

## Divalent Transition Metal Complexes Derived from Thiocarbohydrazide and Dimedone†

D.P. SINGH<sup>1,\*</sup>, PARVEEN<sup>1</sup>, CHETAN SHARMA<sup>2</sup> and K.R. ANEJA<sup>2</sup>

<sup>1</sup>Department of Chemistry, National Institute of Technology, Kurukshetra-136 119, India

<sup>2</sup>Department of Microbiology, Kurukshetra University, Kurukshetra-136 119, India

\*Corresponding author: E-mail: dpsinghchem@yahoo.co.in

AJC-11716

A new series of macrocyclic metal complexes have been synthesized by the template reaction of thiocarbohydrazide and dimedone resulting into the formation of complexes of the type:  $[M(C_{18}H_{28}N_8S_2)X_2]$ ; where M = Co(II), Ni(II), Cu(II), Zn(II) and X = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>. The synthesized complexes have been characterized by elemental analyses, conductance measurements, magnetic susceptibility measurements and fluorescence, electronic, infrared, <sup>1</sup>H NMR and mass spectral studies. The *in vitro* antibacterial activities of these macrocyclic complexes have also been investigated.

**Key Words:** Macrocyclic complexes, Thiocarbohydrazide, Spectroscopic studies.

### INTRODUCTION

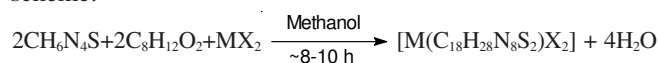
Macrocyclic complexes of transition metal ions have attracted considerable attention for many years because of a number of unique properties offered by the macrocyclic complexes, such as extremely high thermostability and ability to exhibit unusual oxidation states of the metal center<sup>1</sup>; act as MRI contrast agents as well as NMR shift reagents *etc.*<sup>2,3</sup>. Prompted from these applications, the macrocyclic complexes of Co(II), Ni(II), Cu(II) and Zn(II) derived from the condensation reaction between dimedone and thiocarbohydrazide are reported. The complexes have been characterized by various physicochemical techniques like elemental analyses, molar conductance, magnetic susceptibility measurements and IR, NMR, Mass, UV, ESR and fluorescence spectral studies. All the synthesized macrocyclic complexes were tested for their *in vitro* antimicrobial activities.

### EXPERIMENTAL

**Isolation of complexes:** Several attempts to isolate the free macrocyclic ligand were unsuccessful. Hence, all the complexes were synthesized by template method *i.e.* by condensation of thiocarbohydrazide and dimedone in the presence of the respective divalent metal salt. To a hot stirring methanolic solution (-50 cm<sup>3</sup>) of thiocarbohydrazide (10 mmol) was added divalent cobalt, nickel, copper or zinc salt (5.0 mmol) dissolved in the minimum quantity of methanol

(20 mL). The resulting solution was refluxed for 0.5 h. Subsequently, Dimedone (10 mmol) was added to the refluxing mixture and refluxing was continued for 6-8 h. The mixture was cooled to room temperature whereby dark coloured precipitates formed which were filtered, washed with methanol, acetone and diethyl ether and dried in vacuum. The purity of complexes was checked by TLC. The yields obtained were 60-70 %. The complexes were soluble in DMSO and DMF. They were thermally stable up to 280 °C after that decomposed.

The synthesis of complexes may be shown by the following scheme:



**Test microorganisms:** Total six microbial strains were selected on the basis of their clinical importance in causing diseases in humans. Two Gram-positive bacteria (*Staphylococcus aureus* MTCC 96 and *Bacillus subtilis* MTCC 121); two Gram-negative bacteria (*Escherichia coli* MTCC 1652 and *Pseudomonas aeruginosa* MTCC 741) and two yeast, *Candida albicans* (MTCC 3017) and *Saccharomyces cerevisiae* (MTCC 170) were screened for evaluation of antibacterial and antifungal activity of the complexes. All the microbial cultures were procured from microbial type culture collection (MTCC), IMTECH, Chandigarh. The bacteria were subcultured on Nutrient agar whereas yeast on Malt yeast agar. The antimicrobial activities and minimum inhibitory concentration (MIC) were determined by reported method<sup>4</sup>.

