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Short communication

Synthesis and spectroscopic studies of biologically active compounds derived from oxalyldihydrazide and benzil, and their Cr(III), Fe(III) and Mn(III) complexes

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Abstract

A new series of complexes have been synthesized by template condensation of oxalyldihydrazide and benzil in methanolic medium in the presence of trivalent chromium, manganese and iron salts forming complexes of the type $[M(C_{32}H_{24}N_8O_4)X]X_2$ where M = Cr(III), Mn(III), Fe(III) and $X = Cl^{-1}$, NO_3^{-1}, CH_3COO^{-1}. The complexes have been characterized with the help of elemental analyses, conductance measurements, magnetic susceptibility measurements, electronic, NMR, infrared and far infrared spectral studies. On the basis of these studies, a five coordinate square pyramidal geometry has been proposed for all these complexes. The biological activities of the metal complexes have been tested *in vitro* against a number of pathogenic bacteria to assess their inhibiting potential. Some of these complexes have been found to exhibit remarkable antibacterial activities.

Keywords: Antibacterial activity; Minimum inhibitory concentration; Macrocyclic complexes; Infrared spectra

1. Introduction

The chemistry of macrocyclic complexes has attracted the interest of both inorganic and bioinorganic chemists in recent years [1]. The field of coordination chemistry of macrocyclic complexes has undergone remarkable growth during the past few decades and become a growing class of research. This enormous growth is due to synthesis of great number and variety of synthetic macrocycles which behave as coordinating agents for metal ions [2]. Template reactions lie at the heart of macrocyclic chemistry and are the best aids for the preparation of macrocyclic complexes [3,4]. Generally transition metal ions have been used as templates [5]. The importance of macrocyclic complexes in coordination chemistry is because of its various applications in biological processes such as photosynthesis and dioxygen transport, catalytic properties, potential applications as metal extractants and radiotherapeutic agents [6]. The importance of macrocyclic complexes is due to their resemblance with many natural systems like porphyrins and cobalamines [7]. Macrocyclic complexes have attracted attention because of their pharmacological properties, i.e. toxicity against bacterial and fungal growth [8,9]. Some macrocyclic complexes have been reported to have anti-inflammatory approach [10]. Several macrocyclic complexes with tetraazamacrocyclic ligands, such as cyclen, cyclam or bicyclam have been reported to exhibit antitumour activity [11]. Macrocyclic metal complexes of lanthanides, e.g. Gd^{+3} are used as MRI contrast agents [12,13]. The chemistry of macrocyclic complexes is also important due to their use as dyes and pigments [14] as well as NMR shift reagents [15]. The amide macrocyclic

Abbreviations: MIC, Minimum Inhibitory Concentration; MTCC, Microbial Type Culture Collection; MHA, Muller Hinton Agar; CFU, Colony Forming Unit; BM, Bohr Magneton; DMF, *N*,*N*-Dimethylformamide; DMSO, Dimethylsulphoxide; BHI, Brain Heart Infusion.

