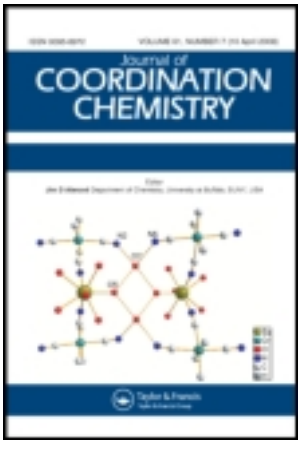

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Divalent metal macrocyclic complexes derived from acetonylacetone and carbohydrazide with their spectroscopic and antibacterial studies

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Divalent metal macrocyclic complexes derived from acetonylacetone and carbohydrazide with their spectroscopic and antibacterial studies

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A series of macrocyclic complexes are synthesized by condensation of acetonylacetone and carbohydrazide in the presence of divalent metal salts in methanol. The complexes are $[M(TML)X_2]$, where M = Co(II), Ni(II), Cu(II), and Zn(II); $X = Cl^-$, NO_3^-, CH_3COO^- and TML is a tetradentate macrocyclic ligand. The complexes have been characterized by elemental analyses, conductance measurements, magnetic measurements, NMR, infrared, and electronic spectral studies. The low value of molar conductance indicates non-electrolytes. A six-coordinate geometry with *trans* coordination of monodentate ligands may be proposed for all the complexes. All the metal complexes were also tested for their *in vitro* antibacterial activities against some bacterial strains. The results obtained were compared with standard antibiotic, *Ciprofloxacin*. Some of the tested complexes show good antibacterial activities against some bacterial strains.

Keywords: Antibacterial activity; Carbohydrazide; Macrocyclic complexes; MIC

1. Introduction

The chemistry of macrocyclic complexes has attracted the interest of both inorganic and bioinorganic chemists [1–3], developing very rapidly because of its importance in coordination chemistry [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 phase transfer catalysis and biological studies [6]. Aza-macrocyclic ligands remain a focus [7] with *in situ* one-pot template condensation at the heart of macrocyclic chemistry [8–10]. Metal ions direct the reaction preferentially toward cyclic rather than oligomeric or polymeric product [11]. Synthetic macrocyclic complexes resemble natural macrocycles like metalloproteins, porphyrins, and cobalamine [12, 13]. Transition metal macrocyclic

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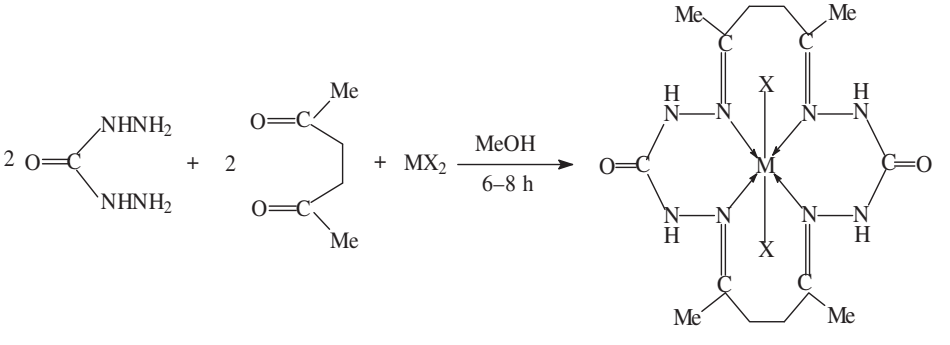
complexes have biological activities, including antiviral, anticarcinogenic [13], antifertile [14], antibacterial, and antifungal [15] and macrocyclic complexes of lanthanides, e.g. Gd^{3+} are used as MRI contrast agents [16]. This article uses template synthesis of macrocyclic complexes of cobalt(II), nickel(II), copper(II), and zinc(II) derived from acetonylacetone and carbahydrazide with characterization by IR, NMR, and elemental analyses, and magnetic susceptibility and conductance measurements. Biological activities of the synthesized complexes have been examined against *Staphylococcus aureus* (MTCC 96), *Bacillus subtilis* (MTCC 121) (Gram-positive), *Escherichia coli* (MTCC 1652), and *Pseudomonas aeruginosa* (MTCC 741) (Gram-negative) and compared with *Ciprofloxacin*.

