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New Series of Complexes of Molybdenum with Biologically Active Schiff Bases

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ABSTRACT

Metal complexes of the type, $[MoO(NCS)_4$ L-L] (where L-L are amine substituted biologically active Schiff bases with general formula , $R_1N = CHR_2$. Here R_1 is 4-aminosalicylic acid & R_2 is 4-chloro-benzaldehyde, 2-chloro-benzaldehyde, salicyladehyde , vanillin and benzaldehyde) have been prepared by reaction of ammonium tetra-isothiocyanato-oxomolybdate (VI) with the corresponding ligand in aqueous medium in the presence of hydrochloric acid. The complexes have been characterized by elemental analysis, molar conductivity, magnetic susceptibility, infrared spectroscopy and ^{1}HNMR spectroscopy. The metal complexes have been screened against different bacteria for their biological activities. The metal complexes show more potent biological activities as compared with Schiff base ligands.

Keywords: Schiff bases, Benzaldehyde, Elemental analysis, Biological activities, ^{1}HNMR spectroscopy.

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INTRODUCTION

Molybdenum is the only essential trace element of the second transition series and is an integral part of oxo-transferase[1] nitrogenase enzymes[2]. The chemistry of molybdenum is quite interesting because of its large number of accessible oxidation states as well as its stability to form stable complexes with oxygen, nitrogen and sulphur donor ligands with diverse co-ordination numbers and stereo-chemistries[3]. It is used in various essential life processes as constituent part of several metallo-enzymes[4]. Apart from their utility as model compounds for enzymes the Mo(V) complexes have also found to be used as catalysts for oxygen transfer. The Schiff bases are a special class of ligands with a variety of donor atoms exhibiting interesting co-ordination modes towards various metals[5-7]. The azomethine linkage in Schiff bases is responsible for the biological activities such as antitumor, antibacterial, antifungal and herbicidal activities[8]. Schiff bases[9] derived from sulfane-thiadizole and salicylaldehyde or thiophene-2-aldehyde and their complexes show toxicities against insects. α-Aminoacid[10] acts as intermediate in synthesis of photo-stable pyrthriod insecticides. The antibacterial, antifungal and antiviral activities of ligands have been increased upon complexation. Metal complexes have a greater effect than the ligands against almost all bacteria[11]. Metal complexes of aroyl-hydrazones have broad applications in biological processes such as in the treatment of tumours, tuberculosis, leprosy[12,13] and mental disorders. The biological activity has been attributed[14] to the complex forming abilities of the ligands with metal ions present in the cells and involvement of molybdenum in molybdenum oxo-transferase enzymes[15]. The enzyme super-family of molybdenum oxotransferases all contain molybdenum, and promote oxygen atom transfer reactions. Enzymes in this family include DMSO reductase, xanthine oxidase, nitrite reductase, and sulfite oxidase. Metal complexes[16] of Mo (VI) and Mn(II) with ligands hydrazine carboxamide and hydrazine carbo-thiamide show anti-bacterial activities against *Staphylococcus aureus* and *Xanthomonas compestris*. Schiff bases[17] derived from salicylaldehyde and boronate esters show antifungal activities against *Aspergillus niger* and *Shigella flexneri*. Schiff bases[18] of salicylaldehyde O,O-dimethyl thiophosphoamide and their complexes with Cu (II), Ni(II) and Zn(II) are effective chemicals to kill Tetranychus bimaculatus. In the present work, we have prepared five new complexes of Mo (VI) with biologically active Schiff base ligands keeping in mind the ability of complexation of Mo and its role in biological processes.