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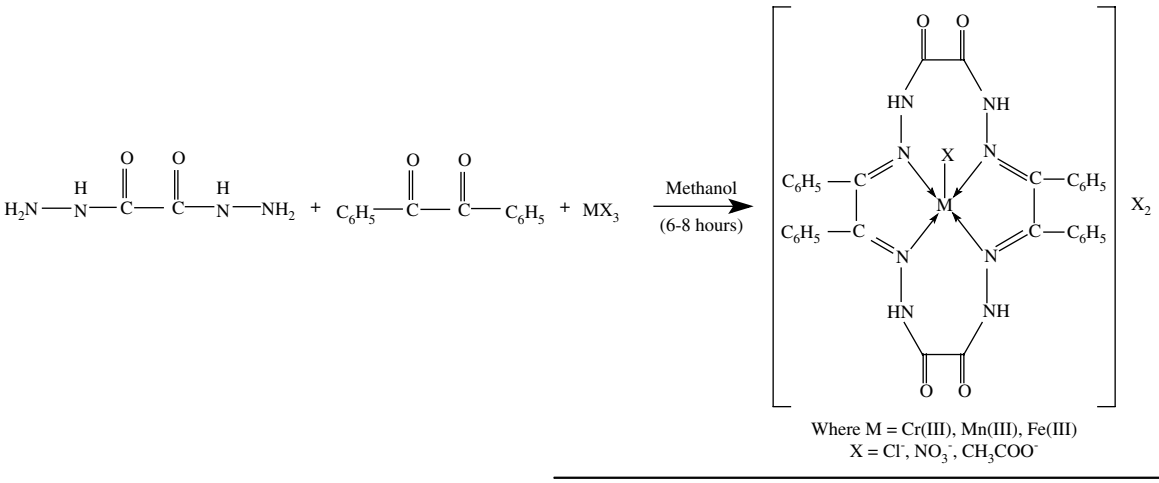
complexes are of special interest since they can function as catalyst in many oxidation reactions [16]. Several macrocyclic complexes containing amide groups have been reported [17,18]. In our previous paper we have reported synthesis of amide macrocyclic complexes of Co(II), Ni(II) and Cu(II) derived from oxalyldihydrazide and benzil [19]. Prompted by these applications, in the present paper template synthesis of amide macrocyclic complexes of Cr(III), Mn(III) and Fe(III) is reported. These complexes were characterized with the help of various physicochemical techniques like IR, NMR, magnetic susceptibilities, elemental analyses, and conductance measurements. Further these complexes were also tested for their biological activities against some pathogenic bacterial strains *viz*. *Bacillus cereus*, *Salmonella typhi*, *Escherichia coli* and *Staphylococcus aureus* and results so obtained were compared with antibacterial activities shown by standard antibiotics such as Cefaclor and Linezolid against the same bacterial strains.

2. Chemistry

The complexes were synthesized using template method by condensing oxalyldihydrazide and benzil in the presence of the respective trivalent metal salt. To a hot stirring methanolic solution (−50 ml) of oxalyldihydrazide (10 mmol, 1.18 g) was added trivalent chromium, manganese or iron salt (5 mmol) dissolved in the minimum quantity of methanol (∼20 ml). The resulting solution was boiled under reflux for 0.5 h. Then the benzil (10 mmol, 2.10 g) was added in the same mixture and refluxing was continued for 6–8 h. The mixture was concentrated to half of its volume and kept in a desiccator overnight. The complexes obtained as solid were then filtered, washed with methanol, acetone and diethylether, dried *in vacuo*. Yield obtained ∼1.5–2.2 g. The complexes are soluble in DMF and DMSO, but are insoluble in common organic solvents and water. The complexes were found thermally stable up to ∼240–260 °C and then decomposed.

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



3. Pharmacology

3.1. In vitro antibacterial activity

Some of the synthesized macrocyclic complexes were tested for *in vitro* antibacterial activity against some bacterial strains using spot-on-lawn on Muller Hinton Agar.

3.2. Test pathogens

Four test pathogenic bacterial strains *viz B. cereus* (MTCC 1272), *S. typhi* (MTCC 733), *E. coli* (MTCC 739) and *S. aureus* (MTCC 1144) were considered for determination of MIC (Minimum Inhibitory Concentration) of selected complexes.

3.3. Culture conditions

The test pathogens were subcultured aerobically using Brain Heart Infusion Agar (HiMedia, Mumbai, India) at 37 °C/24 h. Working cultures were stored at 4 °C in Brain Heart Infusion (BHI) broth (HiMedia, Mumbai, India), while stock cultures were maintained at −70 °C in BHI broth containing 15% (v/v) glycerol (Qualigens, Mumbai, India). Organism was grown overnight in 10 ml BHI broth, centrifuged at 5000 g for 10 min and the pellet was suspended in 10 ml of phosphate buffer saline (PBS, pH 7.2). Optical density at 545 nm (OD-545) was adjusted to obtain 10^8 cfu/ml followed by plating serial dilution onto plate count agar (HiMedia, Mumbai, India).