†Presented at International Conference on Global Trends in Pure and Applied Chemical Sciences, 3-4 March, 2012; Udaipur, India

TABLE-I  
ANALYTICAL DATA OF THE SYNTHESIZED Co(II), Ni(II), Cu(II) AND Zn(II) COMPLEXES  
DERIVED FROM THIOCARBOHYDRAZIDE AND DIMEDONE

S. No.	Complexes	Colour	M. wt.	Found (calcd.) (%)			
				M	C	H	N
1	[Co(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )Cl <sub>2</sub> ]	Brown	550.4	10.61 (10.71)	39.25 (39.28)	5.11 (5.12)	20.34 (20.36)
2	[Co(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(NO <sub>3</sub> ) <sub>2</sub> ]	Brown	603.4	9.78 (9.76)	35.84 (35.83)	4.59 (4.67)	18.50 (18.57)
3	[Co(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(OAc) <sub>2</sub> ]	Black	597.5	9.79 (9.86)	36.16 (36.18)	4.70 (4.72)	18.75 (18.75)
4	[Ni(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )Cl <sub>2</sub> ]	Cream	550.2	10.56 (10.67)	39.30 (39.29)	5.09 (5.13)	20.33 (20.37)
5	[Ni(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(NO <sub>3</sub> ) <sub>2</sub> ]	Black	603.2	9.67 (9.73)	34.87 (35.84)	4.65 (4.68)	18.57 (18.58)
6	[Ni(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(OAc) <sub>2</sub> ]	Dark green	597.2	9.91 (9.82)	35.23 (35.19)	4.69 (4.73)	18.75 (18.76)
7	[Cu(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )Cl <sub>2</sub> ]	Green	555.0	11.50 (11.45)	38.79 (38.95)	4.99 (5.08)	20.10 (20.19)
8	[Cu(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(NO <sub>3</sub> ) <sub>2</sub> ]	Green	608.0	10.42 (10.45)	35.41 (35.55)	4.63 (4.64)	18.43 (18.42)
9	[Cu(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(OAc) <sub>2</sub> ]	Black	602.1	9.89 (10.55)	34.99 (35.90)	4.75 (4.68)	18.55 (18.61)
10	[Zn(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(OAc) <sub>2</sub> ]	Grey	603.9	10.64 (10.83)	34.85 (35.80)	4.59 (4.67)	18.59 (18.55)

## RESULTS AND DISCUSSION

The analytical data of the metal complexes (Table-1), show that the formula of macrocyclic complexes may be represented as: [M(C<sub>18</sub>H<sub>28</sub>N<sub>8</sub>S<sub>2</sub>)X<sub>2</sub>]; where M= Co(II), Ni(II), Cu(II) and Zn(II) and X= Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and CH<sub>3</sub>COO<sup>-</sup>. The test for anions was positive only after decomposing the complexes, indicating their presence inside the coordination sphere. The monomeric nature of these complexes was confirmed by the molecular weight measurements. Conductivity measured in DMSO indicated them to be non-electrolyte (4-20 Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>)<sup>5</sup>. Several attempts to obtain a single crystal, suitable for X-ray crystallography were unsuccessful.

