*Journal of Enzyme Inhibition and Medicinal Chemistry*, April 2007; 22(2): 177–182



# Template synthesis, spectroscopic studies and biological activities of macrocyclic complexes derived from thiocarbohydrazide and glyoxal

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*(Received 20 June 2006; accepted 5 September 2006)*



**Abstract**

A novel series of complexes of the type $[M(TML)X_2]$; where TML is Tetradentate Macrocyclic Ligand; M = Co(II), Ni(II), Cu(II), Zn(II)or Cd(II); $X = Cl^-$, $CH_3COO^-$ or $NO_3^-$ have been synthesized by template condensation of glyoxal and thiocarbohydrazide in the presence of divalent metal salts in methanolic medium. The complexes have been characterized by elemental analyses, conductance measurements, molecular weight determination, magnetic measurements, electronic, NMR, infrared and far infrared spectral studies. Electronic spectra along with magnetic moments suggest a six coordinate octahedral geometry for these complexes. The low molar conductance values indicates them to be non-electrolytes. The biological activities of the metal complexes have been tested *in vitro* against a number of pathogenic bacteria to assess their inhibitory potential.

**Keywords:** *Antibacterial activity, glyoxal, divalent metal salts, thiocarbohydrazide, metal complexes, macrocyclic*

**Abbreviations:** *MTCC (Microbial type culture collection); SCDA (soyabean casein digest agar); MHA (Muller Hinton agar); MIC (minimum inhibitory concentration); CFU (colony forming unit); BM (Bohr Magneton)*

## Introduction

Macrocyclic complexes of transition metal ions have attracted considerable attention for many years because of a number of unique properities offered by the macrocyclic environment, such as extremely high thermostability and ability to access unusual oxidation states of the metal center [1]. Template reactions have been widely used for the syntheses of macrocyclic complexes where a transition metal ion is used as templating agent [2,3]. The importance of macrocyclic ligands and their complexes is obvious when seen in relationship to natural products such as metalloproteins, vitamin B12 and chlorophyll [4]. A number of nitrogen donor macrocyclic derivatives have long been used in analytical, industrial and medical applications [5]. Macrocyclic metal complexes are of great importance due to their resemblances to many natural systems such as porphyrins and cobalamines [6]. Macrocyclic nickel complexes find use in DNA recognition and oxidation [7] while macrocyclic copper complexes find use in DNA binding and cleavage [8]. Macrocyclic metal complexes of the lanthanides e.g. $Gd^{+3}$, are used as MRI contrast agents [9,10,11]. Several macrocyclic complexes with a tetra aza macrocyclic ligand, such as cyclen, cyclam or bicyclam were reported to exhibit antitumour activity [12]. The chemistry of macrocyclic complexes is also important due to their use as dyes and pigments [13] as well as NMR shift reagents [14]. Macrocyclic complexes are also well known for their antibacterial and antifungal activities [15,16]. Most of the macrocyclic metal chelates have been derived from aliphatic or aromatic diamines and aliphatic or aromatic diketones. However, work has not been reported on the metal complexes of

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ISSN 1475-6366 print/ISSN 1475-6374 online © 2007 Informa UK Ltd.
DOI: 10.1080/14756360601051399

macrocyclic complexes derived from thiocarbohydrazide and glyoxal. In this paper the divalent cobalt, nickel, copper, zinc and cadmium complexes derived from thiocarbohydrazide and glyoxal are discussed.

## Experimental

### *Chemistry*

*Isolation of the metal complexes*. Any attempt to isolate the free macrocyclic ligand was unsuccessful so that all the complexes were obtained by template synthesis. To a stirring methanolic solution (~50 mL) of thiocarbohydrazide (10 mmol) was added divalent cobalt, nickel, copper, zinc or cadmium salts (5 mmol) dissolved in a minimum quantity of methanol (20 mL). The resulting solution was refluxed for 0.5 h. After that glyoxal (10 mmol) dissolved in ~20 mL methanol was added to the refluxing mixture and refluxing continued for 6–10 h, depending upon the metal salt (6 h in case of nickel and copper and 10 h in case of cobalt salt). The mixture was concentrated to half of its volume and kept in a dessicator for 2 days. The complexes were filtered, washed with methanol, acetone and ether and dried *in vacuo*; Yield ~ 40%.The complexes are soluble in DMF and DMSO, but are insoluble in common organic solvents and water. They were thermally stable up to ~250°C. The syntheses of the complexes may be represented by the following Equation:

$$SC(NH)_2(NH_2)_2 + C_2H_2O_2 + MX_2 \xrightarrow[(6-8\,h)]{MeOH} [M(TML)X_2] \quad (1)$$

Where M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)

$$X = Cl^-, NO_3^-, CH_3COO^-$$

TML = Tetradentate Macrocyclic Ligand

*Analytical and physical measurements:*. The C, H, and N microanalysis was carried out at CDRI Lucknow and the magnetic susceptibility measurements at IIT Roorkee. The IR spectra were recorded on an Infrared spectrophotometer in the range 4000-667 $cm^{-1}$ using KBr pellets. The NMR spectra were recorded on a Bruker NMR spectrometer (300 MHz) at Punjab University, Chandigarh. The conductivity was measured on a digital conductivity meter (HPG System, G-3001).

### *Biological assay*

*Medium*. Media used for the study were Muller Hinton agar (MHA) and soyabean casein digest agar (SCDA) of the following composition; beef infusion 300 g/L, casein acid hydrolysate 17.5 g/L, starch 1.5 g/L, agar-agar 17 g/L and sterile distilled water 1000 mL, adjusted to pH 7.4 and casein enzymatic hydrolysate 17.0 g/L, papain digest of soyabean 3.0 g/L, NaCl 5.0 g/L, dipotassium phosphate 2.5 g/L, dextrose 2.5 g/L, sterile distilled water 1000 mL, adjusted to pH 7.3, respectively.

*Primary screening*. Primary screening of eight synthesized compounds was done against two Gram-positive bacteria (*Staphylococcus aureus* (MTCC 3160) and *Staphylococcus epidermidis* (MTCC 2639)) and two Gram-negative bacteria (*Salmonella typhi* (MTCC 733) and *Pseudomonas aeruginosa* (MTCC 3541)) by the well diffusion assay technique. The overnight cultures of all the bacteria were used for the assay and adjusted to 0.5 McFarland Standard, i.e. $1.5 \times 10^8$ CFU/mL [17]. The test bacterial cultures were set at 0.5 McFarland Standard using Wickerham paper. The stock solution (1 mg/L) of all the test chemicals was prepared in DMSO. DMSO was used as control for all the test compounds.

20 mL MHA and 500 μL of each test bacterial culture of overnight incubation adjusted at 0.5 McFarland were mixed and poured into sterilized petri plates. Wells of 6 mm diameter were punched in the solidified agar plates. 100 μL of test chemicals were added to individual wells and the loaded plates were incubated at 35°C for 24 h. The diameter of the zone of growth inhibition around each well was measured after incubation using a Vernier Caliper.

*Determination of minimum inhibitory concentration (MIC)*. The minimum inhibitory concentration (MIC) is the lowest concentration of the antimicrobial agent that prevents the development of viable growth after overnight incubation [18]. MIC of compounds against Gram-positive and Gram-negative test bacteria was determined by the literature method [19] using MHA. All the test cultures were streaked on the SCDA and incubated overnight at 37°C. Turbidity of all the bacterial cultures was adjusted to 0.5 McFarland Standard by preparing bacterial suspension of 4–6 isolated colonies. The cultures were further diluted 10-fold to get an inoculum size of $1.2 \times 10^7$ CFU/mL. Stock solutions of compounds of 4 mg/mL was prepared in DMSO and was appropriately diluted to get final concentrations of 64, 32, 16, 8, 4, 2, 1, 0.5, 0.25 and 0.12 μg/mL. Standard antibiotics (linezolid and cefuroxime axetial) were similarly diluted for comparison. 320 μL of each dilution was added to 20 mL molten MHA at 45°C (separate flask for each dilution) and after thorough mixing, the medium was poured into sterilized petri plates. The test bacterial

cultures were spotted in a pre-defined pattern by ascetically transferring 10 μL of each culture onto the surface of pre-solidified agar plates. The spotted plates were incubated at 35°C for 24 h.

