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Antibacterial activity of complexes of Cu (II), Fe (III) and UO_2 (II) with pyrazine-2-carboxylic acid hydrazide and its derivatives

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Abstract

Metals combine with ligands to form complexes. Mono-dentate ligands posses single donor site and form simple i.e. non- chelated complexes whereas polydentate ligands posses more than one donor sites to form close ring or chelated complexes particularly with transition metal ion. The transition metals and the chelated complexes formed by the metal ions and polydentate ligands have evolved greater interest due to their biological potential,(Haidue ,1990) and (Cleare,1974) unusual structural aspects, unique stereo and magneto chemistry (Singh et al., 1985). Thus they constitute one of the most important classes of biologically active ligands providing potential binding sites through nitrogen and sulphur/oxygen donor atoms. The case of formation of a variety of metal complexes from these ligands like thiosemicarbazones, semicarbazones, dithiocarbazates and benzothiazolines speak for their spectacular progress in coordination and bioinorganic chemistry. The alteration in biological properties of chelating ligands when complexed with the metal ions is of great significance. In view of these facts here we have undertaken the screening of metal complexes formed by combination of Cu (II), Fe (III) and UO_2 (II) with ligands 2-pyrazinoyl hydrazide and its derivatives with various aromatic and heterocyclic aldehydes against various bacteria. The present paper deals with the characterization and screening of metal-complexes of hydrazones derivatives of 2-pyrazinoyl hydrazide with various aromatic and heterocyclic aldehydes such as benzaldehyde, anisaldehyde, 4-hydroxy-3-methoxy benzaldehyde, p- (N,N-diethyl amino) benzaldehyde, cinnamaldehyde, 4-methyl salicyldehyde and 2-furfuraldehyde against some gram (+ve) and gram (–ve) bacteria.

Keywords: *Antibacterial, Aromatic and heterocyclic aldehydes, Monodentate Ligands, Polydentate Ligands, Chelated-complexes, Hydrazones.*

1. Introduction

The different modes of bonding between metal ion and ligand produce appreciable changes in the biochemical properties of the metal complexes. These complexes prepared are of tremendous interest due to the current focus in the study of sulphur and nitrogen donor ligands and their complexes. Subsequently azomethines and their derivatives are gaining importance due to their unique structural and stereochemical aspects, and their use as models in industrial, biological, analytical and antimicrobial systems (Mishra and Srivastava, 1994) and Deshmuck, 1995). To illustrate a few examples, azomethines and their derivatives are known to exhibit a wide range of pharmacological properties such as anticancerous, antibacterials anti-fungal (More et al., 2001) and (Singh W M and Dash B C, 1988), anti-inflammatory activities (Singh et al., 2009),(Kumar et al., 2010),(Kulkarni et al., 2009), (Bagihalli et al.,2008), (Singh et al., 2007) and (Ramesh and Maheswaran, 2003), anti-diabetic (Vanco et al.,2008), anti-tumor (de Silveira et al., 2008) and (Zhong et al.,2006), anti-proliferative (Chaviara et al.,2004) and (Illan-Cabeza et al., 2008), herbicidal (Samadhiya and Halve , 2001), anti-corrosion etc. Simultaneously they are known to act as catalysts in many reactions (Yamada et al., 2006), (Mirkhani et al., 2008) and (Mirkhani et al., 2008).

The importance of these biologically active complexes led us to synthesize and characterize a new class of unsymmetrical Cu (II), Fe (III) and UO_2 (II) complexes (Chauhan, 2015) using ligands like 2-pyrazinoyl hydrazide and its derivatives with

various aromatic and heterocyclic aldehydes such as benzaldehyde, anisaldehyde, 4-hydroxy-3-methoxy benzaldehyde, p- (N,N-diethyl amino) benzaldehyde, cinnamaldehyde, 4-methyl salicyldehyde and 2-furfuraldehyde. The change in biological properties of synthesized metal complexes as compared to ligand or metal may be any one or more of the following facts (Chauhan, 2016).

(a) Due to increase in the liposoluble nature of metal complex in comparison to the free metal ion or the ligand molecule alone.
(b) By the replacement of the metal ion of the metal enzyme present in biological system with the foreign metal ion of the more liposoluble metal complex.
(c) By the displacement of protein molecule from the metal enzyme by the foreign ligand of the more liposoluble metal ligand complex.
(d) By an increased activity of a complex as a whole as compared to constituent metal ion and the ligand.
(e) Apart from the above facts, a comparative faster, diffusion of the metal complex as a whole through the cells of fungi and bacteria. It is evident that their complexes are stable.

Due to potentially multidentate ligational behaviour of pyrazine-2-carboxylic acid hydrazides and its derivatives considerable interest has been shown in the study of the complexes of transition metal ions with various aromatic and heterocyclic derivatives of pyrazine-2-carboxylic acid hydrazide. More recently interest has been growing in the synthesis and studies of their chemotherapeutical behavior particularly their antibacterial activity.

In view these facts the Schiff base ligands 2-pyrazinoyl hydrazones were synthesized by reacting 2-pyrazinoyl hydrazide with benzaldehyde and substituted benzaldehydes (1:1) (Chauhan, 2015) and a series of metal complexes using these ligands were synthesized by reaction with Cu (II), Fe (III) and UO_2 (II) metal salt. The Schiff base ligands and the complexes have been characterized (Chauhan, 2015) with the help of elemental analysis, conductance measurements, magnetic measurements and their structure configuration have been determined by various spectroscopic (Electronic, IR, 1H NMR) techniques. Electronic and magnetic moments of the complexes indicate that the geometries of the metal centers were square planer for Cu (II), octahedral for Fe (III) and distorted octahedral for UO_2 (II) (Chauhan, 2015).

2. Material and Method

The ligands Pyrazine-2-carboxylic acid hydrazide (PAH;$C_5H_6N_4O$) and its hydrazones derivatives with different aldehydes viz. Benzy1lidene-2-Pyrazinoyl hydrazone (PAH- BENZ ;$C_{12}H_{10}N_4O$), Anisalidene-2- pyrazinoyl hydrazone (PAH- ANSL ;$C_{13}H_{12}N_4O_2$;) 4- Hydroxy-3-methoxy benzylidene-2-pyrazinoyl hydrazone (PAH-VANI;$C_{13}H_{12}N_4O_3$), p - (N, N - diethyl amino) benzy1lidene–2-pyrazinoyl hydrazone (PAH-PDEAB ;$C_{16}H_{19}N_5O$), Cinnamalidene-2-pyrazinoyl hydrazone (PAH-CAH; $C_{14}H_{12}N_4O$), 4-Methyl salicylidene-2-pyrazinoyl hydrazone (PAH- MSALI ;$C_{13}H_{12}N_4O_2$), 2- Furfuralidene-2'- pyrazinoyl hydrazone (PAH- FURAL ;$C_{11}H_{10}N_4O_2$) were synthesized by treating ethanolic solutions of 2-pyrazinoyl hydrazide with benzaldehyde and substituted benzaldehydes (1:1) (Chauhan, 2015). They were characterized with the help of elemental analysis, conductance measurements and magnetic measurements. These ligands were treated with metal salts of Cu (II), Fe (III) and UO_2 (II) to synthesize complexes which have been characterized (Chauhan, 2015). All these complexes have been screened for their antibacterial activity against human pathogens like Escherichia coli, Staphylococcus aureus, Klebsiella pneumoniae, Bacillus pumilus and Bacillus subtilis.