**IR spectra:** The presence of a single medium band present in the range 3310-3243 cm<sup>-1</sup> may be assigned to (N-H) stretch<sup>6,7</sup> of thiocarbonylhydrazide. It was noted that a pair of bands were present in the spectrum of thiocarbonylhydrazide at 3387 and 3260 cm<sup>-1</sup> corresponding to ν(NH<sub>2</sub>), which were absent in the infrared spectra of all the complexes. Furthermore, no strong absorption band was observed near 1715 cm<sup>-1</sup>, indicating the absence of the C=O group of the dimedone. The disappearance of these bands and appearance of a new strong band near 1630-1590 cm<sup>-1</sup> confirms the condensation of the carbonyl group of dimedone and the amino group of thiocarbonyl-drazide<sup>8,9</sup> and the formation of macrocyclic Schiff's base<sup>10</sup>, as these bands may be assigned to ν(C=N) stretching vibrations<sup>11</sup>. The lower value of ν(C=N) may be explained on the basis of a drift of the lone pair density of the azomethine nitrogen towards the metal atom<sup>11</sup> indicating that coordination occurred through the nitrogen of the C=N groups. The medium intensity bands present in the region 2950-2830 cm<sup>-1</sup> may be assigned to ν(C-H) stretching vibrations of the methyl groups of the dimedone moiety. The presence of the absorption bands at 1440-1408, 1320-1290 and 1030-1010 cm<sup>-1</sup> in the IR spectra of all the nitrate complexes suggest that both nitrate groups are coordinated to the central metal ion in a unidentate fashion<sup>1</sup>. The IR spectra of all the acetate complexes show an absorption band in the region 1680-1650 cm<sup>-1</sup> *i.e.* assigned to the ν(COO<sup>-</sup>) as asymmetric stretching vibrations of the acetate ion and another in the region 1290-1258 cm<sup>-1</sup> that can be assigned to the ν(COO<sup>-</sup>) symmetric stretching vibrations of the acetate ion. The difference between ν<sub>asym</sub> and ν<sub>sym</sub>, which was around 390-370 cm<sup>-1</sup> *i.e.* greater than 144 cm<sup>-1</sup>, indicates the unidentate coordination of the acetate group with the central metal ion<sup>12</sup>.

The band present near 760 cm<sup>-1</sup> in thiocarbonyl-drazide may be assigned to the free ν(C=S). This band is also present in all complexes, which indicate that sulphur is not coordinated to the metal atom<sup>13</sup>. The absence of bands near 2550 cm<sup>-1</sup> (characteristic of thiol group) rule out the possibility of thione-thiol tautomerism<sup>14</sup>. The C-N stretch occurs in the range 1350-1000 cm<sup>-1</sup>.

The far infrared spectra show bands in the region 450-420 cm<sup>-1</sup> corresponding to ν(M-N) vibrations<sup>15</sup>. The presence of bands in all complexes in the region 450-420 cm<sup>-1</sup>, originating from (M-N) azomethine vibrational modes, identify coordination of the azomethine nitrogen<sup>16</sup>. The bands present in the range 320-300 cm<sup>-1</sup> may be assigned to ν(M-Cl) vibrations. The bands present in the region 250-220 cm<sup>-1</sup> in all nitrate complexes are related to ν(M-O) stretching vibrations<sup>16</sup>.

**<sup>1</sup>H NMR Spectra:** The <sup>1</sup>H NMR spectra of the zinc(II) complex shows broad singlet at 12.3-12.7 ppm may be assigned due to -NH protons<sup>17</sup>. The multiplet at 1.5 ppm may be assigned to the methyl protons (12H) of dimedone. The two methine groups (-CH<sub>2</sub>) of dimedone give broad singlet at 2.04-2.17 ppm (8H) whereas one methine group gives singlet at 3.56 ppm (4H).