3.4. Determination of minimum inhibitory concentration

Antimicrobial activity of the compounds was evaluated using spot-on-lawn on Muller Hinton Agar (MHA, HiMedia, Mumbai, India). Soft agar was prepared by adding 0.75% agar in Muller Hinton Broth (HiMedia, Mumbai, India). Soft agar was inoculated with 1% of 10^8 cfu/ml of the test pathogen and 10 ml was overlaid on MHA. From 1000X solution of compound (1 mg/ml of DMSO) 1, 2, 4, 8, 16, 32, 64 and

128X solutions were prepared. Dilutions of standard antibiotics (Linezolid and Cefaclor) were also prepared in the same manner. Five microlitres of the appropriate dilution was spotted on the soft agar and incubated at 37 °C for 24 h. Zone of inhibition of compounds were considered after subtraction of inhibition zone of DMSO. Negative control (with no compound) was also observed.

4. Results and discussion

The analytical data of the metal chelates are given in Table 1, which shows that metal chelates derived from oxalyldihydrazide and benzil may be represented by the formula: $[M(C_{32}H_{24}N_8O_4)X]X_2$ where M = Cr(III), Mn(III), Fe(III) and $X = Cl^{-1}$, NO_3^{-1}, CH_3COO^{-1}. The measurements of molar conductance in DMSO show that these chelates are 1:2 electrolytes [20] (conductance 150–185 $ohm^{-1}\,cm^2\,mol^{-1}$). The tests for anions are positive before decomposing and after decomposing the chelates showing their presence outside as well as inside of coordination sphere. All complexes give satisfactory elemental analyses results as shown in Table 1.

4.1. IR spectra

The presence of a single medium band in the region ~3210–3280 cm^{-1} in the spectra of all complexes may be assigned to N–H stretching [17,21,22]. It was noted that a pair of bands corresponding to $\nu(NH_2)$ at ~3300 and 3310 cm^{-1} were present in the spectrum of oxalyldihydrazide but were absent in the infrared spectra of all the complexes. The disappearance of these bands and appearance of absorption band near ~1605–1610 cm^{-1} indicates the formation of macrocyclic Schiff's base [23,24] as these bands may be assigned to ν(C=N) [25,26]. The value of ν(C=N) is lower than that usually found for azomethine linkage which may be explained on the basis of drift of lone pair density of azomethine nitrogen towards the metal atom [27,28] indicating the involvement of the pi-electrons throughout the macrocyclic framework [17] and confirm that coordination takes place through nitrogen of C=N groups. The bands present ~2960–3050 cm^{-1} may be assigned to ν(C–H) stretching [17]. The band present in the range at 1660–1685 cm^{-1} may be assigned to the C=O group of the CONH moiety [17,29] in all complexes. It may be noted that C=O group of CONH moiety is not shifted from its position in the IR spectra of the complexes which indicates that carbonyl group is not coordinated. The bands present in the range ~1350–1000 cm^{-1} in all complexes are assigned to ν(C–N) stretching. The far IR spectra show bands in the region ~410–460 cm^{-1} corresponding to ν(M–N) vibrations [30–32]. The presence of bands in all the complexes in the region 410–460 cm^{-1} originate from (M–N) azomethine vibrational modes and gives idea about coordination of azomethine nitrogens [33]. The bands present at 310–325 cm^{-1} may be assigned to ν(M–Cl) vibrations [30,32]. The bands present at 215–240 cm^{-1} in all nitrato complexes are assignable to ν(M–O) [30].

4.2. NMR spectra

The ^{1}H NMR spectrum of complex of zinc(II) shows broad signal at 8.02–8.20 ppm due to amide (–CON*H*) protons [17,29]. The multiplets in the region 7.34–7.86 ppm may be assigned to aromatic protons [6,34].