MATERIALS AND METHOD

All the chemicals used were of reagent grade. 4-Amino-salicylic acid (Himedia), 4-Chloro-

benzaldehyde (Himedia), 2-Chloro- benzaldehyde (Himedia), Salicylaldehyde (Aldrich), Vanillin (Himedia) and Benzaldehyde (Himedia) were used as supplied. The Schiff base ligands were prepared as described in the literature[19]. The analysis of Molybdenum was carried out by gravimetric method. The complex (0.2g) was decomposed by repeated treatment with concentrated nitric acid. Excess HNO_3 was evaporated and residue was dissolved in an alkali solution (0.1N NaOH) and finally the volume of the solution was made to 200ml. The pH of the solution was adjusted to 7 and the solution was heated to boiling. A 3% solution of Oxime (8-hydroxy quinoline) in ethanol and acetic acid was added dropwise until present in slight excess with constant stirring, resulting into yellow colouration of mother liquid. The precipitates was allowed to digest at about 60-70^{0}C, filtered through sintered glass crucible and washed with hot water. The precipitates was dried at 130-140 ^{0}C and weighed as molybdenum oxinate [Mo O_2 $(C_9H_6ON)_2$]. Carbon, hydrogen, nitrogen and sulphur were analyzed micro-analytically using CHNS analyser of Leco-model 932. Melting points for the prepared complexes were obtained by electric melting point apparatus. Molar conductivity in DMF at room temperature was measured by an Elico conductivity bridge of type CM82T having a conductivity cell with a cell constant of 0.90 using 10^{-3}mol L^{-1}solution of complexes. IR spectra of complexes over the region 4000-400 cm^{-1} were recorded on an FTIR spectrophotometer made of Shimdz, using KBr discs. ^{1}HNMR of the complexes were determined in DMSO on Bruker spectrophotometer. Antimicrobial activity was studied against various bacterial strains grown on nutrient agar medium. The medium was prepared in a dish by adding 0.5% peptone, 0.3% beef extract, 1.5% agar, 0.5% NaCl and distilled water. The pH of the medium was maintained at 6.8.The medium was then placed in the laminar air flow chamber for some time and well was prepared with the help of well borer.

RESULTS AND DISCUSSION

Ammonium Molybdate (0.00363mol) and ammonium thiocyanate (0.38mol) were dissolved in water (30ml) at room temperature and 7.5 ml of 11M HCl was added to the reaction mixture. The resulting yellow solution was cooled in an ice bath and an equimolar solution of the corresponding ligand (L), where L= Schiff base, was added to the solution. The reaction mixture was left undisturbed for one hour in an ice bath. The precipitates formed were filtered under suction, washed three to four times with water containing a few drops of HCl and dried in *vacuo*.

$(NH_4)_6Mo_7O_{24}.4H_2O + 4\,NH_4SCN \rightarrow (NH_4)_2[MoO_2(NCS)_4] + 8NH_4OH$

$(NH_4)_2[MoO_2(NCS)_4] + L\text{-}L \rightarrow [MoO(SCN)_4L\text{-}L] + NH_4OH$

All the complexes are coloured, stable, insoluble in water but soluble in organic solvents like DMF and DMSO. The complexes have characteristic colours and melting points, table 1.

Table 1: Physical data of Complexes

S.No.	Compound	Colour	Melting point (^{0}C)	Elemental analysis, found (calculated)				
				Mo	C	H	N	S
1	$Mo(SCN)_4$-L_1	Dark yellow	240	16.60 (16.90)	31.80 (38.02)	1.55 (1.76)	12.20 (12.32)	22.45 (22.53)
2	$Mo(SCN)_4$-L_2	Dark red	255	15.20 (15.63)	37.00 (37.13)	1.80 (1.95)	11.35 (11.40)	20.72 (20.84)
3	$Mo(SCN)_4$-L_3	Light green	274	15.60 (15.94)	35.80 (35.88)	1.40 (1.49)	11.50 (11.62)	21.20 (21.26)
4	$Mo(SCN)_4$-L_4	brown	252	15.65 (15.94)	35.70 (35.88)	1.35 (1.49)	11.55 (11.62)	21.18 (21.26)
5	$Mo(SCN)_4$-L_5	brown	273	16.20 (16.43)	36.80 (36.98)	1.60 (1.71)	11.88 (11.98)	21.80 (21.91)