## Magnetic measurements and electronic spectra

**Cobalt complexes:** The magnetic moment of cobalt complexes at room temperature were 4.90-4.92 BM, corresponding to three unpaired electrons<sup>18</sup>. The electronic spectra of cobalt complexes showed bands at ~ 8000-9150 (ν<sub>1</sub>), 12,570-15,850 (ν<sub>2</sub>) and 18,570-20,650 (ν<sub>3</sub>) cm<sup>-1</sup>, similar to those reported for distorted octahedral complexes<sup>18</sup>. Thus, the bands may be assigned to <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>T<sub>2g</sub> (F) (ν<sub>1</sub>); <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>A<sub>2g</sub> (F) (ν<sub>2</sub>) and <sup>4</sup>T<sub>1g</sub> (F) → <sup>4</sup>T<sub>1g</sub> (P) (ν<sub>3</sub>); respectively. It appears that the symmetry of these complexes is not idealized O<sub>h</sub>, but is D<sub>4h</sub>. The assignment of the first spin allowed band seems plausible since the first band appears at approximately half the energy of the visible band<sup>19</sup>.

**Nickel complexes:** The magnetic moment of nickel complexes at room temperature were observed in the range of 2.91-2.98 BM. These values were in tune with high spin configuration and show the presence of an octahedral environment around the Ni(II) ion in all the complexes<sup>19</sup>. The solution spectra of Ni(II) complexes exhibit a well discerned band with a shoulder on the low energy side. The other two bands generally observed in the region 16,500-17,200 cm<sup>-1</sup> (ν<sub>2</sub>) and 26,150-28,430 cm<sup>-1</sup>

TABLE-2  
MASS SPECTRAL DATA OF THE DIVALENT COBALT, NICKEL, COPPER AND ZINC  
COMPLEXES DERIVED FROM THIOCARBOHYDRAZIDE AND DIMEDONE

S. No.	Complexes	Molecular ion peak [M] <sup>+</sup> and [M+2] <sup>+</sup> at m/z	Important peaks due to another fragments
1	[Co(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )Cl <sub>2</sub> ]	[M] <sup>+</sup> = 550.4( <sup>35</sup> Cl), [M+2] <sup>+</sup> = 552.4( <sup>37</sup> Cl)	[Co(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )Cl] <sup>+</sup> = 514.9; [Co(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )] <sup>+</sup> = 479.4; [C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> ] <sup>+</sup> = 420.5; (C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> -H) = 419.5
2	[Co(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(NO <sub>3</sub> ) <sub>2</sub> ]	[M] <sup>+</sup> = 603.4	[Co(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(NO <sub>3</sub> )] <sup>+</sup> = 541.4; [Co(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )] <sup>+</sup> = 479.4; [C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> ] <sup>+</sup> = 420.5; (C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> -2H) = 418.5
3	[Co(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(OAc) <sub>2</sub> ]	[M] <sup>+</sup> = 597.5	[Co(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(OAc)] <sup>+</sup> = 538.5; [Co(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )] <sup>+</sup> = 479.4; [C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> ] <sup>+</sup> = 420.5; (C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> -H) = 419.5
4	[Ni(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )Cl <sub>2</sub> ]	[M] <sup>+</sup> = 550.2( <sup>35</sup> Cl), [M+2] <sup>+</sup> = 552.2( <sup>37</sup> Cl)	[Ni(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )Cl] <sup>+</sup> = 514.7; [Ni(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )] <sup>+</sup> = 479.2; [C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> ] <sup>+</sup> = 420.5; (C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> -2H) = 418.6
5	[Ni(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(NO <sub>3</sub> ) <sub>2</sub> ]	[M] <sup>+</sup> = 603.2	[Ni(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(NO <sub>3</sub> )] <sup>+</sup> = 541.2; [Ni(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )] <sup>+</sup> = 479.2; [C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> ] <sup>+</sup> = 420.5; (C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> -H) = 419.5
6	[Ni(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(OAc) <sub>2</sub> ]	[M] <sup>+</sup> = 597.2	[Ni(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(OAc)] <sup>+</sup> = 538.3; [Ni(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )] <sup>+</sup> = 479.2; (C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> -2H) = 417.5
7	[Cu(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )Cl <sub>2</sub> ]	[M] <sup>+</sup> = 555.0( <sup>35</sup> Cl), [M+2] <sup>+</sup> = 557.0( <sup>37</sup> Cl)	[Cu(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )Cl] <sup>+</sup> = 519.5; [Cu(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )] <sup>+</sup> = 484.0; [C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> ] <sup>+</sup> = 420.4; (C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> -H) = 419.3
8	[Cu(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(NO <sub>3</sub> ) <sub>2</sub> ]	[M] <sup>+</sup> = 608.0	[Cu(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(NO <sub>3</sub> )] <sup>+</sup> = 545.9; [Cu(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )] <sup>+</sup> = 483.9; [C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> ] <sup>+</sup> = 420.4; (C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> -H) = 419.1
9	[Cu(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(OAc) <sub>2</sub> ]	[M] <sup>+</sup> = 602.1	[Cu(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(OAc)] <sup>+</sup> = 543.1 [Cu(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )] <sup>+</sup> = 484.0; [C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> ] <sup>+</sup> = 420.5; (C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> -H) = 419.5
10	[Zn(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(OAc) <sub>2</sub> ]	[M] <sup>+</sup> = 603.9	[Zn(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )(OAc)] <sup>+</sup> = 649.1; [Zn(C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> )] <sup>+</sup> = 590.1; [C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> ] <sup>+</sup> = 420.5; (C <sub>18</sub> H <sub>28</sub> N <sub>8</sub> S <sub>2</sub> -H) = 419.4