(I)Description of Test Organisms(Chauhan,2016) **viz. Escherichia coli, Staphylococcus aureus, Klebsiella pneumonia, Bacillus pumilus and Bacillus subtilis:**

(a) **Escherichia coli:** They inhabit humans and animals intestinal tract (Singleton, 1999). They are Gram-negative, non-sporing, occasionally encapsulated, variably motile bacilli, 0.5 to 0.7µm in width and 1 to 4µm in length, occur either singly, in pair, or in long chains. E. coli is not only very pathogenic for either men or animals, but it is a major source of vitamin K(Bentley and Meganathan, 1982) and in some persons a secondary source (Hudault et al.,2001) and (Reid et al.,2001) of vitamin B2. Infection with E. coli occurs occasionally in the appendix and gall bladder wounds.

(b) Staphylococcus aureus: The staphylococci are a group of Gram-positive, spherical bacteria that form irregular cellular aggregation or group like clusters but seldom form chains when grown in liquid medium. S. aureus is a parasitic and pathogenic (Kluytmans et al., 1997) and (Lowy, 1998). It causes a wide variety of diseases in man. It is a common inhabitant of human skin, throat (Cole, 2001) and mucous membrane. In its relevance the most common type of food poisoning is generally referred as staphylococcus or staph food poisoning (Le Loir, 2003).

(c)Klebsiella pneumoniae: Kiepsiella pneumoniae called friend landor's bacilli was first isolated from

the lung of a patient dying with pneumonia. It is a normal inhabitant of nasal, oral cavities and the intestinal tract (Ryan and Ray, 2004). It is involved in respiratory and some supportive infections (Nordmann et al., 2009). It is a Gram-positive. K. Pneumoniae is present in less than 5% of all normal human respiratory tracts. Pneumonia by K. pneumoniae is highly dangerous.

Table 1. NCBI No, ATCC No and NCTC No. of these organisms are given in table as below.

	NCBI No.	ATCC No.	NCTC No.
Escherichia coli		10536	
Staphylococcus aureus		29737	
Klebsiella pneumoniae	9111	10031	
Bacillus pumilus		14884	8241
Bacillus subtilis		6633	8236

(II). Techniques Used for Bacteriological Studies

After sterilizing the whole apparatus the bacteriostatic action of test organisms was measured using the cup plate method (Chauhan, 2015). The experimental broths were prepared using suitable nutrient media. In heated medium (nearly 45-50°C) the measured quantities of the cultures of the test organisms (0.2 ml per 100 ml) were added and the inoculated media was immediately poured into the sterilized Petri dishes to give a uniform depth of 3 to 4 mm. After setting it was transferred to a refrigerator maintained at 5 ± 2°C (to minimize the effect of variation in time between the applications of the different solutions).To avoid the growth or death of the test organisms before dishes are used and the surface of the agar layer is dry at the time of use, the prepared plates were stored in a smooth way.

Table 2: Incubation temperature of Bacteria (Test organisms)

S.No.	Bacteria	Incubation temp. (°C)
1.	Escherichia coli	35.40
2.	Staphylococcus aureus	32.00
3.	Klepsiella pneumoniae	35.40
4.	Bacillus pumilus	38.00
5.	Bacillus subtilis	32.00

The solutions of metal complexes were prepared (1.0 mg/ml) in dimethyl sulphoxide (DMSO). The

(d)Bacillus pumilus: It is rod-like in shape, with zig-zag twisting, 0.2 to 2.5 µm by 1.32 to 7.2 µm. It is aerobic, Gram-positive, found in moist soil (Priest et al., 1993) and sewage.

(e)**Bacillus subtilis:** It is rod-shaped, 0.3 to 2.2 µm by 1.27 to 7.0 µm. It is Gram-positive. It is found in soil (Priest et al., 1993) and gastrointestinal tract of ruminants (cattle, goats and sheep) and humans. 0.2 ml of each solution was poured into the cups made by using a sterilized cutter. All the Petri dishes were again put in the refrigerator for about an hour in order to allow smooth diffusion of the solutions and then transferred to incubator maintained at specified temperatures (Table 2.) for about eighteen hours. Consecutively three tests were carried out and the average zones of inhibition were measured around the holes, using Vernier Caliper. The data was summarized in the tables (6a and 6b) in term of diameter of zone of inhibition (mm).

3. Results and Discussion

Infrared spectral studies

Comparison of the Infrared spectra of free ligands pyrazine-2-carboxylic acid hydrazide ($C_5H_6N_4O$); benzylidene 2-pyrazinoyl hydrazone ($C_{12}H_{10}N_4O$); anisalidene-2-pyrazinoyl hydrazone ($C_{13}H_{12}N_4O_2$); 4-hydroxy-3-methoxy benzylidene-2-pyrazinoyl hydrazone ($C_{13}H_{12}N_4O_3$); p-(N,N-diethylamino) benzylidene-2-pyrazinoyl hydrazone ($C_{16}H_{19}N_5O$); cinnamalidene-2-pyrazinoyl hydrazone($C_{14}H_{12}N_4O$); 4-methyl salicylidene-2-pyrazinoyl hydrazone ($C_{13}H_{12}N_4O_2$); and 2-furfuralidene-2'- pyrazinoyl hydrazone ($C_{11}H_{10}N_4O_2$) and their complexes with Fe (III), Cu (II) and UO_2 (II) show that all ligands are bidentate with carbonyl oxygen and azomethine nitrogen as coordinating sites except 4-methyl salicylidene-2-pyrazinoyl hydrazone ($C_{13}H_{12}N_4O_2$) and 2-furalidene-2'-pyrazinoyl hydrazone ($C_{11}H_{10}N_4O_2$) which are found to be tridentate, third coordinating site being phenolic-oxygen and furan oxygen respectively.

The UV-spectra of ligands and their complexes show bands at Ca 274 and 300 nm assignable to (π-π^*) electronic transitions within the pyrazoline ring. Another band observed at ~370 nm in the spectra of the said 1igands is due to (n-π^*) transition of the azomethine (>C=N) group. However in the spectra of complexes, this band shifts to lower wavelength due to coordination of azomethine nitrogen to the metal atom, indicating the delocalization of the electronic charge within the chelate ring and thereby stabilizing the resulting complex. The complexes also exhibit a strong band at 390-400 nm due to L→M charge transfer

transitions between the lowest empty metal 'd' orbital and the highest occupied ligand molecular orbital, as reported earlier (Mittal et al., 1981). IR-spectrum of the ligand, 2-pyrazinoyl hydrazone shows bands at 3500 (m, br), 3270 (s, sh), 1700(s), 1520(s) & 1000-1060 cm^{-1} tentatively assigned to νNH, amide-I (C=O), amide-II [δ NH + ν(CN)] and ν(N-N) plus ring breathings modes respectively (Pelizzi et al., 1987) and (Burger et al., 1965).In the complex the amide-I band get shifted indicating that the keto oxygen is coordinated to metal ion. Upward shift of the ν(N-N) band suggests coordination through nitrogen of the azomethine group (-CH=N). The pyrazine ring out of plane bending vibration at 385, 430 cm^{-1}, do not shifted either side indicating that the ring nitrogen is not coordinated (Pelizzi and Pelizzi ,1976) and (Agarwal et al.,1981).