2. Experimental

2.1. *Isolation of complexes*

Several attempts to isolate free macrocyclic ligand were unsuccessful. Therefore, all the complexes were synthesized by template method. To a hot, well-stirred methanolic solution (~50 cm^3) of carbohydrazide (10 mmol) divalent cobalt (Cl^- and CH_3COO^-), nickel (Cl^-, NO_3^-, and CH_3COO^-), copper (Cl^-, NO_3^-, and CH_3COO^-), and zinc (CH_3COO^-) salts (5 mmol) dissolved in minimum methanol were added. The resulting solutions were refluxed for 0.5 h and then acetonylacetone (10 mmol) dissolved in ~20 cm^3 methanol was added and refluxing continued for 6–8 h. The mixture was concentrated to half of its original volume and kept in a desiccator overnight, resulting in precipitation of the product. The complexes were filtered, washed with methanol, acetone, and diethylether and dried *in vacuo*, giving 40–60% yield. The complexes are soluble in DMF and DMSO but insoluble in water and thermally stable to ~250°C.

The template syntheses of the macrocyclic complexes may be shown by the following scheme:



where M = Co(II), Ni(II), Cu(II), and Zn(II); X = Cl^-, NO_3^-, CH_3COO^-.

2.2. *Analytical and physical measurements*

Microanalyses of C, H, and N were carried out at Sophisticated Analytical Instrument Facility, CDRI, Lucknow. The metal contents were determined by standard

EDTA methods. Electronic spectra (DMF) were recorded on a Cary 14 spectrophotometer. Magnetic moments were measured at room temperature by Gouy's method using $Hg[Co(NCS)_4]$ as calibrant. Magnetic susceptibility measurements were carried out at IIT Roorkee. IR spectra were recorded from 4000–200 cm^{-1} using Nujol Mull/KBr pellets. NMR spectra were recorded on a Bruker NMR spectrometer (300 MHz). Conductivity was measured on a digital conductivity meter (HPG System, G-3001).

3. Results and discussion

3.1. *Chemistry*

Analytical data show the macrocyclic complexes as $[M(C_{14}H_{24}N_8O_2)X_2]$, where M = Co(II), Ni(II), Cu(II), and Zn(II); X = Cl^-, NO_3^-, CH_3COO^-. Conductivity in DMSO indicated non-electrolytes [17] (15–20 $Ohm^{-1}\,cm^2\,mol^{-1}$). Attempts at crystallization using mixtures of solvents 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.

3.2. *IR spectra*

The presence of single medium intensity bands at ~3240–3300 cm^{-1} in the complexes may be assigned to N–H stretching vibrations [18]. A pair of medium intensity bands

Table 1. Analytical data of divalent Co, Ni, Cu, and Zn complexes derived from carbohydrazide and acetonylacetone.

		Found (Calcd), %					
No.	Complex	M	C	H	N	Color	Molecular weight
1	$[Co(C_{14}H_{24}N_8O_2)Cl_2]$	12.08 (12.66)	36.00 (36.05)	5.03 (5.15)	23.99 (24.03)	Brown	466
2	$[Co(C_{14}H_{24}N_8O_2)(OAc)_2]$	11.01 (11.05)	42.05 (42.10)	5.50 (5.85)	21.20 (21.83)	Dark green	513
3	$[Ni\ (C_{14}H_{24}N_8O_2)Cl_2]$	12.39 (12.60)	35.61 (36.07)	5.02 (5.15)	24.01 (24.05)	Dark brown	465
4	$[Ni(C_{14}H_{24}N_8O_2)(NO_3)_2]$	11.26 (11.31)	32.29 (32.39)	14.36 (14.63)	26.42 (26.99)	Grey	518
5	$[Ni(C_{14}H_{24}N_8O_2)(OAc)_2]$	11.31 (11.45)	42.10 (42.13)	5.42 (5.85)	21.53 (21.85)	Dark green	512
6	$[Cu(C_{14}H_{24}N_8O_2)Cl_2]$	13.21 (13.49)	35.20 (35.70)	4.99 (5.01)	23.2 (23.8)	Dark brown	470
7	$[Cu(C_{14}H_{24}N_8O_2)(NO_3)_2]$	12.08 (12.13)	32.02 (32.09)	4.24 (4.58)	26.42 (26.74)	Black	523
8	$[Cu(C_{14}H_{24}N_8O_2)(OAc)_2]$	12.15 (12.27)	41.47 (41.74)	5.51 (5.79)	21.40 (21.64)	Blackish green	517
9	$[Zn(C_{14}H_{24}N_8O_2)(OAc)_2]$	12.35 (12.58)	41.40 (41.58)	5.39 (5.77)	21.00 (21.05)	Blackish blue	519