(v<sub>3</sub>) are assigned to <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub> (F) (v<sub>2</sub>) and <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub> (P) (v<sub>3</sub>) respectively. The first two bands result from the splitting of one band, v<sub>1</sub> and were in the range of ~9,750-10,500 and 11,700-12,300 cm<sup>-1</sup> which may be assigned to <sup>3</sup>B<sub>1g</sub> → <sup>3</sup>E<sub>g</sub> and <sup>3</sup>B<sub>1g</sub> → <sup>3</sup>B<sub>2g</sub>, assuming the effective symmetry to be D<sub>4h</sub> (component of <sup>3</sup>T<sub>2g</sub> in octahedral symmetry)<sup>19</sup>. The intense higher energy bands at 34560 cm<sup>-1</sup> may be due to π → π\* transition of the (C=N) group. The spectra were consistent with distorted octahedral nature of these complexes.

**Copper complexes:** The magnetic moment of copper complexes at room temperature were observed in the range of 1.77-1.80 BM, corresponding to one unpaired electron. The electronic spectra of the copper complexes exhibit bands at ~17,425-19,685 cm<sup>-1</sup> with a shoulder at ~14,500-16,050 cm<sup>-1</sup> and showed that these complexes have distorted octahedral geometry<sup>19</sup>. Assuming tetragonal distortion in the molecule, the δ-orbital energy level sequence may be represented as: x<sup>2</sup>-y<sup>2</sup> > z<sup>2</sup> > xy > xz > yz and the shoulder may be assigned to z<sup>2</sup> → x<sup>2</sup>-y<sup>2</sup> (<sup>2</sup>B<sub>1g</sub> → <sup>2</sup>B<sub>2g</sub>) and the broad band contains both xy → x<sup>2</sup>-y<sup>2</sup> (<sup>2</sup>B<sub>1g</sub> → <sup>2</sup>E<sub>g</sub>) and xz, yz → x<sup>2</sup>-y<sup>2</sup> (<sup>2</sup>B<sub>1g</sub> → <sup>2</sup>A<sub>2g</sub>) transitions<sup>19</sup>. Band separation in the spectra of these complexes was of the order of 2,500 cm<sup>-1</sup>, which was consistent with the proposed geometry<sup>20</sup>. Therefore, it may be concluded that all the copper complexes are distorted octahedral.