The IR-spectrum of the ligand exhibits a medium band at 3300 cm^{-1}, which is assigned to ν(NH) mode. This band is present in the spectra of the complexes also in the same region suggesting that imino nitrogen atom do not participate in coordination. The sharp band at 1660 cm^{-1} is assigned to ν (C=O) of the carbonyl group, is shifted to 1600 cm^{-1} indicate that the ligand exists exclusively in the keto form in the complexes bonding through the carbonyl oxygen. The pyrazine ring stretching vibrations appear at 1550 and 1470 cm^{-1} and the out of plane bending of CH of the pyrazine ring at 830 cm^{-1} in the spectrum of the ligand. In the spectra of the complexes the band due to ν (C=C) and the two bands at 1470 and 830 cm^{-1} due to the pyrazine ring remain unaltered, where as the ν (C=N) mode is sifted to 1560 cm^{-1}. The band at 1550 cm^{-1} of the ligand is shifted to 1540 cm^{-1}. The shift of ν (C=N) mode indicates that the azomethine nitrogen take part in complex formation. Since the positions of the bands due to the pyrazine ring do not change appreciably in spectra of the complexes, it is suggested that pyrazine ring does not take part in coordination.

The spectra of ligand 4-methylsalicylidene-2-pyrazinoyl hydrazone ($C_{13}H_{12}N_40_2$) show two bands around 1520 and 1280 cm^{-1} assignable to ν(C-O) (phenolic) and amide-Ill band (Nonoyama et al., 1975). On complexation these bands exhibit an upward shift of 20-25 cm^{-1} indicating the existence of phenoxide bond in the metal complexes. The shift to higher frequencies is probably due to the increase in (C-O) bond strength by extended delocalization of the π-system of the azine moiety.

The disappearance of the bands in the ranges 3200-3280 cm^{-1} and 3000-3080 cm^{-1} in the compounds indicates the involvement of bond formation by phenolic -OH group. The coordinated nature of azomethine N-can be inferred from the lowering of the ν (C=N) band by 10-15 cm^{-1} in the complexes from the ligand value.

The infrared spectra of the ligand 2-furfuralidene-2'- pyrazinoyl hydrazone and their complexes have been recorded in KBr-phase. The infra red spectra of the complexes show bands at 3040-3060 cm^{-1}, 1600-1610 cm^{-1} and 1515-1540 cm^{-1} assignable to ν(NH), ν(C=N) or amide-I and amide-II modes. Both the amide-I and azomethine bands are lowered in comparison to bands in the present ligands; amide-II band is raised from ~ 1515 cm^{-1} to 1530-1545 cm^{-1} in the metal complexes. These interpretations are tentative as the presence of (C=C) / (C=O) chromophore might interfere.

A sharp band at ~1620 cm^{-1} due to ν(C=N) shifts slightly towards lower frequency (10-20 cm^{-1}) in the complexes indicating the coordination of azomethine nitrogen to the metal atom. The bands observed in the region 3350-3430 cm^{-1} attributed to asymmetric and symmetric modes of the NH-group in the ligand pyrazine-2-carboxylic acid hydrazide ($C_5H_6N_4O$) shifted in position in the spectra of complexes, revealing its participation in chelation.

A band at 1080 cm^{-1} in the ligand spectra is assigned to ν(C-O-C) mode of furan moiety. This band position is changed in all the complexes indicating the involvement of oxygen atom of furan moiety in coordination (Lever and Ramaswamy, 1973) and (Syamal and Maurya, 1985).

The uranyl complex exhibit three bands at 930, 840 and 265 cm^{-1} assigned to ν_3, ν_1 and ν_4-modes respectively of dioxouranium ion (Hsieh et al.,1975) and (El. Saied et al., 2000).

Finally the UV-spectrum of the uranyl complexes shows a band at 21270-22222 cm^{-1} assigned to $^1E_9^+ \rightarrow \pi_u^3$. This band is similar to the OUO-symmetric stretching frequency for the first excited state (Nakamoto, 1970).The spectra of uranyl complexes show two bands near 1605-1612 and 1400-1410 cm^{-1} attributed to ν_{asym} COO and ν_{sym} COO respectively. This indicates that acetate group coordinates as a monodentate ligand (Dhanwad et al., 1994), (Clarke, 2002) and (Clarke et al., 1999).

Far Infra red spectra (600-200 cm^{-1})

In UO_2 (VI) complex, the bands at 550 cm^{-1} and 500 cm^{-1} have been assigned to ν(U-O) and ν(U-N) vibrations respectively (Sharma and Mishra, 2005) while in other complexes the bands in the range 470-490 cm^{-1} and 410-440 cm^{-1} have been assigned to ν(M-O) and ν(M-N) vibrations respectively (Balzani and Juris, 2001).The strong band at 915 cm^{-1} in UO_2 (VI) complexes are assigned to ν(O=U=O) vibrations (Panja et al., 2003) and (Naik and Revankar, 2004).

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Infra red spectra of Fe (III), Cu (II) and UO2 Complexes (Fig 4.1-4.8)

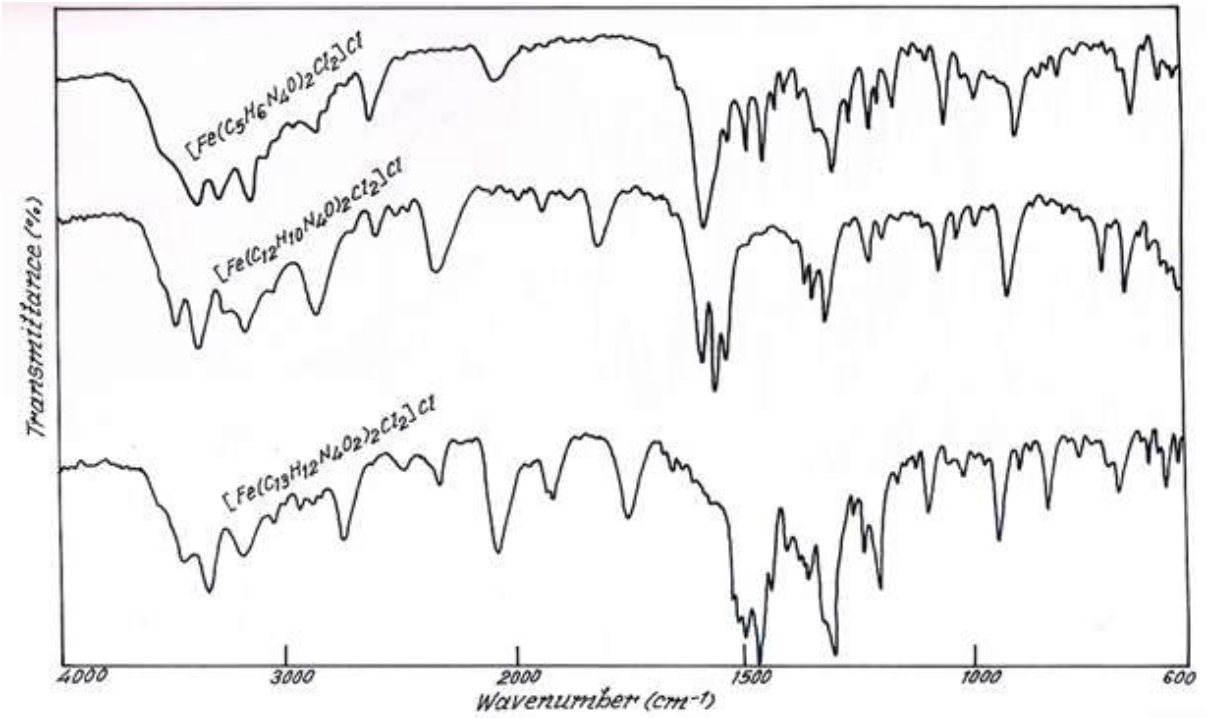

Fig. (4.1) : I. R. Spectra of Fe(III) complexes.