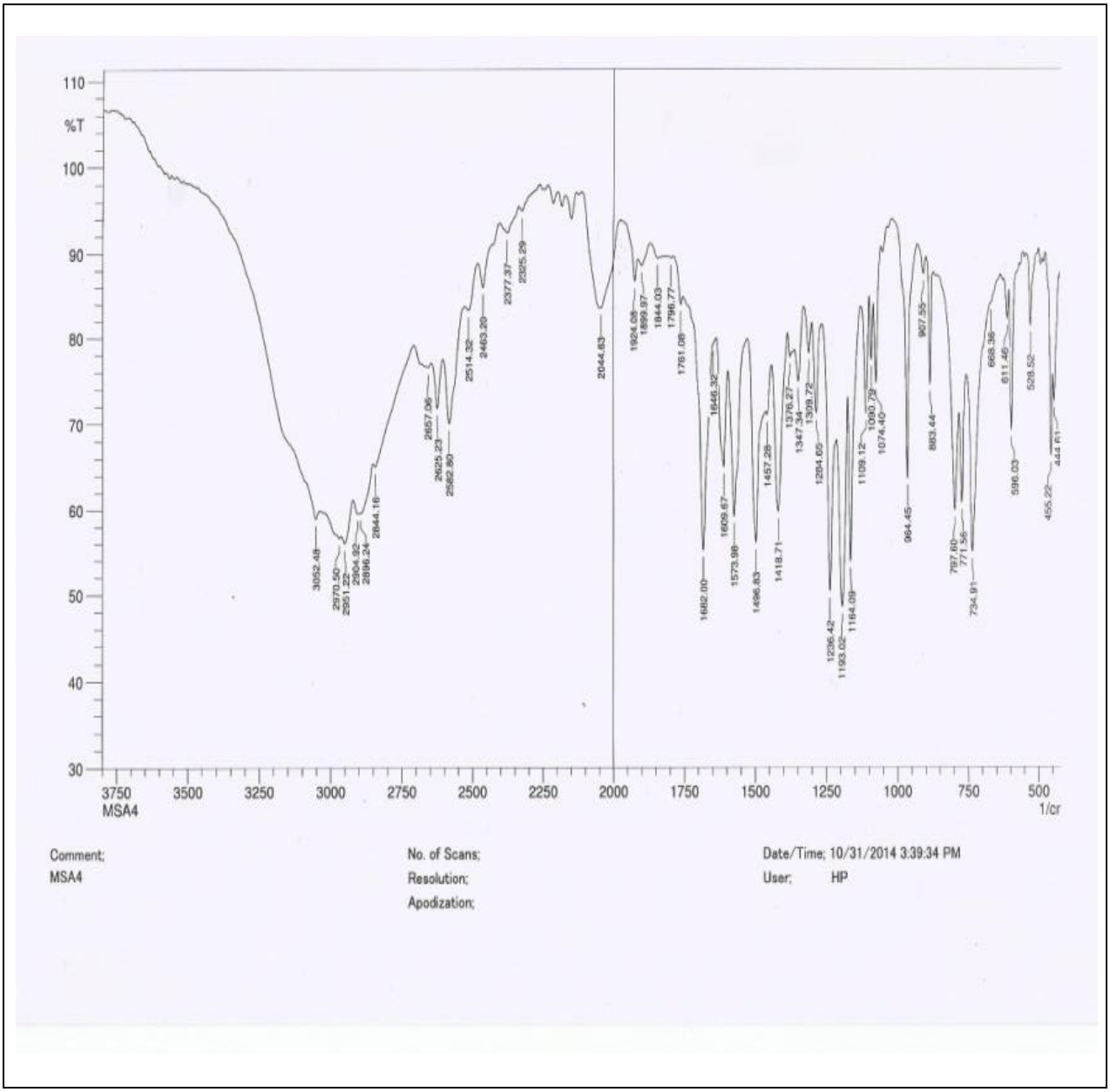

Figure: 1: IR Spectrum of metal complex, MoSA4

Conductance Measurement

The metal complexes are non-electrolytic in nature. The molar conductance is in the range 15-21 mho cm^2mol^{-1} when molar conductance of these complexes was measured in 10^{-3} M DMF, which is much less than the value for 1:1 electrolytes in DMF.