## Results and discussion

### *Chemistry*

The analytical data for the metal chelates are given in Table I, which show that the chelates may be represented by the formula: $[M(C_6H_8N_8S_2)X_2]$. The measurements of molar conductance in DMSO showed that the chelates are non-electrolytes (conductance below 10 mho $cm^2$ $mol^{-1}$).The test for anions are positive after decomposing the chelates showing their presence inside the coordination sphere.

*IR spectra*. The presence of a single medium band in the region ~3243–3300 $cm^{-1}$ in the complexes may be assigned to the N-H stretch [20,21]. It was noted that a pair of bands corresponding to $\nu(NH_2)$ at 3270 $cm^{-1}$ and 3306 $cm^{-1}$ are present in the spectrum of thiocarbohydrazide but are absent in the infrared spectra of all the complexes. Furthermore no strong absorption band was observed near 1700 $cm^{-1}$ indicating the absence of >C═O of glyoxal and confirms the condensation of the carbonyl groups of glyoxal and amino groups of thiocarbohydrazide [22,23]. These results provide strong evidence for the formation of a macrocyclic frame [24]. A strong absorption band in the region ~1615-1640 $cm^{-1}$ may be attributed to the C═N group [25]. The lower values of $\nu$(C═N) may be explained on the basis of a drift of the lone pair density on the azomethine nitrogen towards the metal atom [23,26]. The band present near 760 $cm^{-1}$ in thiocarbohydrazide may be assigned to the free $\nu$(C═S). This band is also present in all complexes which indicates that sulphur is not coordinated to the metal atom [25,27,28].The absence of bands near 2550 $cm^{-1}$ (characteristic of a thiol group) rule out the possibility of thione-thiol tautomerism [29]. The C-N stretch occurs in the range 1350-1000 $cm^{-1}$.

*NMR spectra*. The $^1$H NMR spectrum of the zinc complex shows a broad singlet at 8.01–8.20 ppm corresponding to NH protons [30,31].The singlet at 4.10–4.40 ppm may be assigned to protons of the glyoxal moiety [32].

*Far IR spectra*. The far IR spectra show bands in the region ~430–450 $cm^{-1}$ corresponding to $\nu$(M-N) vibrations [33–35]. The presence of bands in all complexes in the 430–450 $cm^{-1}$ region originate from (M-N) azomethine vibrational modes and identify coordination of azomethine nitrogens [36]. The bands present at 300–310 $cm^{-1}$ may be assigned to $\nu$(M-Cl) vibrations [33,35]. The bands present at 230–260 $cm^{-1}$ in all nitrate complexes are assignable to $\nu$(M-O) [33]. The characteristic bands due to $\nu$(M-S) are not present in the far IR spectra, which again rule out the possibility of coordination through a sulphur atom.

### *Magnetic measurements and electronic spectra*

*Cobalt complexes*. The magnetic moment of the cobalt complexes was measured at room temperature and lie in the range 4.85–4.94 B.M. which corresponds to three unpaired electrons. The solution spectra of the cobalt(II) complexes exhibit absorption in the region ~ 8095–9070($\nu_1$), 12500–15700($\nu_2$) and 18700–20300 $cm^{-1}$($\nu_3$) respectively. The spectra resemble those complexes reported to be octahedral [37]. Thus, assuming the effective symmetry to be $D_{4h}$, the various bands can be assigned to: $^4T_{1g} \rightarrow {}^4T_{2g}$ (F), ($\nu_1$) 8095–9070 $cm^{-1}$, $^4T_{1g} \rightarrow {}^4A_{2g}$(F), ($\nu_2$) 12500–15700 $cm^{-1}$, $^4T_{1g} \rightarrow {}^4T_{1g}$ (P), ($\nu_3$), 18700–20300 $cm^{-1}$, respectively. It appears that the symmetry of these complexes is not idealized $O_h$, but is $D_{4h}$. The