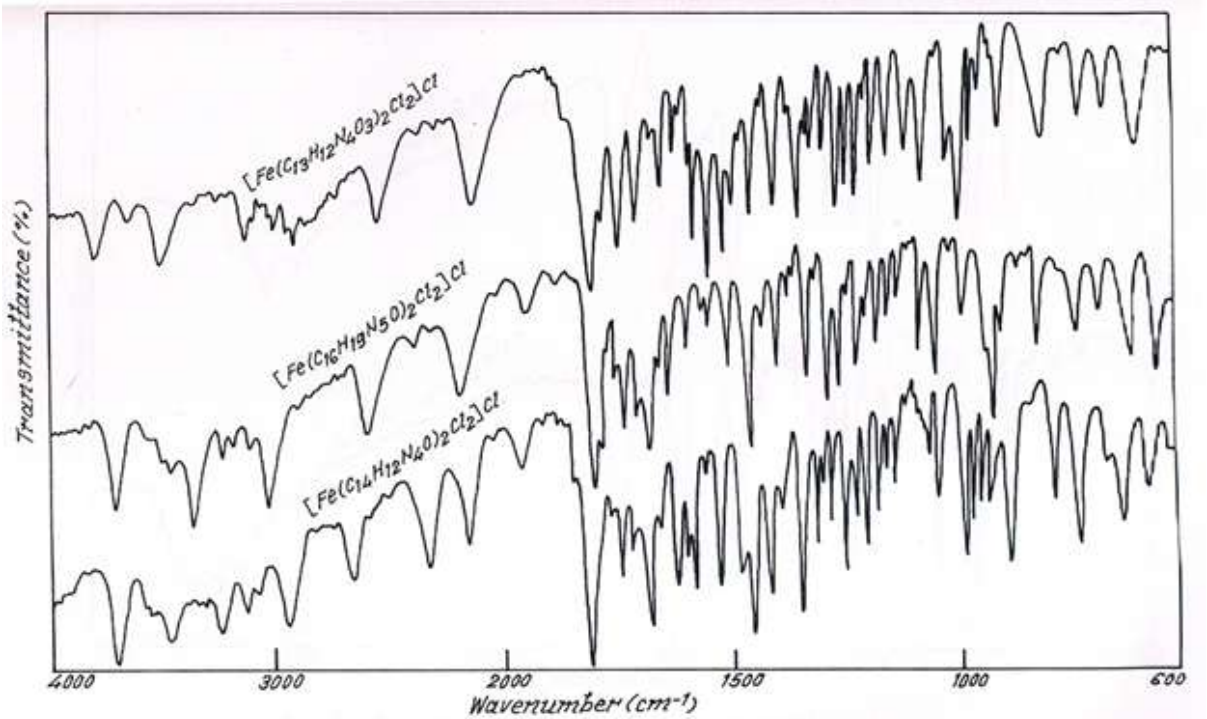

Fig. (4.2) : I. R. Spectra of Fe(III) complexes.

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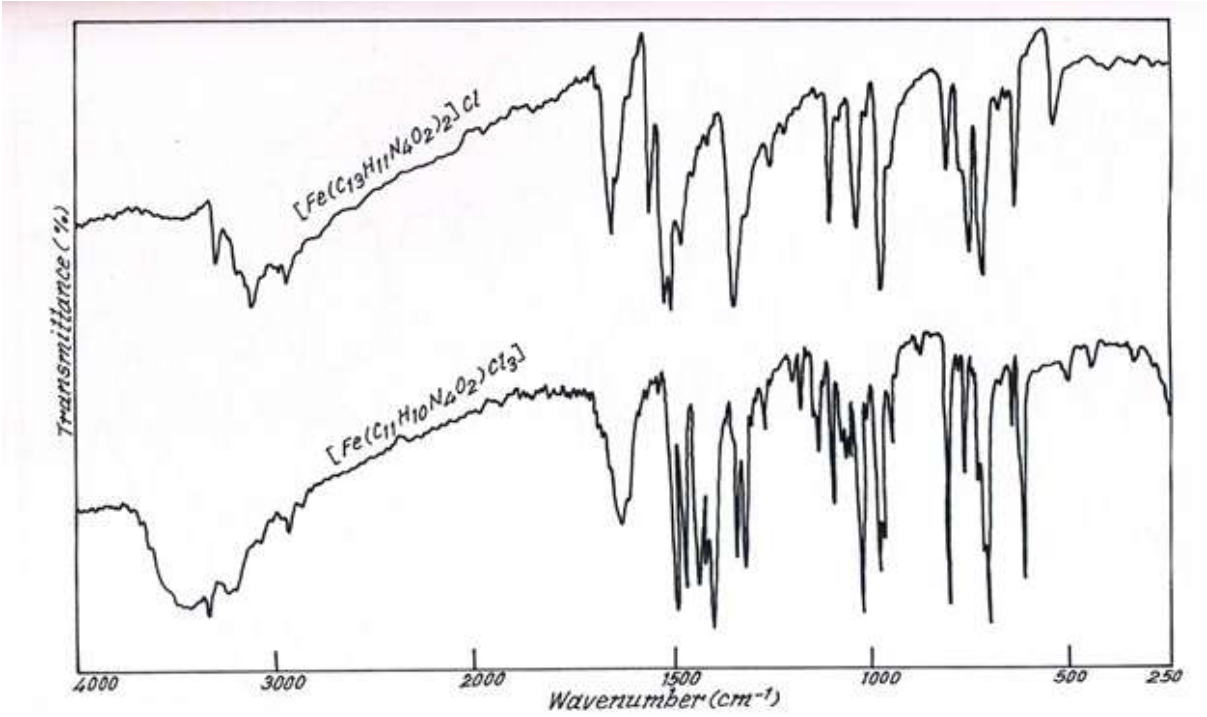

Fig.(4.3) : I. R. Spectra of Fe(III) complexes.