**ESR spectra:** ESR spectra of the Cu(II) complexes were recorded at room temperature in the solid state, on X-band at frequency of 9.1 GHz under the magnetic field strength of 3,000 G using TCNE as reference. The complex showed a broad anisotropic signal. The observed data showed that g<sub>||</sub> = 2.186 and g<sub>⊥</sub> = 2.098. The trend g<sub>||</sub> > g<sub>⊥</sub> > 2.003 observed for the complexes indicated that unpaired electron was localized in dx<sup>2</sup>-y<sup>2</sup> orbital of the Cu(II) ion, this suggests distortion in the Cu(II) complex from O<sub>h</sub> symmetry to D<sub>4h</sub> symmetry. The observed g<sub>||</sub> values for the Cu(II) complex are less than 2.3 which is in agreement with the covalent character of the metal ligand bond. G = (g<sub>||</sub>-2)/(g<sub>⊥</sub>-2), which measures the exchange of interaction between copper centers in the polycrystalline

solids has been calculated. If G > 4, the exchange interaction is negligible and if G < 4, it indicates considerable exchange interaction in solid complexes<sup>21,22</sup>. The calculated G-value is 1.9167, which is less than 4 and indicate the exchange interaction in the solid Cu(II) complex.

**Mass spectra:** The EIMS mass spectra of Co(II), Ni(II), Cu(II) and Zn(II) macrocyclic complexes exhibit parent peaks due to molecular ions [M]<sup>+</sup> and [M+2]<sup>+</sup>. The proposed molecular formulas of these complexes were confirmed by comparing their molecular formula weights with m/z values. The molecular ion peak [M]<sup>+</sup> and [M+2]<sup>+</sup> peaks obtained for various complexes has been shown in Table-2. The data were in good agreement with the proposed molecular formula for these complexes that is [M(C<sub>18</sub>H<sub>28</sub>N<sub>8</sub>S<sub>2</sub>)X<sub>2</sub>]. In addition to the molecular ion peaks, the spectra exhibit other peaks assignable to various fragments arising from the thermal cleavage of the complexes (Table-2).

**Fluorescence spectra:** The fluorescence excitation and emission spectra of the macrocyclic complexes (the excitation and emission slit width were 10.0 nm) were recorded at room temperature. Among all the synthesized complexes, fluorescence spectra of the complex **4** and **7** were more intense and have λ<sub>max</sub> at higher wavelength as compared to the other complexes, whereas some of the complexes were highly quenched. So, the fluorescence spectra indicate that some of the macrocyclic complexes (**4** and **7**) show very good luminescence as compared to the others.

**Biological results and discussion:** All the macrocyclic complexes were screened for their antibacterial and antifungal activity. Of the tested complexes, eight complexes (**2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**) possessed variable antibacterial activity against the Gram-positive (*Staphylococcus aureus* and *Bacillus subtilis*) bacteria while only two complexes **2** and **4** displayed activity against Gram-negative bacteria (*E. coli*). Two complexes [Co(C<sub>18</sub>H<sub>28</sub>N<sub>8</sub>S<sub>2</sub>)Cl<sub>2</sub>] and [Zn(C<sub>18</sub>H<sub>28</sub>N<sub>8</sub>S<sub>2</sub>)(OAc)<sub>2</sub>] do not displayed any activity against any of the tested bacteria. All the complexes exhibit activity against *Candida albicans* while