4.3. Magnetic measurements and electronic spectra

Magnetic moment of chromium(III) complexes were found in the range of 4.20–4.50 BM. The electronic spectra of chromium(III) complexes show bands at ~9020–9300, 13,040–13,330, 17,470–18,310, 27,430–27,840 and 34,810 cm^{-1}. However, these spectral bands cannot be interpreted in terms of four or six coordinated environment around the metal atom. In turn, the spectra are consistent with that of five coordinated Cr(III) complexes, whose structure have been confirmed with the help of X-ray measurements [35]. Thus keeping in view, the analytical data and electrolytic nature of these complexes, a five coordinated square pyramidal geometry may be assigned for these complexes. Thus, assuming the symmetry C_{4V} for these complexes [36], the various spectral bands may be assigned as: $^4B_1 \rightarrow {}^4E^a$, $^4B_1 \rightarrow {}^4B_2$, $^4B_1 \rightarrow {}^4A_2$ and $^4B_1 \rightarrow {}^4E^b$.

The magnetic moment of manganese(III) complexes lie in the range 4.85–4.90 BM. The electronic spectra of manganese(III) complexes show three d–d bands which lie in the range 12,260–12,580, 16,060–18,910 and 35,430–35,740 cm^{-1}. The higher energy band at 35,450–35,750 cm^{-1} may be assigned to charge transfer transitions. The spectra resemble to those reported for five coordinate square pyramidal manganese

Table 1
Analytical data of trivalent chromium, manganese and iron complexes derived from oxalyldihydrazide and benzil

S. No.	Complexes	Found (calcd.)				Colour	Mol. wt.
		M	C	H	N		
1	$[Cr(C_{32}H_{24}N_8O_4)Cl]Cl_2$	6.91(6.99)	51.61(51.68)	3.09(3.23)	15.03(15.07)	Light green	743
2	$[Cr(C_{32}H_{24}N_8O_4)(NO_3)](NO_3)_2$	6.17(6.32)	46.50(46.71)	2.82(2.91)	18.57(18.73)	Light grayish	822
3	$[Cr(C_{32}H_{24}N_8O_4)(OAc)](OAc)_2$	6.27(6.39)	55.91(56.08)	3.92(4.05)	13.71(13.77)	Light yellow	813
4	$[Mn(C_{32}H_{24}N_8O_4)Cl]Cl_2$	7.18(7.37)	50.89(51.47)	3.17(3.21)	14.96(15.01)	Brown	746
5	$[Mn(C_{32}H_{24}N_8O_4)(OAc)](OAc)_2$	6.68(6.74)	55.23(55.88)	4.00(4.04)	13.54(13.72)	Light brown	816
6	$[Fe(C_{32}H_{24}N_8O_4)Cl]Cl_2$	7.33(7.49)	51.24(51.40)	3.08(3.21)	14.84(14.99)	Light yellow	747
7	$[Fe(C_{32}H_{24}N_8O_4)(NO_3)](NO_3)_2$	6.74(6.81)	46.40(46.48)	2.74(2.90)	18.49(18.64)	Pale yellow	826
8	$[Fe(C_{32}H_{24}N_8O_4)(OAc)](OAc)_2$	6.73(6.83)	55.48(55.67)	3.89(4.02)	13.32(13.67)	Light brown	817

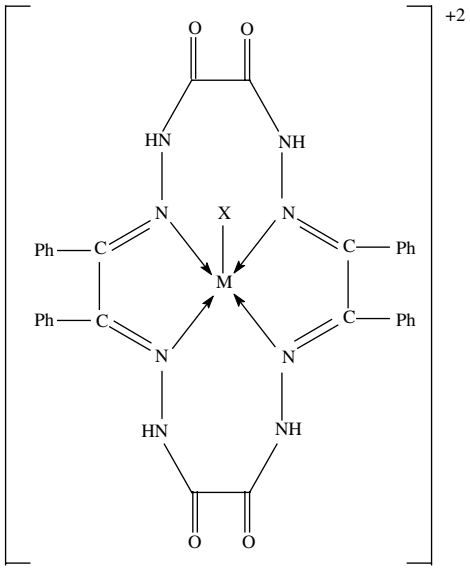


Fig. 1. Comparison of MIC of complexes with standard antibiotics up to the concentration of 64 μg/ml. (a) *Bacillus cereus* (MTCC 1272), (b) *Staphylococcus aureus* (MTCC 1144), (c) *Escherichia coli* (MTCC 739), (d) *Salmonella typhi* (MTCC 733). Cefaclor and Linezolid are standard antibiotics.

