



Synthesis, Characterization and Antimicrobial Study of Metal Complexes with N, N-Dimethylformamide

Sanjay R. Kale*, Sonali P. Nale, Pravin Kale, Suraj Dhende, Prerna Dhaygude

Department of chemistry, Tuljaram Chaturchand College, Baramati, Dist. Pune, (M.S.)

ABSTRACT:

In present study, the two metal N, N-Dimethylformamide complexes $[M (DMF)_9]^{2+}$ where, M = Mn and Cu, were synthesized by treatment of metal sulphate and N, N-Dimethylformamide as a ligand. The metal Complexes were characterized by using various characterization techniques including IR and XRD. The magnetic moment data confirmed that all metal complexes were magnetically dilute and octahedral. The antimicrobial study on these metal complexes against Escherichia Coli, Pseudomonas aeruginosa showed that all the metal complexes had broad spectrum antimicrobial activity against selected microbes.

KEYWORDS:

N, N-Dimethylformamide, X ray diffraction, $[M (DMF)_9]^{2+}$, Magnetic moment

INTRODUCTION:

Dimethylformamide is an organic compound with formula, $(CH_3)_2NC(O)H$, miscible with water and majority of organic liquids. The various organic & organometallic transformations are carried out with N, N dimethylformamide where it is used as a source of carbon monoxide ligands. The DMF is a polar (hydrophilic) aprotic solvent with high boiling point, commonly used in the solvothermal synthesis of Metal-Organic framework. It facilitates reactions that follow polar mechanisms. [1]. One review shows that DMF act as either a nucleophilic or electrophilic reagent or leads to natural, ionic or radical species [2]. It was disclosed that DMF also act as stabilizer in reaction. In this regard, synthesis of stabilized metal-DMF nanoparticles were reported. The Copper(Cu), Iridium (Ir), Gold (Au), Palladium (Pd), Silver (Ag) and Iron oxide (Fe_2O_3) nanoparticles are stabilized with DMF molecules through interaction of amide group of DMF with N-Cs. [3]. DMF used as reducing agent in metal nanoparticle synthesis [4]. The study in 2020 shows transformation of lanthanide metal iodide with DMF is possible [5]. Interest of DMF is not only their dissolution power but also coordination to metal center, the oxygen atom act as donor may favor the efficiency of transition-metal-mediated reactions [6]. The combination of DMF with Thiourea has the remarkable ability to form intermediate stability acid base complexes with a wide number of metal chlorides, Lewis acid to form high-concentration stable molecular inks [7].

In present study the various metal complexes with N, N Dimethylformamide has been synthesized by chemical method. Metal form coordinate bond with DMF through metal oxygen linkage with coordination number 6. Each N, N Dimethylformamide (DNF) ligand coordinates via its O atom in the SP^2 lone pair direction. Although the vicinity of metal is crowded with six planer ligands, no serious steric hindrance is found in the coordination structure. It is confirmed by structural and spectroscopic analysis by XRD and FTIR study. The magnetic dipole moment is determined by Gouy method. Lastly, the antimicrobial behavior of thus synthesized metal complexes was tested against selected microbes by agar disc diffusion technique.

MATERIALS AND METHOD:

Materials and reagents:

In the present work, N, N-Dimethylformamide, Manganese (II) Sulphate monohydrate and Copper (II) Sulphate pentahydrate, were purchased from Loba Chemie. These chemicals were used as received without any further purification.

Preparation of $[Mg(DMF)_6]^{2+}$:

An aqueous solution of Manganese (II) sulphate monohydrate is prepared by dissolving specific amount in minimum amount of water. Then this solution is concentrated to expel water by slow heating for 15 min. After cooling the solution, the dropwise addition of 5 mL, N, N-Dimethylformamide is carried out with constant stirring for 30 min. After complete addition stir the solution for more 10 min. and then add 3 mL alcohol dropwise. The resulting homogeneous solution was heated for 20 min. at $80^\circ C$ during which crystal separates out. It was then cooled and dried. This dry product is $[Mn (DMF)_6]^{2+}$ complex. The same procedure was used for the preparation of $[Cu (DMF)_6]^{2+}$, complex from its sulphate salt.