corresponding to $\nu(NH_2)$ appeared at $\sim$3240–3300 cm^{-1} in the IR spectrum of carbohydrazide but were absent in IR spectra of the metal complexes. Further, no strong absorption was observed near 1700 cm^{-1}, indicating the absence of >C=O of acetonylacetone, confirming condensation of carbonyl group of acetonylacetone and amino group of carbohydrazide [19]. These results provide evidence for formation of a macrocyclic frame [20]. A strong absorption at $\sim$1590–1620 cm^{-1} may be assigned to (C=N) stretching vibrations [21]. The lower values of ν(C=N) may be explained as drift of lone-pair density of azomethine nitrogen to metal [22]. A medium intensity band at 1650–1690 cm^{-1} may be assigned to >C=O group of CONH in all the complexes [23]. Absorption bands at 1410–1430, 1280–1320, and 1010–1045 cm^{-1} in IR spectra of the nitrate complexes suggest that nitrate is coordinated unidentate [24]. IR spectra of the acetate complexes show absorptions at 1650–1685 cm^{-1} assigned to $\nu(COO^-)_{as}$ of acetate and at 1258–1295 cm^{-1} to $\nu(COO^-)_s$ of acetate. The difference between $(\nu_{as} - \nu_s)$ of 390–370 cm^{-1}, greater than 144 cm^{-1}, indicates unidentate acetate [24].

Far infrared spectra showed bands at $\sim$425–455 cm^{-1} corresponding to ν(M–N) [25], suggesting coordination of azomethine nitrogen [26]. Bands present at 300–315 cm^{-1} may be assigned to ν(M–Cl) [25] and bands at 230–250 cm^{-1} in nitrate complexes to ν(M–O) [25].

3.3. *NMR spectra*

^{1}H-NMR spectrum of zinc(II) complex showed a singlet at 9.55 ppm corresponding to CO–**NH**– of carbohydrazide [23], while protons of –C**CH$_2$CH$_2$**C– (8H) appear at 2.65 ppm. The –C**H$_3$** protons (12H) are at 2.40 ppm [27].

3.4. *Mass spectra*

The electron impact (EI) mass spectra of Co(II), Ni(II), Cu(II), Zn(II) macrocyclic complexes 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 $m/z = 464.1$ (due to Cl^{35}) and 466.1 (due to Cl^{37}) of $[M]^+$ of $[Co(C_{14}H_{24}N_8O_2)Cl_2]^+$ ion; **2** at $m/z = 512.2$ due to $[Co(C_{14}H_{24}N_8O_2)(OAc)_2\text{-}H]^+$; **3** at $m/z = 463.2$ (due to Cl^{35}) and 465.2 (due to Cl^{37}) of $[M]^+$ of $[Ni(C_{14}H_{24}N_8O_2)Cl_2]^+$ ion; **7** at $m/z = 521.5$ due to $[Cu(C_{14}H_{24}N_8O_2)(NO_3)_2\text{-}2H]^+$; and **10** at $m/z = 518.0$ due to $[Zn(C_{14}H_{24}N_8O_2)(OAc)_2\text{-}H]^+$. The proposed molecular formulas of these complexes were confirmed by comparing their molecular formula weights with m/z values. The data were in good agreement with the proposed molecular formulas, i.e. $[M(C_{48}H_{32}N_4)X_2]$, confirming the formation of the macrocyclic frame.

3.5. *Magnetic measurements and electronic spectra*

3.5.1. Cobalt complexes. The magnetic moments of cobalt(II) complexes measured at room temperature were in the range 4.80–4.85 B.M., which corresponds to three unpaired electrons [28]. The solution spectra (in DMF) of cobalt(II) complexes exhibit absorption bands at $\sim$8200–9150 cm^{-1} (ν_1) ($\varepsilon = 5.0 - 5.4 \times 10^3\ mol^{-1}\ cm^{-1}$), $\sim$12,550–15,600 cm^{-1} (ν_2) ($\varepsilon = 5.3 - 6.1 \times 10^3\ mol^{-1}\ cm^{-1}$), and $\sim$18,500–20,700 cm^{-1}

(ν_3) ($\varepsilon = 4.5 - 5.1 \times 10^3\,mol^{-1}\,cm^{-1}$), respectively. The spectra resemble those reported for distorted octahedral complexes [29]. 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) $^1(\nu_3)$ transitions, respectively. The assignment of the first spin-allowed band seems plausible since the first band appears approximately at half the energy of the visible band [29].