TABLE-3  
*In vitro* ANTIMICROBIAL ACTIVITY OF COMPLEXES THROUGH AGAR WELL DIFFUSION METHOD

Complex no.	Diameter of growth of inhibition zone (mm) <sup>a</sup>					Minimum inhibitory concentration (MIC) (in µg/mL)				
	<i>S. aureus</i>	<i>B. subtilis</i>	<i>E. coli</i>	<i>S. cerevisiae</i>	<i>C. albicans</i>	<i>S. aureus</i>	<i>B. subtilis</i>	<i>E. coli</i>	<i>S. cerevisiae</i>	<i>C. albicans</i>
1	-	-	-	-	12.3	Nt	Nt	Nt	Nt	256
2	15.6	18.3	15.3	14.3	19.0	128	64	128	128	32
3	12.3	13.6	-	-	13.3	512	256	Nt	Nt	128
4	14.3	15.6	14.6	-	13.6	512	256	256	Nt	128
5	12.6	14.3	13.6	-	12.6	256	128	256	Nt	128
6	13.6	12.3	-	-	12.6	256	512	Nt	Nt	128
7	13.6	15.6	-	14.3	15.6	256	128	Nt	128	128
8	12.6	12.6	-	15.6	22.3	512	512	Nt	64	16
9	13.3	14.3	-	-	18.6	256	256	Nt	Nt	32
10	-	-	-	-	12.3	Nt	Nt	Nt	Nt	256
Ciprofloxacin	26.6	24.0	25.0	Nt	Nt	6.25	6.25	6.25	Nt	Nt
Amphotericin-B	Nt	Nt	Nt	19.3	16.6	Nt	Nt	Nt	12.5	12.5

-No activity; <sup>a</sup> Values, including diameter of the well (8 mm), are means of three replicates; Nt- not tested

three of them **2**, **7** and **8** showed activity against *Saccharomyces cerevisiae* (Table-3).

On the basis of maximum inhibitory activity shown against the tested bacteria [Co(C<sub>18</sub>H<sub>28</sub>N<sub>8</sub>S<sub>2</sub>)(NO<sub>3</sub>)<sub>2</sub>] was found to be most effective against *B. subtilis*, *S. aureus* and *E. coli* with zone of inhibition of 18.3 mm, 15.6 mm and 15.3 mm whereas complex [Cu(C<sub>18</sub>H<sub>28</sub>N<sub>8</sub>S<sub>2</sub>)(NO<sub>3</sub>)<sub>2</sub>] was found to be most effective against tested fungi *C. albicans* and *S. cerevisiae* with zone of inhibition of 22.3 mm and 15.6 mm, respectively (Table-3).

In the whole series, the MIC of various tested complexes ranged between 64 µg/mL and 512 µg/mL against Gram positive bacteria. [Co(C<sub>18</sub>H<sub>28</sub>N<sub>8</sub>S<sub>2</sub>)(NO<sub>3</sub>)<sub>2</sub>] was found to be best as they exhibit the lowest MIC of 64 µg/mL against *B. subtilis* and 128 µg/mL against *S. aureus*. However in case of yeast, the MIC of various tested complexes ranged between 16 µg/mL and 512 µg/mL. [Cu(C<sub>18</sub>H<sub>28</sub>N<sub>8</sub>S<sub>2</sub>)(NO<sub>3</sub>)<sub>2</sub>] was found to be best as they exhibit the lowest MIC of 16 µg/mL against *C. albicans* and 64 µg/mL against *S. cerevisiae* (Table-3).

Among all the complexes, complex **2** i.e. [Co(C<sub>18</sub>H<sub>28</sub>N<sub>8</sub>S<sub>2</sub>)(NO<sub>3</sub>)<sub>2</sub>] was found to be best in inhibiting the growth of Gram positive bacteria and complex **8** i.e. [Cu(C<sub>18</sub>H<sub>28</sub>N<sub>8</sub>S<sub>2</sub>)(NO<sub>3</sub>)<sub>2</sub>] was found to be best in inhibiting the growth of tested yeast.

### Conclusion

Based on various studies like elemental analyses, conductance measurements, magnetic susceptibilities, infrared, NMR, electronic, fluorescence and mass spectral studies a distorted octahedral geometry may be proposed for all of these complexes. It has been suggested that chelation/coordination reduces the polarity of the metal ion mainly because of partial sharing of its positive charge with donor group within the whole chelate ring system<sup>23</sup>.