porphyrins [36]. This idea is further supported by the presence of the broad ligand field band at 20,400 cm^{-1} diagnostic of C_{4V} symmetry, and thus the various bands may be assigned as follows: $^5B_1 \rightarrow {}^5A_1$, $^5B_1 \rightarrow {}^5B_2$, and $^5B_1 \rightarrow {}^5E$, respectively. The band assignment in single electron transition may be made as: $d_{z^2} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy}, d_{yz} \rightarrow d_{x^2-y^2}$, respectively, in the order of increasing energy. However, the complexes do not have idealized C_{4V} symmetry.

The magnetic moment of iron(III) complexes lie in the range 5.82–5.90 BM. The electronic spectra of iron(III) complexes show various bands at 9830–9960, 15,520–15,575, 27,620–27,720 cm^{-1} and these bands do not suggest the octahedral or tetrahedral geometry around the metal atom. The spectral bands are consistent with the range of spectral bands reported for five coordinate square pyramidal iron(III) complexes [37]. Assuming C_{4V} symmetry for these complexes, the various bands can be assigned as: $d_{xy} \rightarrow d_{xz}$, d_{yz} and $d_{xy} \rightarrow d_{z^2}$. Any attempt to make accurate assignment is difficult due to interactions of the metal–ligand π-bond systems lifting the degeneracy of the d_{xz} and d_{yz} pair.

5. Biological results and discussion

Six chemically synthesized macrocyclic complexes were screened for their *in vitro* antibacterial activity against four test bacteria *B. cereus* (MTCC 1272), *S. typhi* (MTCC 733), *E. coli* (MTCC 739) and *S. aureus* (MTCC 1144).

Complex **1** showed a minimum inhibitory concentration ranging from 4 to 64 μg/ml. It showed a minimum inhibitory concentration of 4 μg/ml against bacterial strain *S. aureus* (MTCC 1144), which is equal to MIC (Fig. 1) shown by standard antibiotic Linezolid against the same bacterial strain. Further MIC of complex **1** against *S. typhi* (MTCC 733), is registered as 32 μg/ml, which is again equal to the minimum inhibitory concentration shown by standard antibiotic Linezolid against the same bacterial strain. Complex **2** registered a minimum inhibitory concentration of 4 μg/ml against bacterial strain *S. aureus* (MTCC 1144) which is equal to MIC shown by standard antibiotic Linezolid against the same bacterial strain. Complex **4** registered a minimum inhibitory concentration of 16 and 32 μg/ml against bacterial strain *E. coli* (MTCC 739) and *S. typhi* (MTCC 733), respectively, which is equal to MIC shown by standard antibiotic Linezolid against the same bacterial strains. Complex **5** registered a minimum inhibitory concentration of 32 μg/ml against bacterial strain *S. typhi* (MTCC 733) which is equal to MIC shown by standard antibiotic Linezolid against the same bacterial strain (Table 2).

Among all complexes of the series under test for determination of minimum inhibitory concentration (Fig. 1) complex **1** was found to be the most potent. It registered MIC as shown by standard antibiotic Linezolid against two bacterial strains, i.e. *S. aureus* and *S. typhi*. However, complexes **3** and **6** showed poor antibacterial activity or no activity against all bacterial strains among the whole series (Table 2).