CHARACTERIZATION:

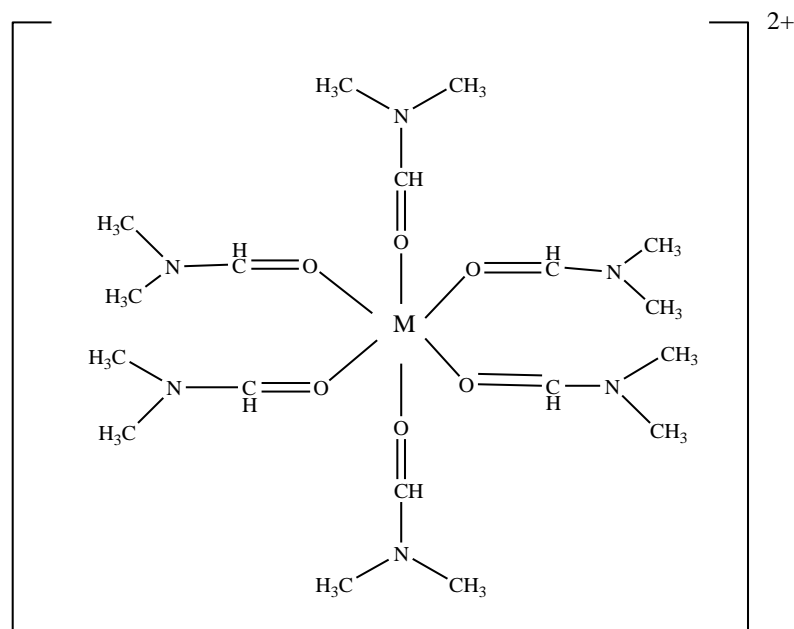
The IR spectra were recorded from FTIR-(Shimadzu, IR affinity-1S WL, Japan) with scan range 200 nm-800 nm. The room temperature magnetic susceptibility at 299 K was measured on Gouy's magnetic susceptibility balance and diamagnetic corrections were calculated using Pascal's constant. The X-ray diffraction spectrum were recorded with scanning angle from 20° to 80° .

ANTIMICROBIAL STUDY:

The antimicrobial activity of synthesized metal complexes was studied by using agar diffusion technique on Escherichia Coli and Pseudomonas bacteria.

RESULT & DISCUSSION:

The reaction of N, N-Dimethylformamide with metal (II) sulphate of Manganese, and Copper gave white/blue colored complexes with low to moderate yields (35 to 45 %) having structure represented in figure 1. The DMF has boiling point $153^\circ C$ whereas the metal complexes decomposed in the range of $170^\circ C$ to $200^\circ C$. The crystalline nature, chemical constitution, structural and magnetic characteristics of metal complex determined by x-ray diffraction technique, Infrared spectroscopy and Gouy's magnetic susceptibility method.



(Where M = Mn, or Cu)

Fig. 1: Octahedral Structure of $[M(DMF)_6]^{2+}$

Table 1 represents the analytical data of synthesized $[M(DMF)_6]^{2+}$

Table 1: Analytical data of synthesized metal complexes

Metal Complex (Empirical formula)	Molecular weight	Color	Melting Point (°C)	% Yield
$[Mn(DMF)_6]^{2+}$	493.47	White	196°C	45
$[Cu(DMF)_6]^{2+}$	502.08	Blue	180°C	35

XRD analysis for crystal structure of synthesized metal complexes:

The XRD pattern of synthesized $[Mn(DMF)_6]^{2+}$ is represent in figure 2,

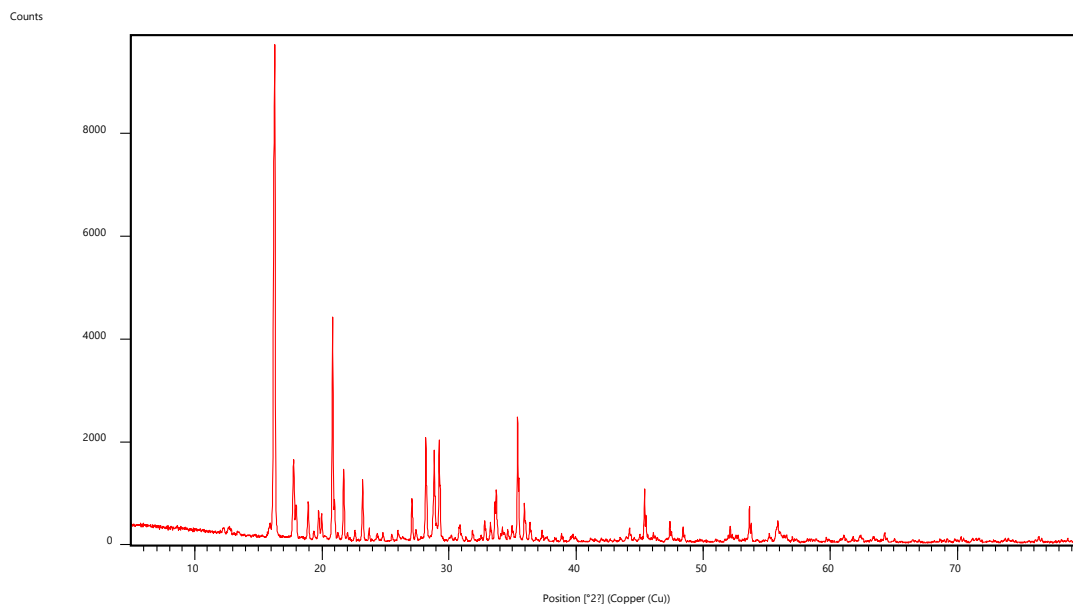
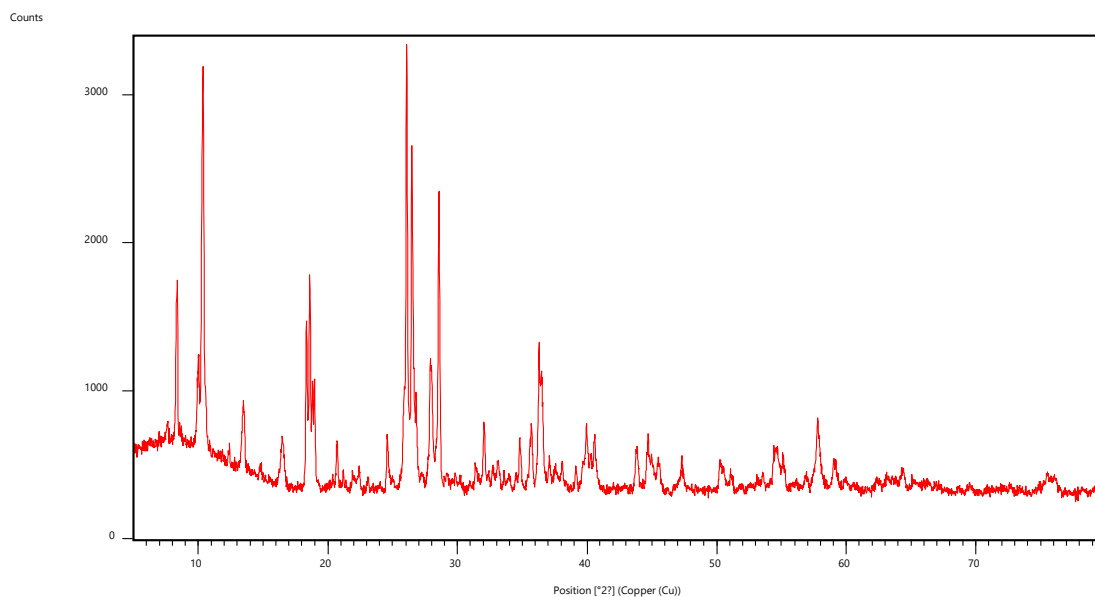


Fig. 2: XRD pattern of [Mn (DMF)₉]²⁺

The XRD patterns show that the intensities of the peaks assigned to planes, [100], [100], [110], [111], [200], [210], [221], [222] are more than that of other peaks.

The XRD pattern of synthesized [Cu (DMF)₉]²⁺ is represent in figure 3,

**Fig. 3: XRD pattern of [Cu (DMF)₉]²⁺**

The XRD patterns shows that intensities of the peaks assigned to planes, [100], [111], [220], [221], [330], [421], and [530] are more than that of other peaks.

The observed intense peaks refer the excellent growth of crystal size and assembly of large clusters. The crystalline size was calculated from the full width at half maximum (FWHM) of strongest diffraction peak by using the Debye-Scherer formula.

$$D = \frac{K \lambda}{\beta \cos \theta}$$

Table 2 and Table 3 represents XRD parameters and mean crystalline size of [Mn (DMF)₆]²⁺ and [Cu (DMF)₉]²⁺

Table 2: XRD parameters and mean crystalline size of [Mn (DMF)₆]²⁺

Plane (hkl)	(2θ)	Rel. Int. (%)	FWHM	D(nm)
[100]	16.2241	77.62	0.0848	17.28nm
[100]	16.3081	100	0.0735	19.94nm
[110]	20.8554	55.31	0.0784	18.51nm
[111]	28.8533	21.48	0.0854	17.54nm
[200]	29.2482	27.81	0.0722	20.77nm
[210]	35.4201	36.24	0.0706	21.58nm
[221]	45.4084	15.70	0.0662	25.29nm
[222]	53.6569	10.36	0.0726	22.40nm

The crystalline size for [Mn (DMF)₉]²⁺ calculated from XRD data is **19.94nm**.

