (6.98)	74.26 (74.28)	4.50 (4.52)	6.58 (6.67)	Black	840.7
7	$[Cu(C_{48}H_{32}N_4)Cl_2]$	7.92 (7.96)	72.00 (72.18)	4.00 (4.01)	6.99 (7.02)	Shiny black	798.5
8	$[Cu(C_{48}H_{32}N_4)(NO_3)_2]$	7.39 (7.46)	67.67 (67.68)	3.74 (3.76)	9.73 (9.87)	Dark green	851.5
9	$[Cu(C_{48}H_{32}N_4)(OAc)_2]$	7.51 (7.52)	73.79 (73.85)	4.29 (4.49)	6.60 (6.63)	Black	845.5
10	$[Zn(C_{48}H_{32}N_4)(OAc)_2]$	7.65 (7.72)	73.59 (73.67)	4.43 (4.48)	6.56 (6.61)	Light grey	847.4

using mixtures of solvents and low temperature crystallization were unsuccessful in obtaining a single crystal suitable for X-ray crystallography. However, the analytical, spectroscopic, and magnetic data enable us to predict the structure of the synthesized complexes. All complexes give satisfactory elemental analyses as shown in table 1.

4.2. *IR spectra*

A pair of bands is present in the spectrum of 1,8-diaminonaphthalene at ~3350 and ~3390 cm^{-1} corresponding to $\nu(NH_2)$ which was absent in the infrared spectra of all the metal complexes. Further, no strong absorption was observed at 1690 cm^{-1}, indicating the absence of >C=O of benzil. The disappearance of these bands and appearance of a new strong absorption at 1590–1629 cm^{-1} indicates condensation of the carbonyl of benzil and amino of diaminonaphthalene [23] with the formation of the macrocyclic frame [24], as these bands may be assigned to ν(C=N) [25]. The value of ν(C=N) was lower (1590–1629 cm^{-1}) than the expected value (1650–1690 cm^{-1}), explained on the basis of shift of electron density of azomethine nitrogen toward the metal [26], indicating that coordination takes place through nitrogen of C=N. Various absorption bands at ~1450–1588 cm^{-1} may be assigned to ν(C=C) of the naphthalene ring [27] as well as phenyl rings [28]. Bands at ~740–785 cm^{-1} may be assigned to ν(C–H) (out of plane bending) of aromatic rings [29]. The presence of absorptions at 1410–1440, 1290–1325, and 1010–1040 cm^{-1} in the IR spectra of the nitrato complexes suggest that the nitrates are unidentate coordinated to the central metal [30]. IR spectra of the acetate complexes showed an absorption at 1650–1685 cm^{-1} assigned to $\nu(COO^-)_{as}$ asymmetric stretch of acetate and another at 1258–1295 cm^{-1} to $\nu(COO^-)_s$ symmetric stretch. A difference $(\nu_{as} - \nu_s)$ of 390–370 cm^{-1} (greater than 144 cm^{-1}) indicates unidentate coordination of acetate [31]. Far IR spectra show bands at ~420–450 cm^{-1}, corresponding to ν(M–N) [32–34] from (M–N) azomethine vibration and identifies coordination of azomethine nitrogen [35]. Bands at 300–320 cm^{-1} may be assigned to ν(M–Cl) [32–34]. Bands at ~220–250 cm^{-1} in all nitrato complexes were assigned to ν(M–O) [32, 33].

4.3. *NMR spectra*

^{1}H-NMR spectrum of the zinc(II) complex showed multiplets at 6.82–7.53 ppm corresponding to aromatic ring protons (12H) of naphthalene [19] and multiplets at 7.40–7.85 ppm due to aromatic ring protons (20H) of benzil [28].

4.4. *Mass spectra*

The EI mass spectra of Co(II), Ni(II), Cu(II), Zn(II) macrocyclic complexes have been recorded. All the spectra exhibit parent peaks due to molecular ions $[M]^+$ and $[M+2]^+$. The molecular ion $[M]^+$ peaks obtained for various complexes were as follows: (1) at $m/z = 792.9$ (due to Cl^{35}) and 794.9 (due to Cl^{37}) of molecular ions $[M]^+$ and $[M+2]^+$ of $[Co(C_{48}H_{32}N_4)Cl_2–2H]^+$ ion; (2) at $m/z = 845.9$ due to molecular ion $[Co(C_{48}H_{32}N_4)(NO_3)_2–H]^+$; (3) at $m/z = 838.9$ due to $[Co(C_{48}H_{32}N_4)(OAc)_2–2H]^+$; (4) at $m/z = 845.6$ due to $[Ni(C_{48}H_{32}N_4)(NO_3)_2–H]^+$; (5) at $m/z = 839.7$ due to $[Ni(C_{48}H_{32}N_4)(OAc)_2–H]^+$; (6) at $m/z = 849.5$ due to $[Cu(C_{48}H_{32}N_4)(NO_3)_2–2H]^+$; (7) at $m/z = 844.4$ due to $[Cu(C_{48}H_{32}N_4)(OAc)_2–H]^+$; and (8) at $m/z = 846.4$ due to $[Zn(C_{48}H_{32}N_4)(OAc)_2–H]^+$. The proposed molecular formulas of these complexes were confirmed by comparing their molecular formula weights with m/z values. The data are in good agreement with the proposed molecular formulas for these complexes, confirming formation of the macrocyclic frame. In addition to peaks due to the molecular ions, the spectra exhibit peaks assignable to various fragments arising from thermal cleavage of the complexes.