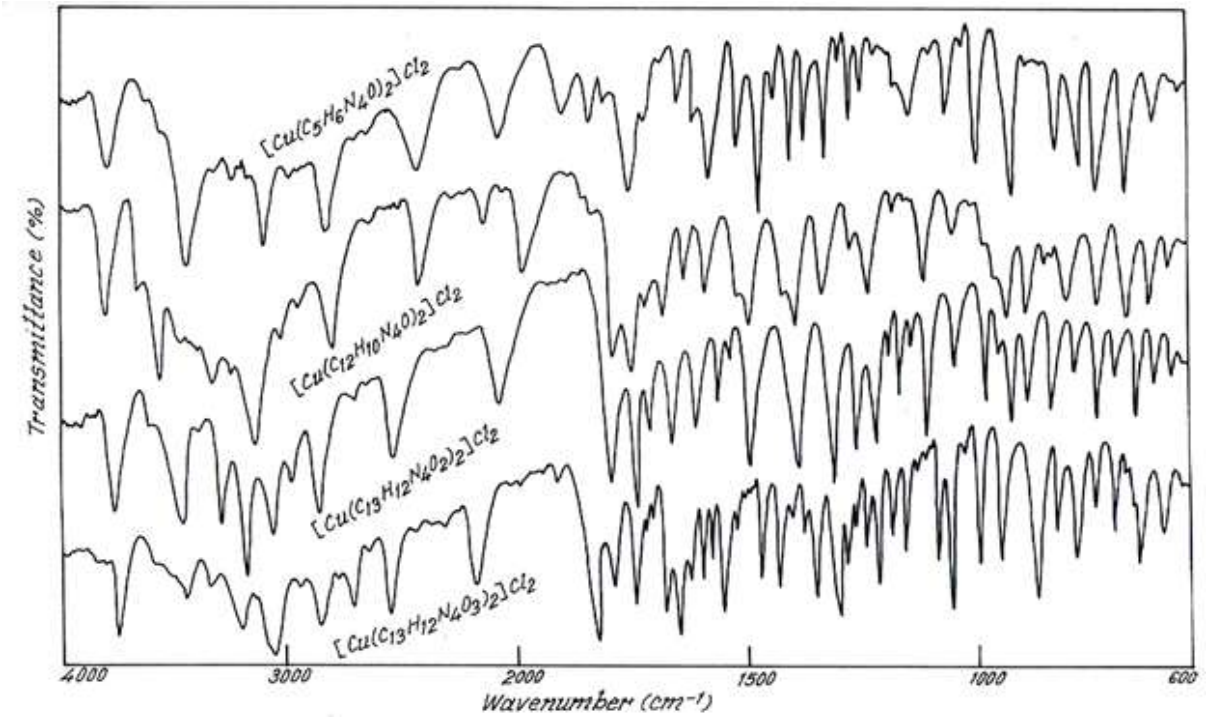

Fig.(4.4) : I. R. Spectra of Cu(II) complexes.

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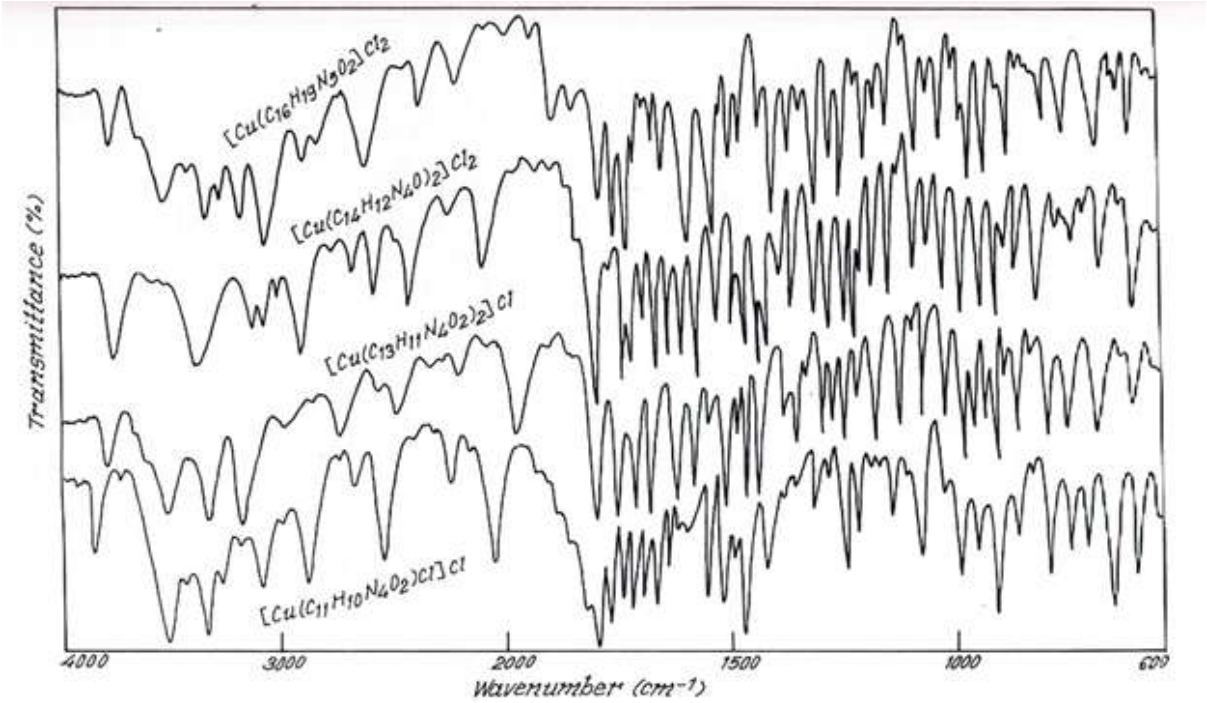

Fig. (4.5): I. R. Spectra of Cu(II) complexes.

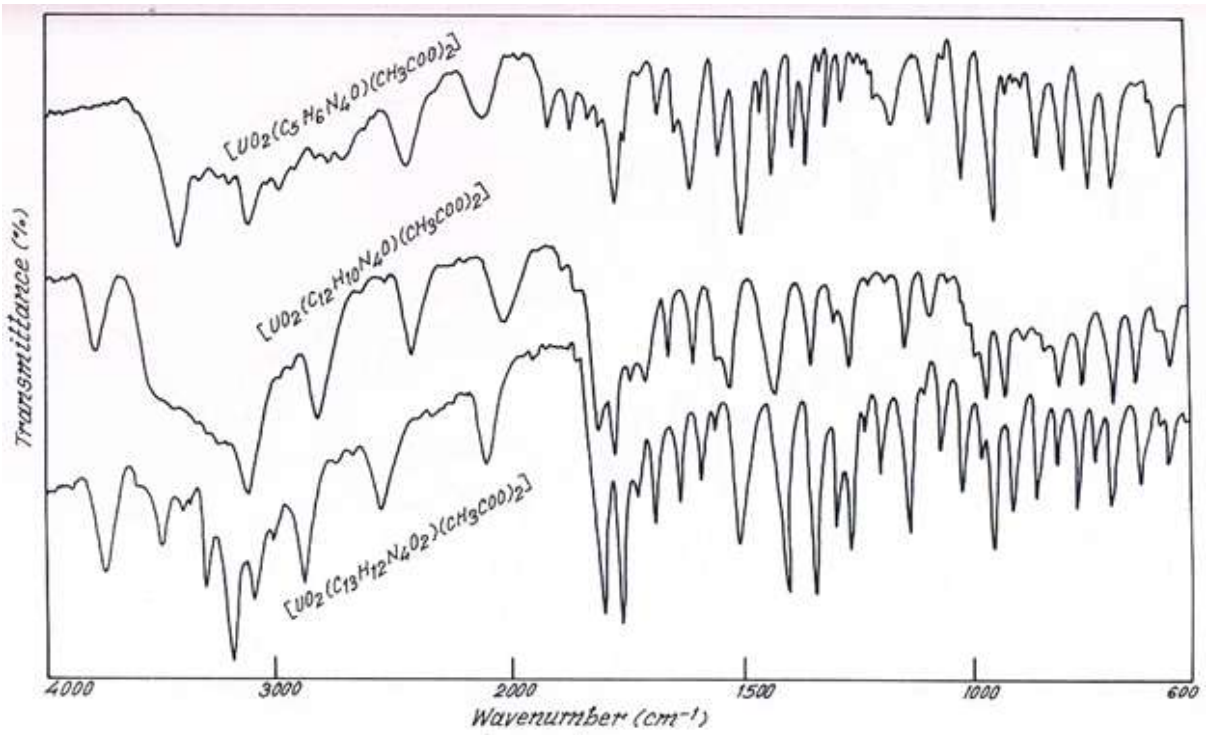

Fig. (4.6): I. R. Spectra of UO_2(II) complexes.