Table 3: XRD parameters and mean crystalline size of [Cu (DMF)₉]²⁺

Plane (hkl)	(2θ)	Rel. Int. (%)	FWHM	D(nm)
[100]	8.3310	35.10	0.1501	9.67nm
[111]	10.3344	76.47	0.1699	8.55nm
[220]	18.3327	33.42	0.1447	10.13nm
[221]	18.5786	43.87	0.1422	10.31nm
[330]	26.0554	100	0.1077	13.79nm
[421]	28.5450	67.46	0.1176	12.70 nm
[530]	36.2732	33.11	0.1315	11.58nm

The crystalline size for [Cu (DMF)₉]²⁺ calculated from XRD data is **13.79nm**.

FTIR spectral analysis for synthesized metal complexes:

Figure 4 and figure 5 represents the IR spectrum of synthesized Metal-DMF complexes.

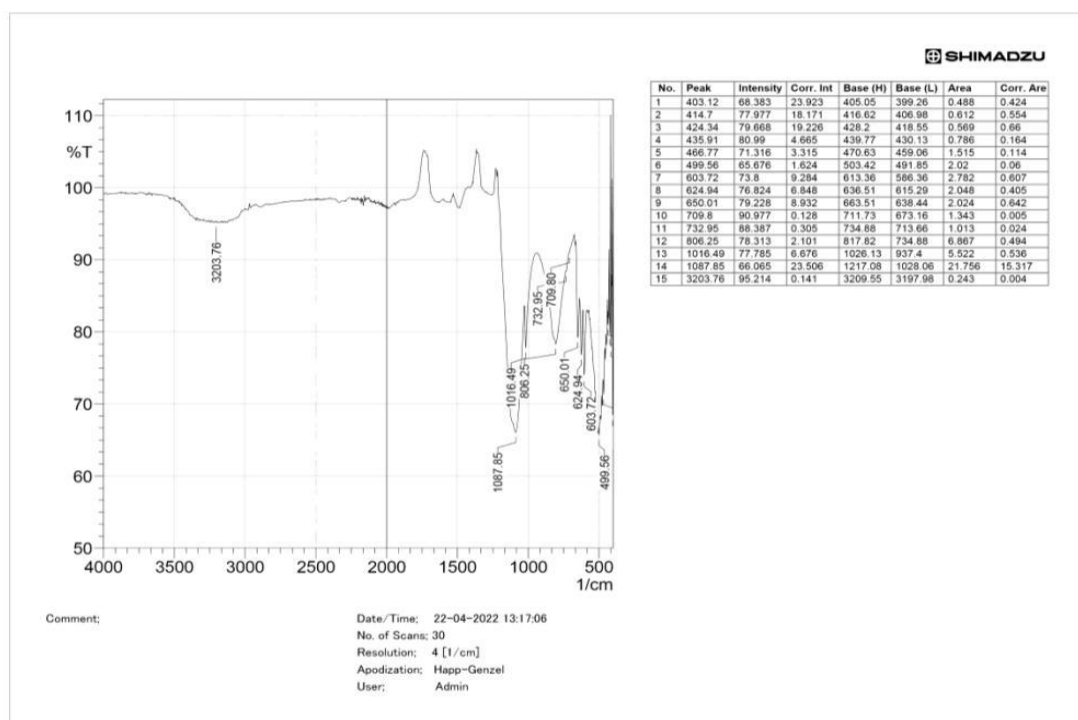
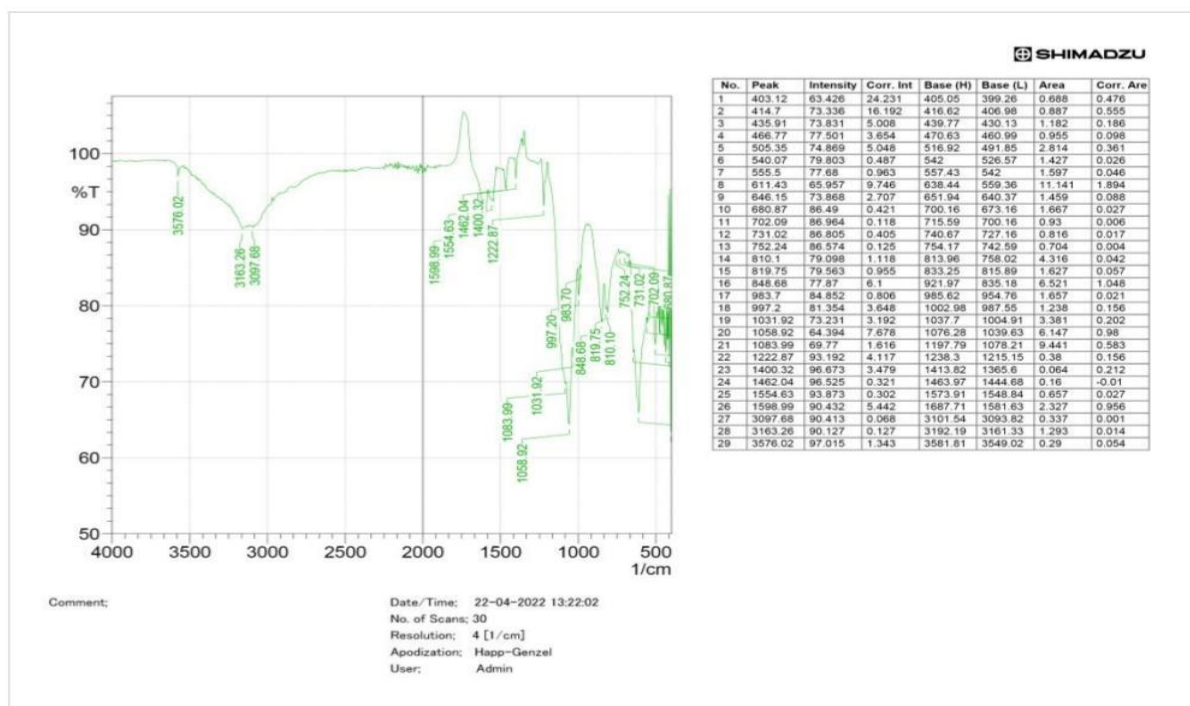