3.5.2. Nickel complexes. The magnetic moment of nickel(II) complexes at room temperature were 2.91–2.96 B.M., indicating two unpaired electrons [28]. The solution spectra (in DMF) of Ni(II) complexes exhibit a band with a shoulder on the low-energy side. The other two bands, generally at ~16,470–17,100 cm^{-1} (ν_2) ($\varepsilon = 4.1 - 4.7 \times 10^3\,mol^{-1}\,cm^{-1}$) and 26,750–28,000 cm^{-1} (ν_3) ($\varepsilon = 4.4 - 4.9 \times 10^3\,mol^{-1}\,cm^{-1}$), 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 ν_1 at ~9650–10,200 ($\varepsilon = 4.3 - 4.8 \times 10^3\,mol^{-1}\,cm^{-1}$) and 11,530–12,480 cm^{-1} ($\varepsilon = 4.2 - 4.8 \times 10^3\,mol^{-1}\,cm^{-1}$), assigned to $^3B_{1g} \rightarrow {}^3E_g$ and $^3B_{1g} \rightarrow {}^3B_{2g}$ transitions [29]. The intense higher energy band at ~34,050 cm^{-1} may be due to a $\pi - \pi^*$ transition of the (C=N) group. The spectra are consistent with distorted octahedral nature of these complexes [29].

3.5.3. Copper complexes. The magnetic moments of copper(II) complexes were 1.75–1.93 B.M., corresponding to one unpaired electron [28]. The absorption spectra of the copper complexes exhibit bands at ~17,600–19,000 cm^{-1} ($\varepsilon = 4.2 - 4.7 \times 10^3\,mol^{-1}\,cm^{-1}$) with a shoulder on the low-energy side at ~14,430–16,000 cm^{-1} ($\varepsilon = 4.4 - 4.9 \times 10^3\,mol^{-1}\,cm^{-1}$), suggesting distorted octahedral [29]. Assuming tetragonal distortion in the molecule, 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 [30]. The band separation of the spectra of the complexes was 2500 cm^{-1}, consistent with the geometry of the complexes [30]. Therefore, it may be concluded that Cu(II) complexes were distorted octahedral in shape.

3.6. *Biological assay*

3.6.1. Test microorganisms. Four bacteria, *S. aureus* (MTCC 96), *B. subtilis* (MTCC 121) (Gram-positive), *E. coli* (MTCC 1652), and *P. aeruginosa* (MTCC 741) (Gram-negative) were used in this study.

3.6.2. *In-vitro* antibacterial activity. The antibacterial activity of the synthesized macrocyclic complexes has been evaluated by the agar well diffusion method [31]. 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}. Mueller Hinton agar medium (20 mL) was poured into each Petri plate and the agar plates were swabbed with 100 µL inocula of each test bacterium 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 loaded with 100 µL of 4.0 mg mL^{-1} of each metal complex in DMSO. All the plates were incubated at 37°C for 24 h. Antibacterial activities of each complex were evaluated

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

	Diameter of growth of inhibition zone (mm)[x]			
Complex	a	b	c	d
1	–	16.6	18.6	14.6
2	14.3	26.3	23.0	19.6
3	–	15.6	14.3	–
4	15.6	18.6	21.6	16.6
5	25.3	21.3	19.6	–
6	19.6	22.6	17.6	20.1
7	16.0	16.3	–	19.2
8	20.3	16.0	–	16.5
9	26.3	18.6	16.3	15.6
Ciprofloxacin	26.3	24.0	25.0	22.0

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

by measuring the zone of growth inhibition against the test microorganisms with zone reader (Hi Antibiotic zone scale). DMSO was used as a negative control and *Ciprofloxacin* was used as a positive control. This procedure was performed in the three replicate plates for each microorganism.

3.6.3. Determination of MIC of synthesized complexes. Minimum inhibitory concentration (MIC) is the lowest concentration of an antimicrobial compound that will inhibit the visible growth of a microorganism after overnight incubation. MICs of the complexes against bacterial strains were tested through a macrodilution tube method as recommended by National Committee for Clinical Laboratory Standards (NCCLS). In this method, various test concentrations of the synthesized metal complexes were made from 128 to 0.25 $\mu g\,mL^{-1}$ in sterile tubes No. 1–10. A 100 µL sterile Mueller Hinton Broth medium was poured in each sterile tube followed by addition of 200 µL test complex in tube 1. Twofold serial dilutions were carried out from tube 1 to tube 10 and excess broth (100 µL) was discarded from tube No. 10. To each tube, 100 µL of the standard inoculum (1.5×10^8 cfu mL^{-1}) was added. The turbidity was observed after incubating the inoculated tubes at 37°C for 24 h.