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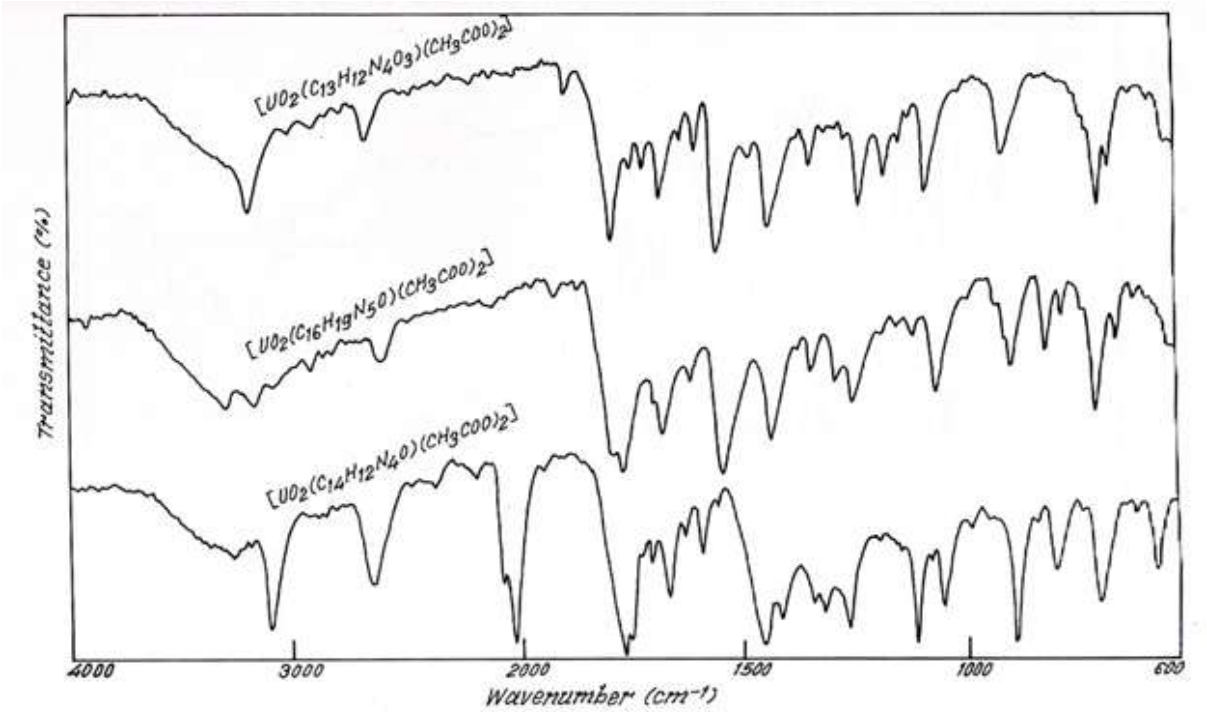

Fig. (4.7): I.R. Spectra of UO_2(II) complexes.

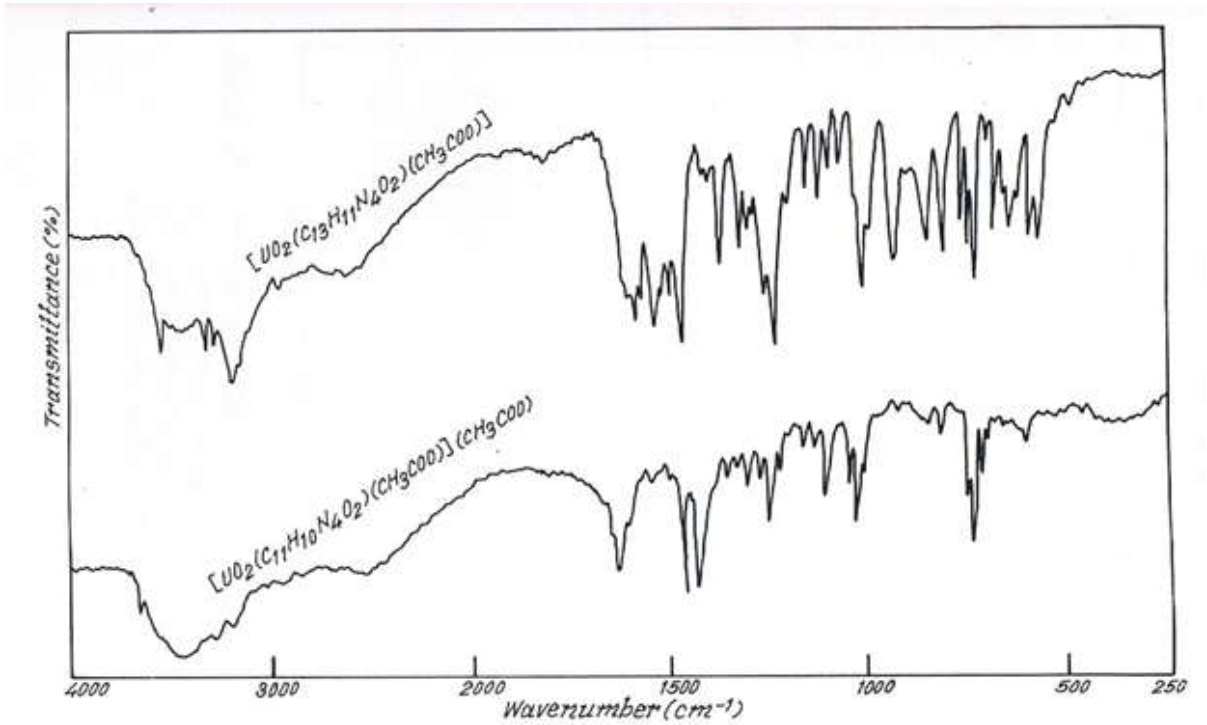

Fig. (4.8): I.R. Spectra of UO_2(II) complexes.

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Table 3a.: Selected I.R. frequencies (cm^{-1}) and their tentative assignments from I.R. spectra of Iron (III) complexes with pyrazine-2-carboxylic acid hydrazide and its derivatives.