Table I. Analytical data for the divalent cobalt, nickel, copper, zinc and cadmium complexes.

| | | Found(calcd) % | | | | | |
|---|---|---|---|---|---|---|---|
| Sr. no. | Complexes | M | C | H | N | Colour | Mol. wt. |
| 1. | $[Co(TML)Cl_2]$ | 15.10 (15.28) | 18.37 (18.65) | 1.96 (2.07) | 28.87 (29.01) | Light orange | 386 |
| 2. | $[Co(TML)(NO_3)_2]$ | 13.21 (13.43) | 16.27 (16.40) | 1.76 (1.82) | 31.66 (31.89) | Light orange | 439 |
| 3. | $[Co(TML)(OAc)_2]$ | 13.50 (13.62) | 27.48 (27.71) | 3.13 (3.23) | 25.60 (25.86) | Brown | 433 |
| 4. | $[Ni(TML)Cl_2]$ | 14.98 (15.06) | 18.56 (18.70) | 1.99 (2.07) | 29.01 (29.09) | Light pink | 385 |
| 5. | $[Ni(TML)(NO_3)_2]$ | 13.14 (13.24) | 16.34 (16.43) | 1.57 (1.82) | 31.32 (31.60) | Light grey | 438 |
| 6. | $[Ni(TML)(OAc)_2]$ | 13.34 (13.42) | 27.70 (27.77) | 3.08 (3.24) | 25.67 (25.92) | Brown | 432 |
| 7. | $[Cu(TML)Cl_2]$ | 16.10 (16.15) | 18.29 (18.46) | 1.91 (2.05) | 28.42 (28.71) | Yellow | 390 |
| 8. | $[Cu(TML)(NO_3)_2]$ | 14.09 (14.22) | 16.13 (16.25) | 1.69 (1.80) | 31.43 (31.60) | Brown | 443 |
| 9 | $[Cu(TML)(OAc)_2]$ | 14.36 (14.41) | 27.39 (27.45) | 3.14 (3.20) | 25.50 (25.62) | Dark green | 437 |
| 10 | $[Zn(TML)(OAc)_2]$ | - | 27.19 (27.33) | 3.10 (3.18) | 25.34 (25.51) | Brown | 439 |
| 11 | $[Cd(TML)(OAc)_2]$ | - | 24.21 (24.69) | 2.59 (2.88) | 22.88 (23.04) | Brown | 486 |

assignment of the first spin-allowed band seems plausible since the first band appears approximately at half the energy of the visible band [38].

*Nickel complexes*. The magnetic moment of the nickel complexes at room temperature lie in the range 2.92–2.97 B.M. showing an octahedral environment around the Ni(II) ion in all complexes. 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 at ~16,650–17,040 $cm^{-1}$($\nu_2$), and 27,730–28200 $cm^{-1}$ ($\nu_3$), are assigned to $^3A_{2g}\rightarrow{}^3T_{1g}$(F) ($\nu_2$), and $^3A_{2g}\rightarrow{}^3T_{1g}$(P) ($\nu_3$), respectively. The first two bands result from the splitting of one band, $\nu_1$ and are in the range ~9700–10,600 and 11,850–12,300 $cm^{-1}$, which can be 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 band at ~34,500 $cm^{-1}$ may be due to a $\pi$-$\pi^\star$ transition of the (C=N) group. Various bands do not follow any regular pattern and seem to be anion-independent. The spectra are consistent with the distorted octahedral nature of these complexes.

*Copper complexes*. The magnetic moments of the copper complexes lie in the range 1.77–1.81 B.M. The electronic spectra of the copper complexes exhibit bands in the region ~ 17,800–19,640 $cm^{-1}$ with a shoulder on the low energy side at ~14,600–16,000 $cm^{-1}$, and show that these complexes are distorted octahedral [37,38]. Assuming tetragonal distortion in the molecule, the d-orbital energy level sequence for these complexes may be: $x^2 - y^2 > z^2 > xy > xz > yz$ and the shoulder can 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 [39]. The band separation of the spectra of the complexes is of the order 2500 $cm^{-1}$, which is consistent with the proposed geometry of the complexes [39].Therefore, it may be concluded that all the complexes formed by the macrocycles with Cu(II) are distorted octahedral.