4.5. *Magnetic measurements and electronic spectra*

4.5.1. Cobalt complexes. The magnetic moments of the cobalt complexes measured at room temperature were in the range 4.88–4.96 B.M., which corresponds to octahedral Co(II) [36]. The electronic spectra of the cobalt(II) complexes in DMSO exhibit three absorptions in the regions 8250–9480 cm^{-1} (ν_1) ($\varepsilon = 5.5–5.9 \times 10^3\ mol^{-1}\ cm^{-1}$), 13,400–15,350 cm^{-1} (ν_2) ($\varepsilon = 4.6–5.6 \times 10^3\ mol^{-1}\ cm^{-1}$) and 18,400–20,600 cm^{-1} (ν_3) ($\varepsilon = 5.1–6.3 \times 10^3\ mol^{-1}\ cm^{-1}$), respectively. The spectra of the complexes were reported to be those of a distorted octahedral [37]. Thus, the various 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 symmetry of these complexes was not idealized octahedral, but was D_{4h}. The assignment of the first spin-allowed band seems plausible since the first band appears approximately at half the energy of the visible band [38].

4.5.2. Nickel complexes. The magnetic moments of the nickel complexes at room temperature were 2.91–2.96 B.M., in agreement with two unpaired electrons [36]. The spectra of nickel(II) complexes in DMSO exhibit a band with a shoulder on the low energy side. The other two bands observed at 16,550–17,300 cm^{-1} (ν_2) ($\varepsilon = 4.2–4.8 \times 10^3\ mol^{-1}\ cm^{-1}$) and 27,600–28,200 cm^{-1} (ν_3) ($\varepsilon = 4.1–5.8 \times 10^3\ mol^{-1}\ cm^{-1}$) were assigned to $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) (ν_3), respectively. The first two bands result from the splitting of one band, ν_1 in the range ~9,650–10,300 ($\varepsilon = 4.5–4.9 \times 10^3\ mol^{-1}\ cm^{-1}$) and 11,900–12,400 cm^{-1} ($\varepsilon = 4.5–5.4 \times 10^3\ mol^{-1}\ cm^{-1}$), assigned

to $^3B_{1g} \rightarrow {}^3E_g$ and $^3B_{1g} \rightarrow {}^3B_{2g}$, assuming the effective symmetry to be D_{4h} (component of $^3T_{2g}$ in O_h symmetry) [38]. The intense higher energy bands at 34,540 cm^{-1} may be due to a π–π^* transition of the (C=N) group. The spectra were consistent with distorted octahedral complexes.

4.5.3. Copper complexes. The magnetic moments of copper complexes were 1.75–1.80 B.M. Electronic spectra of the copper(II) complexes exhibit bands at 17,850–19,500 cm^{-1} ($\varepsilon = 4.1$–4.6×10^3 mol^{-1} cm^{-1}), with a shoulder on the low energy side at ~14,400–16,000 cm^{-1} ($\varepsilon = 3.5$–4.0×10^3 mol^{-1} cm^{-1}), indicating distorted octahedral [37, 38]. Assuming tetragonal distortion, the d-orbital energy level sequence for these complexes may be assigned as: $x^2 - y^2 > z^2 > xy > xz > yz$; 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 $xy - yz \rightarrow x^2 - y^2$ ($^2B_{1g} \rightarrow {}^2A_{2g}$) transitions [39]. The band separation of the spectra of the complexes was of the order of 2500 cm^{-1}, consistent with the proposed geometry of these complexes [39].

4.6. *Biological results and discussion*

The synthesized macrocyclic complexes were evaluated against Gram-positive and Gram-negative bacteria. MIC of these macrocyclic complexes were determined by the method given by Andrews [21]. Standard antibiotic, Ciprofloxacin, was used for comparison with antibacterial activities of these complexes. All complexes possessed good antibacterial activity against Gram-positive bacteria (*S. aureus, B. subtilis*) as well as Gram-negative (*E. coli*, *P. aeruginosa*) except **3**, **4**, and **6** (table 2). Complexes **1**, **2**, and **9** exhibit good activity against all the tested bacteria with zones of inhibition from 29.6 to 16.6 mm. Complexes **5** and **9** showed activity against all bacteria except *P. aeruginosa* and **7** and **8** showed activity against *S. aureus* only. From minimum

Table 2. *In vitro* antibacterial activities of the complexes through agar well diffusion method.