Fig. 4: IR spectrum of $[\text{Mn}(\text{DMF})_6]^{2+}$ Fig. 5: IR spectrum of $[\text{Cu}(\text{DMF})_6]^{2+}$

The FTIR spectrum of the $[\text{M}(\text{DMF})_6]^{2+}$ where $\text{M} = \text{Mn}, \text{Cu}$, indicates the presence of different functional groups. The peaks in between 400 cm^{-1} to 600 cm^{-1} indicate presence of metal oxygen bond. These bonds were absent in IR spectrum of DMF. In IR spectrum of DMF the band at 1850 cm^{-1} indicates the presence of $(\text{C}=\text{O})$ but it disappears in synthesized metal complexes, $[\text{M}(\text{DMF})_6]^{2+}$ which clearly indicating the formation of metal DMF bonding.

Magnetic moment for synthesized metal complexes:

The effective magnetic moment of Mn (II) complexes is expected to be in the range of 5.50 -5.90 B.M. while low spin octahedral Mn (II) complexes have moment in the range of 1.73 -2.20 B.M. [8] Consequently, the calculated magnetic moment for $[\text{Mn}(\text{DMF})_6]^{2+}$ is 2.08 B.M which indicate that complex exhibited low spin Octahedral geometry

The effective magnetic moment of 1.9 - 2.2 B.M. is usually observed for mononuclear copper (II) complexes, regardless of stereochemistry, expectedly higher than the spin only moment due to orbital contribution and spin-orbit coupling. The calculated magnetic moment for the $[\text{Cu}(\text{DMF})_6]^{2+}$ complex in this study is 2.20 B.M.

The number of unpaired electrons in synthesized complexes, $[\text{Mn}(\text{DMF})_6]^{2+}$, $[\text{Cu}(\text{DMF})_6]^{2+}$, are 3, and 4, respectively. It revealed that all metals are present in +2 oxidation state.