S. No.	Compounds	Amide band I ν(C=O)	Amide band II ν(-CH=N-) of immine-N & NH bending modes	Antisymmetric & symmetric ν(C=C)+ ν(C=N) of pyrazine ring	Amide band III ν(C=O) + ν(C=N)+ γ(CO) + γ (CN)	Amide band IV γ (NCO) + γ (C-O)	Pyrazine ring breathings, deformation δ(N-N)*	Metal donor frequencies 1.ν(M-azomethine- N) 2.ν (M-O) 3.ν(M-halogen)
1	2	3	4	5	6	7	8	9
1.	$[Fe(C_5H_6N_4O)_2Cl_2]Cl$	1640ms 1600sh	1560s	1560sh 1540ms	1350ms	1125ms	1035ms 880vs*	1. 500ms 2. 480s
2.	$[Fe(C_{12}H_{10}N_4O)_2Cl_2]Cl$	1605vs	1570ms 1565ms	1540vs	1390vs 1360vs	1180s 1165ms 1135ms	1090b 1070s 1035vs 885s*	1. 510m 2. 470sh 3. 380m
3.	$[Fe(C_{13}H_{12}N_4O_2)_2Cl_2]Cl$	1620vs	1575ms	1540ms 1515s	1370s 1320ms	1195ms 1180vs 1135sh	1080ms 1045vs 870vs*	1. 500m 2. 460s 3. 375s
4.	$[Fe\ (C_{13}H_{12}N_4O_3)_2Cl_2]Cl$	1630vs 1610sh	1580vs 1560ms	1555sh 1505vs	1405ms 1320ms	1200ms 1185ms 1140ms	1065ms 1020ms 880vs*	1. 475ms 2. 338ms 3. 281s
5.	$[Fe\ (C_{16}H_{19}N_5O)_2Cl_2]Cl$	1640s 1590sh	1570vs	1520s	1380vs	1295ms 1165s 1146s	1050s 1020s 910s*	1. 500m 2. 440s 3. 275m

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Table 3b. Selected I.R. frequencies (cm^{-1}) and their tentative assignments from I.R. spectra of Iron (III) complexes with pyrazine-2-carboxylic acid hydrazide and its derivatives.

S. No.	Compounds	Amide band I ν(C=O)	Amide band II ν(-CH=N-) of immine-NH bending modes	Antisymmetric & symmetric ν(C=C)+ ν(C=N) of pyrazine ring	Amide band III ν(C+O) + ν(C=N)+ γ(CO) + γ (CN)	Amide band IV γ (NCO) + γ (C-O)	Pyrazine ring breathings, deformation δ(N-N)*	Metal donor frequencies 1.ν(M-azomethine- N) 2.ν (M-O) 3.ν(M-halogen)
1	2	3	4	5	6	7	8	9
6.	$[Fe(C_{14}H_{12}N_4O)_2Cl_2]Cl$	1630ms 1600s	1600s 1565s	1555ms	1380vs 1325ms	1195s 1165s 1145ms	1065ms 1025vs 900vs*	1. 475ms 2. 340ms 3. 279ms
7.	$[Fe(C_{13}H_{11}N_4O)_2]Cl$	1590s	1590s 1560b	1500ms	1385vs 1355sh 1325vs	1175s 1145b	1070s 1020vs 880vs*	1. 500ms 2. 350s 3. 270m
8.	$[Fe(C_{11}H_{10}N_4O_2)Cl_3]$	1610s 1600s	1590s	1550vb	1415s 1350s	1215s 1175vs 1135s	1060vs 1020ms 900ms*	1. 495m 2. 460s 3. 285m

s- sharp, ms-medium, v s-very sharp, sh-shoulder, b-broad, v b-very broad

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Table 4a. : Selected I.R. frequencies (cm^{-1}) and their tentative assignments from I.R. spectra of Copper (II) complexes with pyrazine-2-carboxylic acid hydrazide and its derivatives.

S. No.	Compounds	Amide band I ν(C=O)	Amide band II ν(-CH=N-) of immine-N& NH bending modes	Antisymmetric & symmetric ν(C=C)+ ν(C=N) of pyrazine ring	Amide band III ν(C=O) + ν(C=N)+ γ(CO) + γ (CN)	Amide band IV γ (NCO) + γ (C-O)	Pyrazine ring breathings, deformation δ(N-N)*	Metal donor frequencies 1.ν(M-azomethine- N) 2.ν (M-O) 3.ν(M-halogen)
1	2	3	4	5	6	7	8	9
1.	$[Cu(C_5H_6N_4O)_2]Cl2$	1630ms 1600sh	1570s	1575sh 1540ms	1360ms	1140ms	1030s 885vs*	1. 480m 2. 400s 3. 325s
2.	$[Cu(C_{12}H_{10}N_4O)_2]Cl_2$	1610ms	1590vs 1560ms	1550ms	1380vs 1365ms	1180ms 1160ms	1060ms 1030vs 885s*	1. 475ms 2. 338ms 3. 300s
3.	$[Cu(C_{13}H_{12}N_4O_2)_2]Cl_2$	1605vs	1580ms	1540ms 1505ms	1370vs 1330vs	1200s 1180vs 1135s	1060vs 1040ms 880vs*	1. 480m 2. 410s 3. 325s
4.	$[Cu(C_{13}H_{12}N_4O_3)_2]Cl_2$	1600vs 1580s	1560vs	1555sh 1505ms	1405vs 1325ms	1200ms 1185ms 1150ms	1080b 1020vs 900vs*	1. 475ms 2. 360s 3. 300m
5.	$[Cu(C_{16}H_{19}N_5O)_2]Cl_2$	1610s 1600s	1565vs	1520s	1380ms	1200ms 1160s 1150s	1040s 1020s 905s*	1. 480m 2. 400m 3. 330s

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Table 4b.Selected I.R. frequencies (cm^{-1}) and their tentative assignments from I.R. spectra of Copper (II) complexes with pyrazine-2-carboxylic acid hydrazide and its derivatives**.**

S. No.	Compounds	Amide band I ν(C=O)	Amide band II ν(-CH=N-) of immine-N& NH bending modes	Antisymmetric & symmetric ν(C=C)+ ν(C=N) of pyrazine ring	Amide band III ν(C=O) + ν(C=N)+ γ(CO) + γ (CN)	Amide band IV γ (NCO) + γ (C-O)	Pyrazine ring breathings, deformation δ(N-N)*	Metal donor frequencies 1.ν(M-azomethine- N) 2.ν (M-O) 3.ν(M-halogen)
1	2	3	4	5	6	7	8	9
6.	$[Cu(C_{14}H_{12}N_4O)_2]Cl_2$	1640vs 1600sh	1590sh 1570s	1560ms	1380vs 1325ms	1220s 1175ms 1150ms	1070ms 1030vs 905vs*	1. 485m 2. 350ms 3. 370s
7.	$[Cu(C_{13}H_{11}N_4O_2)_2]Cl$	1580s	1580s 1565ms	1500ms	1380ms 1355s 1325ms	1170s 1150ms	1060vs 1020vs 885vs*	1. 475s 2. 340ms 3. 275ms
8.	$[Cu(C_{11}H_{10}N_4O_2)Cl]Cl$	1620s 1585s	1585ms	1560vb	1415s 1350ms	1220ms 1180ms 1135s	1080s 1060ms 1020vs 900ms*	1. 490 m 2. 350ms 3. 300s

s- sharp, ms-medium, v s-very sharp, sh-shoulder, b-broad, v b-very broad

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Table 5a.Selected I.R. frequencies (cm^{-1}) and their tentative assignments from I.R. spectra of Dioxouranium (VI) complexes with pyrazine-2-carboxylic acid hydrazide and its derivatives.