Infrared spectra

The IR spectra of ligands and their respective complexes were compared and has been found that all the complexes exhibit a band due to ν (Mo=O) in the region 960-975 cm^{-1} which was absent in the free ligands, indicates the presence of oxo group in all the complexes. The band for ν(C=N), ν(CS) and ν(NCS) were observed in the spectra of the complexes at 2044-2083 cm^{-1}, 1136-1164 cm^{-1} and 471- 490 cm^{-1}. The bands in the region 1682 cm^{-1} is attributed to the ν(C=N) in the spectra of all the complexes, figures. 1 and 2.

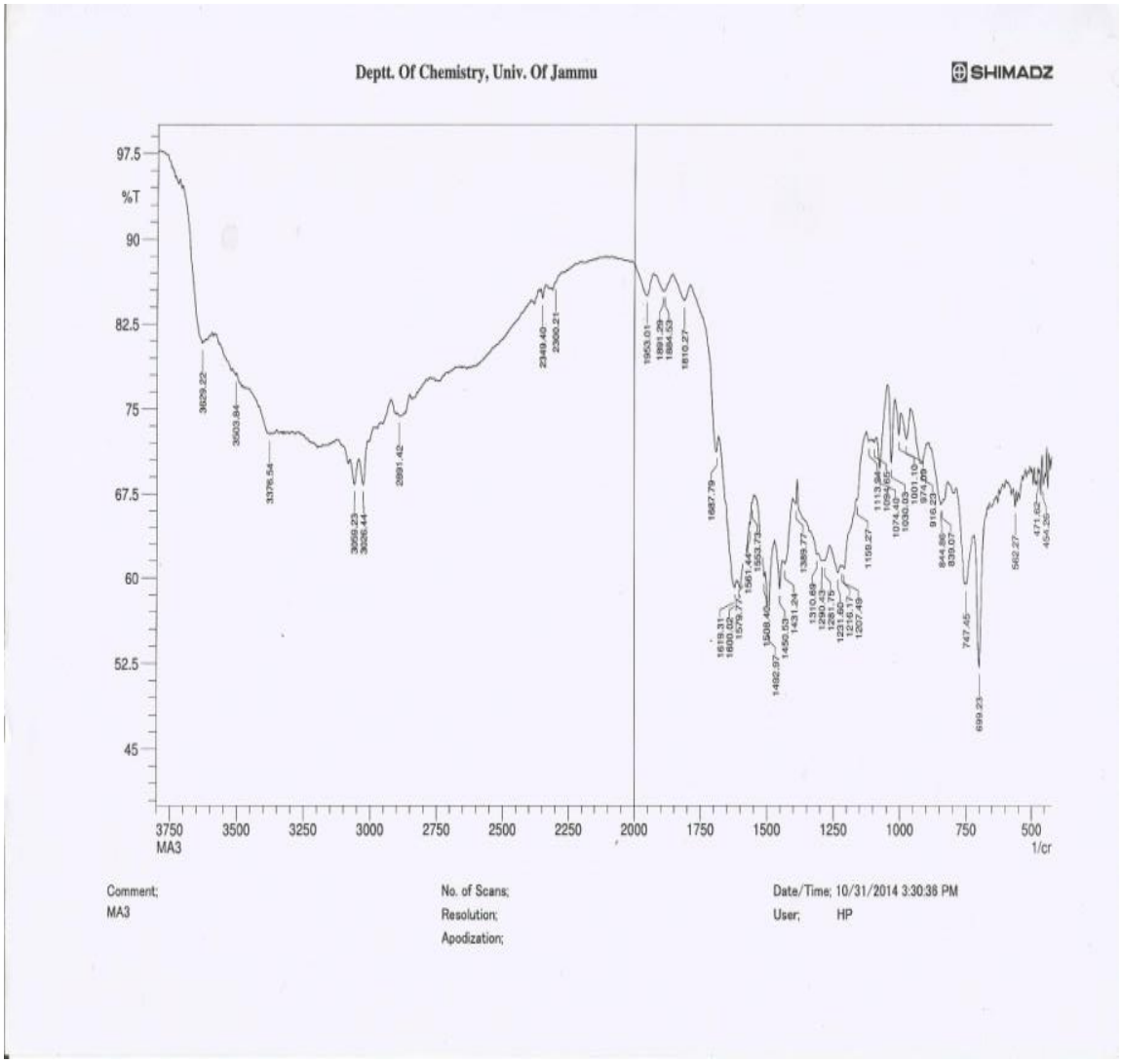

Figure: 2: IR spectrum of metal complex MoSA3

^{1}HNMR spectra

The ^{1}HNMR spectra of ligands and their respective complexes in DMSO solution were also compared. The free NH_2 protons usually show a broad singlet peak in a region of 4-6 ppm[19]. This signal is absent in the observed spectra of Schiff bases which indicates the formation of Schiff bases. The peaks for aromatic proton exhibits signals in the region 6.06 - 7.42 ppm. The ^{1}HNMR spectra of all the complexes exhibits signals at 10.26 and 10.35 ppm due to CH=N- group.(Figure.3).