Therefore based on elemental analyses, conductivity, magnetic, electronic, NMR and IR spectral studies the following structure may be proposed for these complexes:

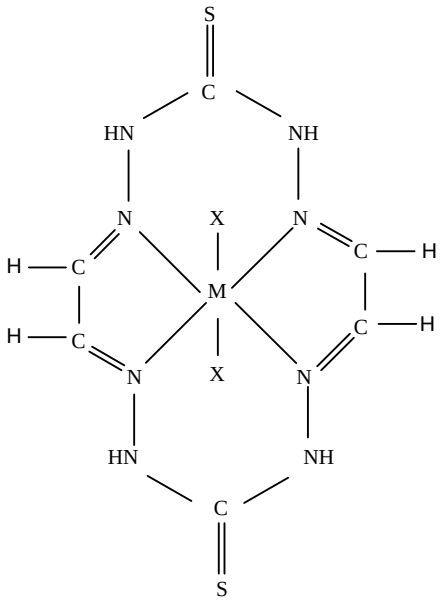


Figure 1. Structure of the complexes.

*Biological assays*

Eight chemically synthesized compounds were tested *in vitro* for their antibacterial activity against five test bacteria namely *Staphylococcus aureus* (MTCC 3160) and *Staphylococcus epidermidis* (MTCC 2639) (Gram-positive); *Salmonella typhi* (MTCC 733) and *Pseudomonas aeruginosa* (MTCC 3541) (Gram-negative) (Tables II & III). Out of eight compounds

Table II. *In vitro* antibacterial spectrum of synthesized compounds using the agar diffusion assay.

| Sr. no. | Compounds | Diameter of zone of growth inhibition (mm)[a] | | | |
|---|---|---|---|---|---|
| | | Sa | Se | Pa | St |
| 1 | $[Co(TML)Cl_2]$ | 15 | – | – | 10 ± .57 |
| 2 | $[Ni(TML)Cl_2]$ | – | – | – | 10 ± .57 |
| **3** | $[Cu(TML)Cl_2]$ | 10.83 ± .37 | 10 ± .81 | 10.83 ± .37 | 10.83 ± .37 |
| 4 | $[Cu(TML)(NO_3)_2]$ | 15 | 15 | 10 ± .57 | 15 |
| 5 | $[Ni(TML)(NO_3)_2]$ | 10.83 ± .37 | – | – | 10 ± .57 |
| 6 | $[Cd(TML)(OAc)_2]$ | 10 ± .81 | 10.83 ± .37 | 20 | 10.83 ± .37 |
| 7 | $[Zn(TML)(OAc)_2]$ | 15 | 10 ± .81 | – | 10.83 ± .37 |
| 8 | $[Co(TML)(NO_3)_2]$ | 10 ± .81 | 10.83 ± .37 | – | 30 |
| | DMSO | 8 | 7.83 | 7.16 | 7.83 |

Sa- *Staphylococcus aureus* (MTCC 3160), Se- *Staphylococcus epidermidis* (MTCC 2639), Pa- *Pseudomonas aeruginosa* (MTCC 3541) and St-*salmonella typhi* (MTCC 733)

[a] Mean of six replicates ± Standard deviation. –No activity.