3.6.4. Biological results and discussion. The macrocyclic complexes were evaluated against two Gram-positive and two Gram-negative bacteria. MICs were determined by the method given by Andrews [32]. *Ciprofloxacin* was used for comparison with antibacterial activities shown by these complexes. Some complexes of the tested series possess good antibacterial activities against Gram-positive (*S. aureus*, *B. subtilis*) as well as Gram-negative bacteria (*E. coli*, *P. aeruginosa*) (table 2). Complexes **2**, **4**, **5**, **6**, **8**, and **9** exhibit good antibacterial activities with zone of inhibition ranges from 26.3 to 20.1 mm. Complexes **1**, **3**, and **7** also show zone of inhibition ranges from 19.2 to 14.3 mm against some bacteria strains.

From MIC's shown by these complexes, **2** and **9** were most effective with MIC of 8 $\mu g\,mL^{-1}$ for *B. subtilis* and *S. aureus* (table 3, figure 1). In the whole series, MIC of **6**

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

	MIC ($\mu g\,mL^{-1}$)			
Complex	a	b	c	d
1	–	>128	64	>128
2	>128	8	16	32
3	–	>128	>128	–
4	>128	64	32	128
5	16	32	64	–
6	64	16	128	16
7	>128	>128	–	64
8	64	>128	–	>128
9	8	128	128	>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).

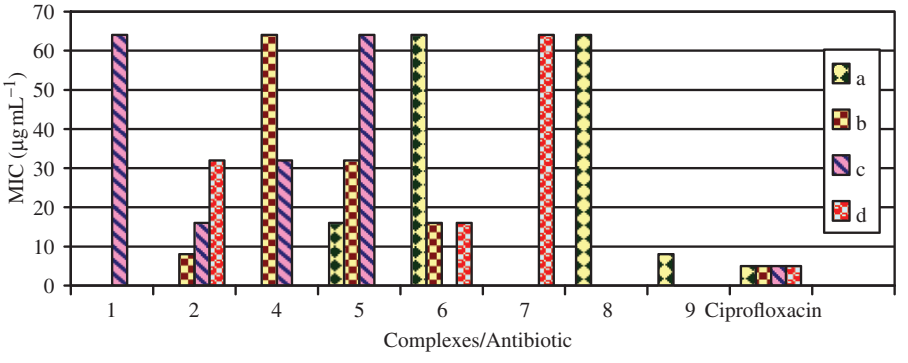


Figure 1. Comparison of MIC ($\mu g\,mL^{-1}$) of the complexes with standard antibiotic. (a, *S. aureus* (MTCC 96); b, *B. subtilis* (MTCC 121); c, *E. coli* (MTCC 1652); d, *P. aeruginosa* (MTCC 741); ciprofloxacin, standard antibiotic).

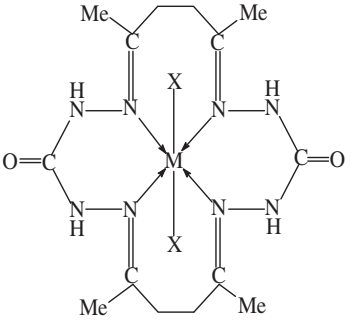


Figure 2. Proposed structure of the macrocyclic complexes (M = Co(II), Ni(II), Cu(II), Zn(II); X = Cl^-, NO_3^-, CH_3COO^-).

was 16 μg mL^{-1} for both the bacterial strains *B. subtilis* and *P. aeruginosa* and 64 μg mL^{-1} for *S. aureus*, whereas MIC of **2** and **5** was 16 μg mL for *E. coli* and *S. aureus*. Complexes **6** and **8** showed MIC of 64 μg mL for *S. aureus* and **1** and **5** showed MIC of 64 μg mL^{-1} for *E. coli*. Complexes **4** and **5** showed MIC of 32 μg mL^{-1} for *E. coli* and *B. subtilis* (table 3, figure 1).

4. Conclusions

Based on elemental analyses, conductance measurements, magnetic susceptibilities, infrared, NMR, and electronic spectra, a distorted octahedral geometry as shown in figure 2 may be proposed for all these complexes.

None of the macrocyclic complexes were as potent as the standard antibiotic; however, some of the complexes possess good antibacterial activities. Chelation [33], solubility, dipole moment, and conductivity influenced by metal ion may be possible reasons for antibacterial activities of these complexes [31].