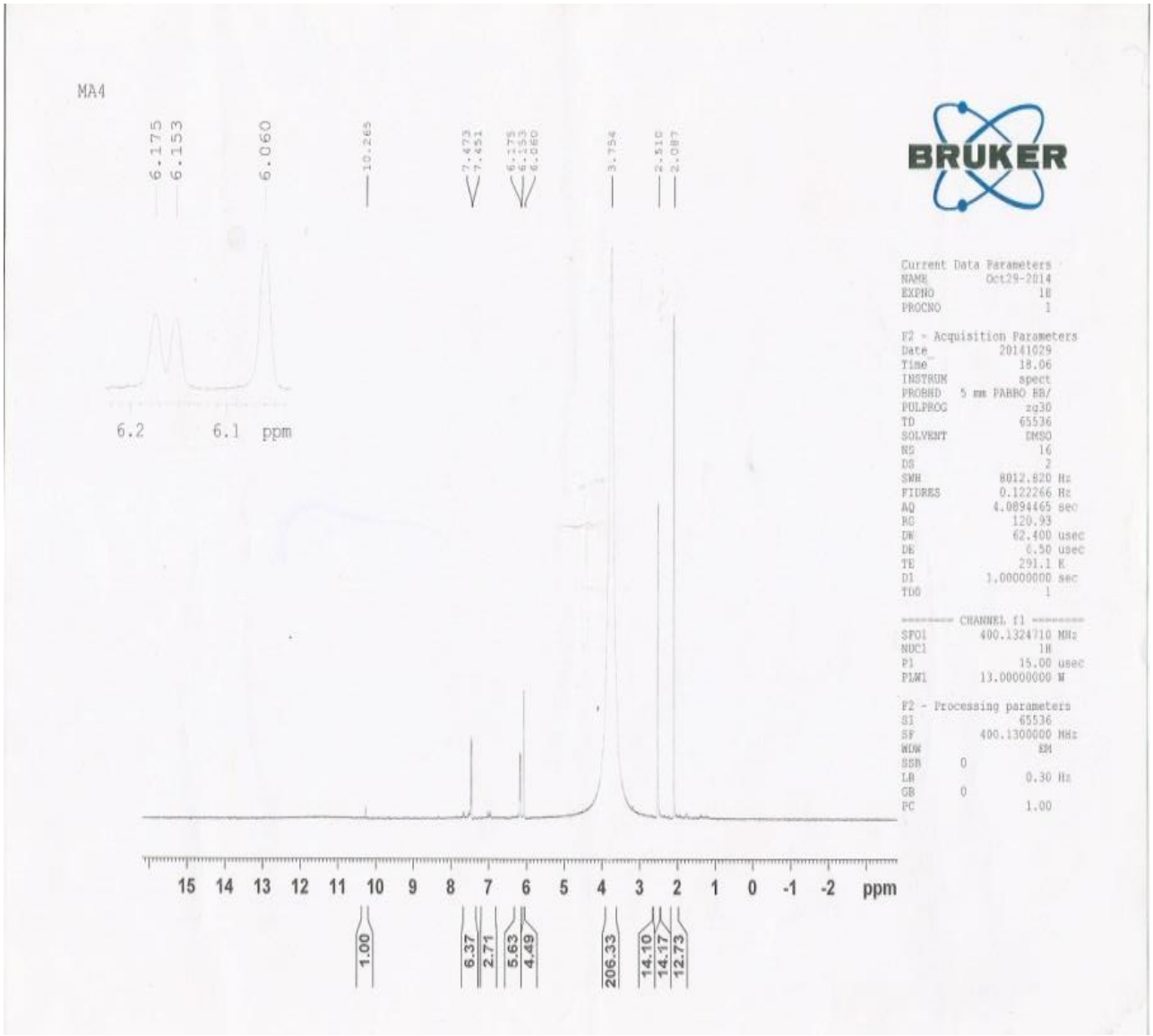

Figure: 3: ^{1}HNMR spectrum of metal complex MoSA3

Antibacterial activity

The bacterial culture for the bacteria namely, *Micrococcus luteus, Enterococcus faecalis, Alcaligenes dinitroficans & Klebsiella pneumonia* was grown on nutrient agar medium. In each plate the central well was filled in with standard antibiotic Chloramphenicol and two wells on the edges are of Schiff base metal complexes. From the result obtained, it has been found that the tested complexes show activity against *E. faecalis, A. dinitroficans & Klebsiella pneumonia* and show a little activity against *A. Luteus*, figures. 4 (a&b).

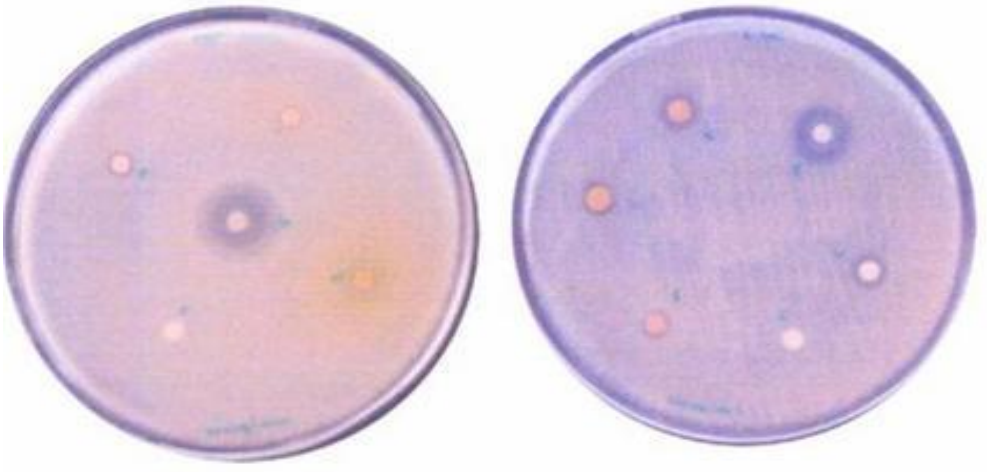

Figure 4 (a&b): Antimicrobial activity of metal Complexes

CONCLUSION

The complexes were studied and was found that all the complexes were monomeric with general formula MoO(SCN)4L-L(Where L-L = Bidentate biologically active Schiff bases) having +6 oxidation state of molybnenum. They show more potent antimicrobial behavior towards most of tested bacteria.

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