Table III. Minimum inhibitory concentration (MIC) of compounds against test bacteria using the agar dilution assay.

| Sr. no. | Compounds | MIC (μg/ mL) | | | |
|---|---|---|---|---|---|
| | | Sa | Se | Pa | St |
| 1 | $[Co(TML)Cl_2]$ | 32 | – | – | >64 |
| 2 | $[Ni(TML)Cl_2]$ | – | – | – | >64 |
| **3** | $[Cu(TML)Cl_2]$ | 64 | >64 | >64 | >64 |
| 4 | $[Cu(TML)(NO_3)_2]$ | 32 | 32 | >64 | 16 |
| 5 | $[Ni(TML)(NO_3)_2]$ | >64 | – | – | >64 |
| 6 | $[Cd(TML)(OAc)_2]$ | >64 | >64 | 16 | >64 |
| 7 | $[Zn(TML)(OAc)_2]$ | 32 | >64 | – | >64 |
| 8 | $[Co(TML)(NO_3)_2]$ | >64 | >64 | – | 4 |
| | Cefuroxime axetial | 32 | 16 | 32 | 16 |
| | Linezolid | 2 | 8 | 16 | 32 |

Sa- *Staphylococcus aureus* (MTCC 3160), Se- *Staphylococcus epidermidis* (MTCC 2639), Pa- *Pseudomonas aeruginosa* (MTCC 3541) and St- *salmonella typhi* (MTCC 733) Cefuroxime axetial and linezolid are standard antibiotics.

the membrane thus causing the metal complex to cross the bacterial membrane more effectively so increasing the activity of the complexes. Besides this many other factors such as solubility, dipole moment, conductivity influenced by metal ion may be possible reasons for the remarkable antibacterial activities of these complexes [42]. It has also been observed that some moieties such as the azomethine linkage or heteroaromatic nucleus introduced into such compounds exhibit extensive biological activities that may be a result of the increase in hydrophobic character and liposolubility of the molecules in crossing the cell membrane of the microorganism and enhance the biological utilization ratio and activity of complexes [43].

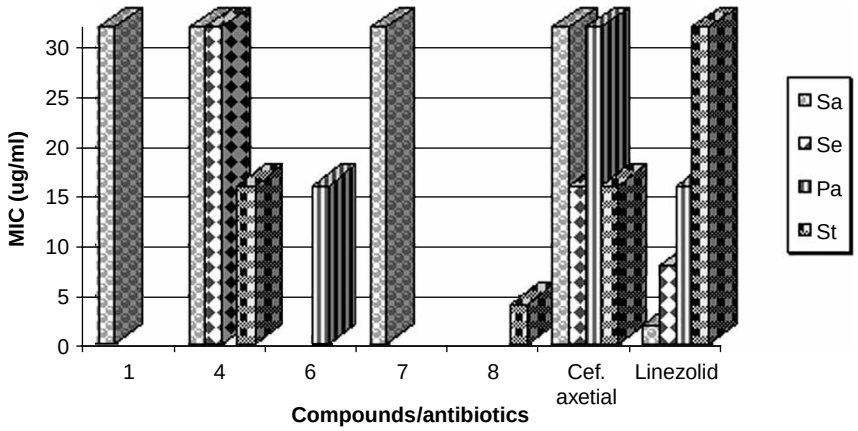


Figure 2. Comparison of minimum inhibitory concentration (MIC) of compounds and standard antibiotics against test microorganisms.

tested, compounds **1**, **4** and **7** showed MIC 32 μg/mL against *S. aureus* and compound **4** against *S. epidermidis* also possessed MIC of 32 μg/mL. Compounds **4** and **6** showed MIC 16 μg/mL against *S. typhi* and *P. aeruginosa*, respectively. In the whole series of these compounds, the best antimicrobial activity i.e. MIC 4 μg/mL was shown by compound **8** against *S. typhi* which can be compared with that of the standard antibiotics (Table III, Figure 2)

## Conclusions

It has been suggested that chelation/coordination reduces the polarity of the metal ion mainly because of partial sharing of its positive charge with a donor group within the whole chelate ring system [40,41]. This process of chelation thus increases the lipophilic nature of the central metal atom, which in turn, favours its permeation through the lipoid layer of

## Acknowledgements

DPS thanks the University Grants Commission, New Delhi for financial support in the form of a Major Research Project (MRP-F.12-62/2003) and RK for the award of a Project Fellow under the above project. Thanks are also due to authorities of N.I.T., Kurukshetra for providing the necessary facilities.

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