### ACKNOWLEDGEMENTS

Ms. Parveen is highly thankful to CSIR, New Delhi for financial support in the form of Junior Research Fellowship (File No. 09/1050 (0001)/2011-EMR-1). Thanks are also due to authorities of N.I.T., Kurukshetra for providing necessary research facilities.

### REFERENCES

- D.P. Singh, V. Grover, K. Kumar and K. Jain, *J. Serb. Chem. Soc.*, **76**, 385 (2011); D.P. Singh, K. Kumar and R.M. Chopra, *Spectrochim. Acta A*, **78**, 629 (2011).
- K. Gloe, *Macrocyclic Chemistry Current Trends and Future Perspective*, Springer, Edition (2005).
- S. Chandra, L.K. Gupta and S. Agarwal, *Transition Met. Chem.*, **32**, 240 (2007); S. Chandra, A. Gautum and M. Tyagi, *Transition Met. Chem.*, **32**, 1079 (2007).
- K.R. Aneja, C. Sharma and R. Joshi, *Jondishpur J. Microbiol.*, **4**, 175 (2011).
- W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
- T.A. Khan, M.A. Rather, N. Jahan, S.P. Varkey and M. Shakir, *Transition Met. Chem.*, **23**, 283 (1998).
- A.K. Singh, A. Panwar, R. Singh and S. Beniwal, *Transition Met. Chem.*, **28**, 160 (2003).
- S.S. Nivasan and P. Atheppan, *Transition Met. Chem.*, **26**, 588 (2001).
- Q. Zeng, J. Sun, S. Gou, K. Zhou, J. Fang and H. Chen, *Transition Met. Chem.*, **23**, 371 (1998).
- A.K. Mohamed, K.S. Islam, S.S. Hasan and M. Shakir, *Transition Met. Chem.*, **24**, 198 (1999).
- L.K. Gupta and S. Chandra, *Transition Met. Chem.*, **31**, 368 (2006).
- K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed. Part B, Wiley Interscience Publication, New York, (1997).
- O.V. Mikhailov, *Transition Met. Chem.*, **29**, 732 (2004); D.P. Singh and R. Kumar, *J. Serb. Chem. Soc.*, **72**, 1069 (2007).
- S. Chandra, Sangeetika and S. Thakur, *Transition Met. Chem.*, **29**, 925 (2004).
- S. Candra and R. Kumar, *Transition Met. Chem.*, **29**, 269 (2004).
- V.B. Rana, D.P. Singh, P. Singh and M.P. Teotia, *Transition Met. Chem.*, **6**, 36 (1981); *Polyhedron*, **1**, 377 (1982).
- A.D. Naik, S.M. Annigeri, U.B. Gangadharmath, V.K. Revankar and V.B. Mahale, *J. Inclusion Phenom. Macrocyc. Chem.*, **43**, 291 (2002).
- R.L. Dutta and A. Syamal, *Elements of Magnetochemistry*, East-West Press, New Delhi, edn. 2, p. 42 (1993).
- A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, edn. 2, p. 317 (1984); D.P. Singh, K. Kumar, S.S. Dhiman and J. Sharma, *J. Enzym. Inhib. Med. Chem.*, **24**, 795 (2009).
- A.B.P. Lever and E. Mantovani, *Inorg. Chem.*, **10**, 40 (1971).
- I.M. Proctor, B.J. Hathway and P. Nicholls, *J. Chem. Soc. (A)*, 1678 (1968).
- R.-H. Hui, P. Zhou and Z.-L. You, *Indian J. Chem.*, **48A**, 1102 (2009).
- Z.H. Chohan, H. Pervez, A. Rauf, K.M. Khan and C.T. Supuran, *J. Enzym. Inhib. Med. Chem.*, **19**, 417 (2004); Z.H. Chohan, A. Scozzafava and C.T. Supuran, *J. Enzym. Inhib. Med. Chem.*, **17**, 261 (2002).