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References

[1] S. Chandra, L.K. Gupta, S. Agrawal. *Transition Met. Chem.*, **32**, 240 (2007).
[2] A.I. Hanafy, A.B.K.T. Maki, M.M. Mostafa. *Transition Met. Chem.*, **32**, 960 (2007).
[3] M.C. Fernandez, R. Bastida, A. Macias, V. Lalencia, P. Lourida. *Polyhedron*, **25**, 783 (2006).
[4] S. Ilhan, H. Temel. *Transition Met. Chem.*, **32**, 1039 (2007).
[5] S. Chandra, A. Gautum, M. Tyagi. *Transition Met. Chem.*, **32**, 1079 (2007).
[6] L.T. Bozic, E. Marotta, P. Traldi. *Polyhedron*, **26**, 1663 (2007).
[7] L.F. Lindoy. *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge (1989).
[8] N.F. Curtis. *Coord. Chem. Rev.*, **3**, 3 (1968); M.S. Niasari, M. Bazarganipour, M.R. Ganjali, P. Norouzi. *Transition Met. Chem.*, **32**, 9 (2007).
[9] D.P. Singh, K. Kumar, S.S. Dhiman, J. Sharma. *J. Enzyme Inhib. Med. Chem.*, **24**, 795 (2009).
[10] R.N. Prasad, S. Gupta, S. Jangir. *J. Indian Chem. Soc.*, **84**, 1191 (2007).
[11] T.A. Khan, S.S. Hasan, A.K. Mohamed, M. Shakir. *Indian J. Chem.*, **37A**, 1123 (1998).
[12] M. Shakir, S. Khatoon, S. Parveen, Y. Azim. *Transition Met. Chem.*, **32**, 42 (2007).
[13] S. Chandra, M. Pundir. *Spectrochim. Acta, Part A*, 69, 1 (2008).
[14] S. Chandra, R. Gupta, N. Gupta, S.S. Bawa. *Transition Met. Chem.*, **31**, 147 (2006).
[15] D.P. Singh, K. Kumar, C. Sharma. *Eur. J. Med. Chem.*, **44**, 3299 (2009).
[16] D.P. Singh, R. Kumar, V. Malik, P. Tyagi. *J. Enzyme Inhib. Med. Chem.*, **22**, 177 (2007).
[17] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
[18] A.K. Singh, R. Singh, P. Saxena. *Transition Met. Chem.*, **28**, 160 (2003).
[19] S. Srinivasan, P. Athappan. *Transition Met. Chem.*, **26**, 588 (2001).
[20] D.P. Singh, R. Kumar, P. Tyagi. *Transition Met. Chem.*, **31**, 970 (2006).
[21] A.K. Mohamed, K.S. Islam, S.S. Hasan, M. Shakir. *Transition Met. Chem.*, **24**, 198 (1999).
[22] D.P. Singh, R. Kumar, M. Kamboj, K. Jain. *J. Coord. Chem.*, **62**, 2995 (2009).
[23] P. Souza, M.A. Mendiola, A.I. Matesanz, V. Fernandez. *Transition Met. Chem.*, **20**, 157 (1995).

[24] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Part B, 5th Edn, Wiley, New York (1997).
[25] D.P. Singh, V. Malik, R. Kumar, K. Kumar, J. Singh. *Russ. J. Coord. Chem.*, **35**, 740 (2009).
[26] D.P. Singh, R. Kumar, V. Malik, P. Tyagi. *Transition Met. Chem.*, **32**, 1051 (2007).
[27] D.P. Singh, R. Kumar, M. Kamboj, K. Jain. *Acta Chim. Slov.*, **56**, 780 (2009).
[28] R.L. Dutta, A. Syamal. *Elements of Magnetochemistry*, 2nd Edn, East-West Press, New Delhi (1993).
[29] A.B.P. Lever. *Inorganic Electronic Spectroscopy*, Amsterdam, Elsevier (1984).
[30] A.B.P. Lever, E. Mantovani. *Inorg. Chem.*, **10**, 40 (1971).
[31] D.P. Singh, R. Kumar, J. Singh. *Eur. J. Med. Chem.*, **44**, 1731 (2009).
[32] J.M. Andrews. *J. Antimicrob. Chemother.*, **48**, 5 (2001).
[33] D.P. Singh, V. Malik, R. Kumar, J. Singh. *J. Enzyme Inhib. Med. Chem.*, **24**, 1201 (2009).