Antimicrobial activity of synthesized metal complexes:

The antimicrobial activity of $[\text{M}(\text{DMF})_6]^{2+}$ complexes were performed by agar disc diffusion method on Escherichia Coli and Pseudomonas aeruginosa Bacteria. [9] The surface of agar in a petri dish was uniformly inoculated with 0.2 ml of 18hr old test microbial culture. Using a sterile cork borer, 5mm wells were bored into agar, then 0.06 mL

of 10 mg/mL concentration of each metal complex in water was introduced into wells and plates were allowed to stand on the bench for 30 minutes before incubation at 37°C for 24 hours. After which inhibitory zones (in mm) were taken as measure of antimicrobial activity. [Table 4] All the metal complexes showed inhibitory zone hence all are having antibacterial properties. [10]

Table 4: Metal complexes and Inhibition zone diameter against *P. aeruginosa* and *E. Coli*.

Microorganisms	Metal complexes with Inhibition zone diameter (mm)	
	[Mn (DMF) ₆] ²⁺	[Cu(DMF) ₆] ²⁺
<i>P. aeruginosa</i>	32	12
<i>E. Coli</i>	16	25

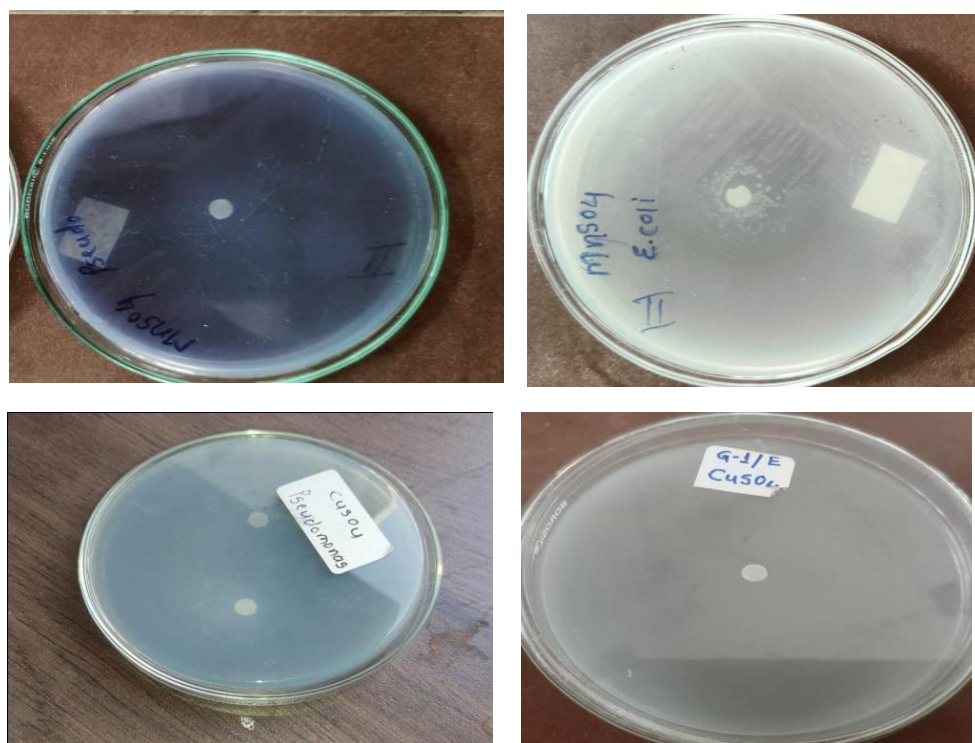


Fig. 6: Inhibition of *P. aeruginosa* and *E. Coli* due to [M (DMF)₆]²⁺

CONCLUSION:

The N, N Dimethylformamide formed low spin octahedral complexes with Manganese, and Copper. These complexes were crystalline, magnetically dilute and having octahedral structure containing Metal-Oxygen coordinate framework, has been proved by XRD analysis, room temperature magnetic moment and IR analysis. XRD analysis showed the metal complexes having crystalline size 19.94 nm and 13.79 nm for [Mn (DMF)₆]²⁺ and [Cu(DMF)₆]²⁺ respectively. FTIR spectrum confirmed the metal oxygen bonds due to presence of an intense peaks in the range of 400-600 cm⁻¹. All metal complexes show broad spectrum antimicrobial activities against *E. coli* and *P. aeruginosa* microbes. The present study confirms that this method is suitable and effective for large scale synthesis of metal DMF complexes and their applications in biomedical field.

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CONFLICT OFINTEREST:

The authors have no conflicts of interest regarding this investigation.

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