	Diameter of growth of inhibition zone (mm)[a]			
Complexes	a	b	c	d
1	25.3 ± 0.05	21.6 ± 0.07	19.3 ± 0.06	16.3 ± 0.05
2	27.6 ± 0.04	23.3 ± 0.02	21.6 ± 0.03	17.6 ± 0.04
3	–	–	–	–
4	–	–	–	–
5	25.6 ± 0.01	22.3 ± 0.02	17.6 ± 0.03	–
6	–	–	–	–
7	23.3 ± 0.08	–	–	–
8	17.6 ± 0.03	–	–	–
9	29.6 ± 0.05	24.3 ± 0.02	23.6 ± 0.03	16.6 ± 0.04
10	26.3 ± 0.06	21.6 ± 0.04	16.6 ± 0.02	–
Ciprofloxacin	26.3 ± 0.05	24.0 ± 0.01	25.0 ± 0.04	22.0 ± 0.05

–, No activity; a, *S. aureus* (MTCC 96); b, *B. subtilis* (MTCC 121); c, *E. coli* (MTCC 1652); d, *P. aeruginosa* (MTCC 741); Ciprofloxacin, Standard antibiotic.
[a]Values, including diameter of the well (8 mm), are means of three replicates.

Table 3. Minimum inhibitory concentrations (in $\mu g\,mL^{-1}$) of the complexes obtained using macro dilution method.

	MIC ($\mu g\,mL^{-1}$)			
Complexes	a	b	c	d
1	32	64	64	128
2	16	64	64	128
5	32	64	128	–
7	64	–	–	–
8	128	–	–	–
9	16	32	32	128
10	32	64	128	–
Ciprofloxacin	05	05	05	05

–, No activity; a, *S. aureus* (MTCC 96); b, *B. subtilis* (MTCC 121); c, *E. coli* (MTCC 1652); d, *P. aeruginosa* (MTCC 741); Ciprofloxacin, Standard antibiotic.

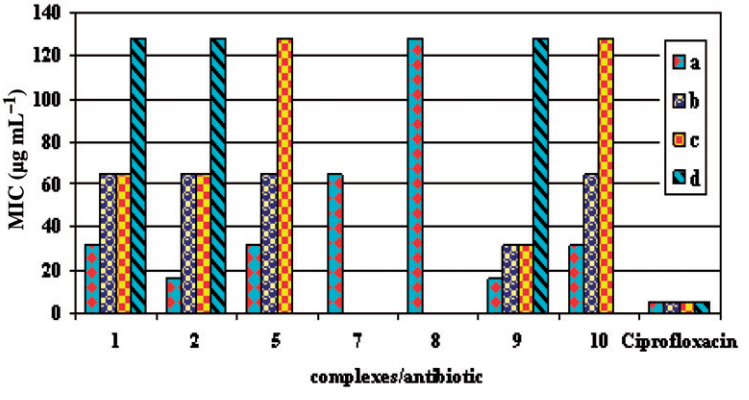


Figure 2. Comparison of MICs ($\mu g\,mL^{-1}$) of synthesized complexes with standard antibiotic. a, *S. aureus* (MTCC 96); b, *B. subtilis* (MTCC 121); c, *E. coli* (MTCC 1652); d, *P. aeruginosa* (MTCC 741); ciprofloxacin, Standard antibiotic.

inhibitory activities, **2** and **9** were most effective with MIC of $16\,\mu g\,mL^{-1}$ for *S. aureus* (table 3; figure 2). MICs of **1**, **5**, and **10** were $32\,\mu g\,mL^{-1}$ for *S. aureus* and $64\,\mu g\,mL^{-1}$ for *B. subtilis* whereas MIC of **9** was $32\,\mu g\,mL^{-1}$ for both *B. subtilis* and *E. coli* (table 3; figure 2). Complex **2** also shows an MIC of $64\,\mu g\,mL^{-1}$ for both *B. subtilis* and *E. coli*.

5. Conclusions

Based on elemental analyses, conductance measurements, magnetic susceptibilities, IR, NMR and electronic, and mass spectral studies, a distorted octahedral geometry, as shown in figure 1, is proposed for the complexes.

Some macrocyclic metal complexes do not show good antibacterial activities against all bacterial strains, but some cobalt and copper complexes show good antibacterial activities against *S. aureus*, *B. subtilis*, and *E. coli*.

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