S. No.	Compounds	Amide band I ν(C=O)	Amide band II ν(-CH=N-) of immine-N& NH bending modes	Antisymmetric & symmetric ν(C=C)+ ν(C=N) of pyrazine ring	Amide band III ν(C=O) + ν(C=N)+ γ(CO) + γ (CN)	Amide band IV γ (NCO) + γ (C-O)	Pyrazine ring breathings, deformation δ(N-N)*	Metal donor frequencies 1.ν(M-azomethine- N) 2.ν (M-O)
1	2	3	4	5	6	7	8	9
1.	$[UO_2(C_5H_6N_4O)_2$	1600ms 1600sh	1570ms	1560sh 1545ms	1360vs	1130ms	1025vs 880vs*	1. 450ms 2. 325ms
2.	$[UO_2(C_{12}H_{10}N_4O)_2$ $(CH_3COO)_2$	1580vs	1570s 1560ms	1555vs	1385vs 1365ms	1210s 1190ms 1165ms	1090b 1035vs 875vs*	1. 500s 2. 325ms
3.	$[UO_2(C_{13}H_{12}N_4O_2)_2$ $(CH_3COO)_2]$	1600vs	1575ms	1540ms 1515vs	1370ms 1360s 1335vs	1190ms 1190vs 1150s	1070vs 1040ms 890vs*	1. 510s 2. 450m
4.	$[UO_2 (C_{13}H_{12}N_4O_3)_2$ $(CH_3COO)_2]$	1600vs 1595sh	1570ms	1560sh 1500ms	1390ms 1330ms	1200ms 1190ms 1150vs	1080b 1020vs 900ms*	1. 500s 2. 480m
5.	$[UO_2 (C_{16}H_{19}N_5O)_2$ $(CH_3COO)_2]$	1605ms 1600s	1580ms	1520ms	1380ms	1200vs 1165ms 1145s	1040s 1020s 905s*	1. 450ms 2. 400m

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Table 5b. Selected I.R. frequencies (cm^{-1}) and their tentative assignments from I.R. spectra of Dioxouranium (VI) complexes with pyrazine-2-carboxylic acid hydrazide and its derivatives.

S. No.	Compounds	Amide band I ν(C=O)	Amide band II ν(-CH=N-) of immine-N& NH bending modes	Antisymmetric & symmetric ν(C=C)+ ν(C=N) of pyrazine ring	Amide band III ν(C=O) + ν(C=N)+ γ(CO) + γ (CN)	Amide band IV γ (NCO) + γ (C-O)	Pyrazine ring breathings, deformation δ(N-N)*	Metal donor frequencies 1.ν(M-azomethine- N) 2.ν (M-O)
1	2	3	4	5	6	7	8	9
6.	$[UO_2(C_{14}H_{12}N_4O)_2$ $(CH_3COO)_2$	1620vs 1600sh	1600sh 1575ms	1560vs	1380ms 1325ms	1215ms 1170s 1145s	1060ms 1030vs 905vs*	1. 500m 2. 460s
7.	$[UO_2(C_{13}H_{11}N_4O_2)_2$ $(CH_3COO)_2]$	1580s	1600ms 1570b	1500s	1385ms 1325vs	1180ms 1150b	1070s 1020vs 880vs*	1. 510m 2. 470m
8.	$[UO_2$ $(C_{11}H_{10}N_4O_2)$ $(CH_3COO)](CH_3COO)$	1650s 1600s	1590s	1540b	1420vs 1350s	1220sh 1190vs	1060vs 1020ms 900ms*	1. 500m 2. 470m

s- sharp, ms- medium, v s-very sharp, sh-shoulder, b-broad, v b-very broad

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Table 6a. Antibacterial activity of Iron (III), complexes of pyrazine-2-carboxylic acid hydrazide and its hydrazones derivatives against gram positive and gram negative organisms.

S.No.	Compounds	Gram-positive Organisms			Gram-negative Organisms	
		S.aureus	B.subtilis	B.pumilus	E.coli	K.pneumoniae
		Diameter of zone of inhibition (mm)	Diameter of zone of inhibition (mm)	Diameter of zone of inhibition (mm)	Diameter of zone of inhibition (mm)	Diameter of zone of inhibition (mm)
1	2	3	4	5	6	7
1.	$[Fe\ (C_5H_6N_4O)_2Cl_2]Cl$	10.0	7.8	7.8	12.2	12.1
2.	$[Fe(C_{13}H_{12}N_4O_3)_2Cl_2]Cl$	13.4	7.8	13.0	12.6	7.8
3.	$[Fe\ (C_{16}H_{19}N_5O)_2Cl_2]Cl$	16.4	7.8	7.8	12.4	15.4
4.	$[Fe\ (C_{14}H_{12}N_4O)_2Cl_2]Cl$	15.0	7.8	7.8	12.0	7.8
5.	$[Fe(C_{13}H_{11}N_4O_2)_2]Cl$	10.0	7.8	10.0	12.3	17.2
6.	$[Fe(C_{11}H_{10}N_4O_2)Cl_3]$	13.8	7.8	14.8	13.2	7.8

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Table 6b. Antibacterial activity Copper (II) and Dioxouranium (VI) complexes of pyrazine-2-carboxylic acid hydrazide and its hydrazones derivatives against gram positive and gram negative organisms.

S.No.	Compounds	Gram-positive Organisms			Gram-negative Organisms	
		S.aureus	B.subtilis	B.pumilus	E.coli	K.pneumoniae
		Diameter of zone of inhibition (mm)	Diameter of zone of inhibition (mm)	Diameter of zone of inhibition (mm)	Diameter of zone of inhibition (mm)	Diameter of zone of inhibition (mm)
1	2	3	4	5	6	7
1.	$[Cu(C_5H_6N_4O)_2]Cl_2$	11.0	7.8	7.8	12.4	14.1
2.	$[Cu(C_{13}H_{12}N_4O_3)_2]Cl_2$	7.8	7.8	15.4	13.0	15.2
3.	$[Cu(C_{16}H_{19}N_5O)_2]Cl_2$	12.4	7.8	24.6	14.8	7.8
4.	$[Cu(C_{14}H_{12}N_4O)_2]Cl_2$	11.2	7.8	8.0	12.4	12.0
5.	$[UO_2 (C_{13}H_{12}N_4O_3)(CH_3COO)_2]$	11.4	7.8	16.2	12.8	12.4
6.	$[UO_2(C_{16}H_{19}N_5O)CH_3COO)_2]$	11.4	7.8	8.0	14.6	7.8
7.	$[UO_2(C_{14}H_{12}N_4O)CH_3COO)_2]$	13.8	7.8	12.0	12.8	7.8
8.	$[UO_2(C_{13}H_{11}N_4O_2)CH_3COO)_2]$	13.6	12.3	15.6	13.6	7.8
9.	$[UO_2(C_{11}H_{10}N_4O_2)(CH_3COO)](CH_3COO)$	13.3	7.8	15.4	14.7	7.8

Evaluation of antibacterial activity

All the iron (III), Copper (II) and uranyl (II) complexes of pyrazine-2-carboxylic acid hydrazide and its hydrazones were screened their antibacterial activity against gram positive (**Staphylococcus aureus, Bacillus subtilis and Bacillus pumilus)** and gram negative organisms (**Escherichia coli and Klebsiella pneumonia) organisms** (Table 6a.-6b.). Their activities are represented by diameter of zones of inhibition (mm), based on average of three experimental values.

From diameter of zone of inhibition it is evident that all the chelates are almost inactive against B.subtilis and general trend of activity is E .coli > S.aurius > B. Pumilus > K.pneumoniae and about 50% of chelates does not show activity against B.pumilus and K.pneumoniae and in general activity is decreased on chelation.

4. Conclusion

The ligands possess antibacterial properties. In view of these facts the present studies were carried out to analyze the antibacterial behavior of metal ligand complexes. The antibacterial behaviour may alter after formation of complexes. In present case after formation of complex antibacterial activity has decreased. This is probably due to lesser antibacterial activity of individual metal in comparison to the free ligands.

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