6. Conclusions

Based on the elemental analyses, conductivity, magnetic, electronic, NMR and IR spectral studies the structure as shown in Fig. 2 may be proposed for 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 [38,39]. This process of chelation thus

Table 2
Minimum Inhibitory Concentration (MIC) shown by complexes against test bacteria

S. No.	Complexes	MIC in μg/ml (mmol/L)			
		a	b	c	d
1	$[Cr(C_{32}H_{24}N_8O_4)Cl]Cl_2$	32 (0.043)	4 (0.005)	64 (0.086)	32 (0.043)
2	$[Cr(C_{32}H_{24}N_8O_4)(NO_3)](NO_3)_2$	32 (0.038)	4 (0.004)	128 (0.155)	64 (0.077)
3	$[Cr(C_{32}H_{24}N_8O_4)(OAc)](OAc)_2$	>128 (>0.157)	64 (0.078)	–	–
4	$[Fe(C_{32}H_{24}N_8O_4)Cl]Cl_2$	64 (0.085)	128 (0.171)	16 (0.021)	32 (0.042)
5	$[Fe(C_{32}H_{24}N_8O_4)(NO_3)](NO_3)_2$	128 (0.155)	>128 (>0.155)	64 (0.077)	32 (0.038)
6	$[Fe(C_{32}H_{24}N_8O_4)(OAc)](OAc)_2$	64 (0.078)	64 (0.078)	32 (0.039)	>128 (>0.156)
	Cefaclor	8 (0.020)	2 (0.005)	8 (0.020)	16 (0.041)
	Linezolid	4 (0.011)	4 (0.011)	16 (0.047)	32 (0.094)

(–) No activity; (a) *Bacillus cereus* (MTCC 1272), (b) *Staphylococcus aureus* (MTCC 1144), (c) *Escherichia coli* (MTCC 739), (d) *Salmonella typhi* (MTCC 733). Cefaclor and Linezolid are standard antibiotics.

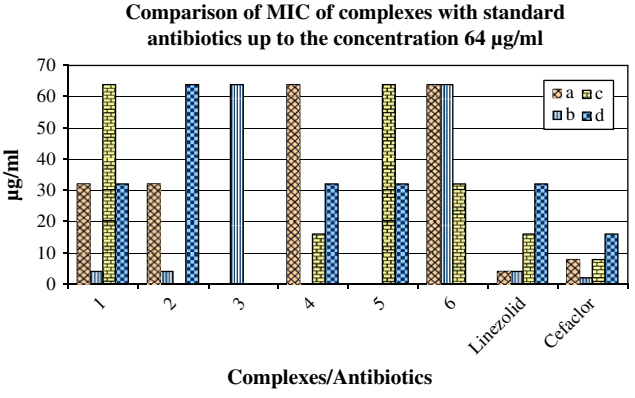


Fig. 2. M = Cr(III), Mn(III), Fe(III), X = Cl^{-1}, NO_3^{-1}, CH_3COO^{-1}.

increases the lipophilic nature of the central metal atom, which in turn, favours its permeation through the lipoid layer of the membrane thus causing the metal complex to cross the bacterial membrane more effectively thus 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 remarkable antibacterial activities of these complexes [40–42]. It has also been observed that some moieties such as azomethine linkage or heteroaromatic nucleus introduced into such compounds exhibit extensive biological activities that may be responsible for the increase in hydrophobic character and liposolubility of the molecules in crossing the cell membrane of the microorganism and enhance biological utilization ratio and activity of complexes [43,44].

7. Experimental protocols

7.1. Chemistry

Melting points were determined using capillaries in electrical melting point apparatus.

The metal contents were estimated using standard methods [45].

Electronic spectra of metal complexes were recorded in the region 1100–200 nm on a Hitachi U-2000 spectrophotometer.

IR spectra were recorded on Beckman IR-20 spectrophotometer in KBr/Nujol mull in the range 4000–200 cm^{-1}.

Proton NMR spectra was recorded in d_6-DMSO on Brucker ACF 300 spectrometer at 300 MHz with reference to Me_4Si (0.0 ppm).

Magnetic moment studies were carried out at SAIF, IIT, Roorkee, on Vibrating Sample Magnetometer (Model PAR 155).

The conductivity was measured on digital conductivity meter (HPG System, G-3001).

7.2. Biological activity

Antimicrobial activity of the compounds was evaluated using spot-on-lawn on Muller Hinton Agar. Zone of inhibition of compounds were considered after subtraction of inhibition zone of DMSO. Negative control (with no compound) was also observed.

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