

Synthesis and Characterization of Transition Metal complexes with pyrimidine based ligand derivative

Ruchita Awate¹, Ashutosh Mishra², A Mansuri²

¹Bangalore Technological Institute, Bangalore, 560 035

²School of Physics, Devi Ahilya University, Khandwa road, Indore 452 001

E-mail: ruchita.awate@gmail.com

Abstract. The article deals with a study of Synthesis Transition Metal Complexes Like copper and iron with Pyrimidine based ligand derivatives. The synthesized complex were characterized by XRD, SEM, FTIR. Mossbauer Spectra of Iron complex has also taken out to find oxidation state of iron after complexation. The aim of this study is to preparation and characterization with Transition Metal complexes by different physical and chemical characterization techniques.

1. Introduction

Pyrimidines are probably the most widely distributed heterocyclic compounds in nature. They show the immense commercial applications in medicine as antioxidant, antibacterial, antifungal, antiviral and hepatoprotective agents. The heterocyclic complexes are significant due to their use as models in naturally occurring systems; they also have greater biological importance. The coordination properties of pyrimidine are important in understanding the role of metal ions in biological system and its physicochemical importance creates great interest in complexation.[1] In view of the broad-spectrum importance associated with these metal complexes, it was considered worthwhile to prepare interesting complexes derived from hitherto unsubstantiated pyrimidine as the complexing agent. These complexes were characterized by XRD, SEM, FTIR, and Mossbauer Spectroscopy measurements corroborated towards the structure of both the synthesized compounds.

2 Experimental Techniques

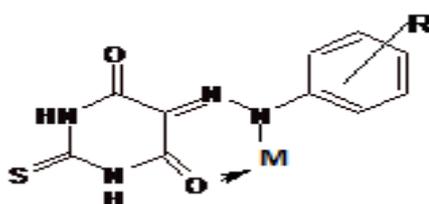
2.1 Materials and methods

Elemental analyses (C, H, N, S) were performed by using a Carlo Erba 1160 elemental analyzer. Melting points were recorded in open capillaries and are uncorrected. Grain size of the powdered sample was measured by X-ray diffractometer (Philips X-pert pro diffractometer, PW 1830) at room temperature with CuK α radiation. Surface morphological study was observed by scanning electron microscopy (SEM, Philips XL 30). IR spectra were recorded using a Perkin-Elmer instrument (using KBr disks, 4000-400cm⁻¹). Mossbauer Measurement were carried out using a standard PC-based spectrometer equipped with a Weissel velocity drive operating in the constant acceleration mode. The data was fitted with the NORMOS-SITE program, and the obtained parameters are with respect to natural iron.



2.2 Synthesis of the complexes

Both the complexes were prepared in a similar way by the usual diazotization process. [2] 6-Methyl-5-arylhydrazone-2thio-4-oxo-pyrimidine (ligand) were prepared by dissolving (0.01 mol) of Aniline in a mixture of concentrated hydrochloric acid (3ml) and water (4ml) and cooled to 0-5°C in ice bath. To it a cold aqueous solution of sodium nitrite (0.01mol) was then added. The Diazonium salt so obtained was filtered into a cold mixture of sodium acetate (7gms) and ethylacetoacitate (0.01mol) in ethanol (25ml) the resulting solid is 1-ethoxy-2-arylhydrezo-2-butene-1, 3dione was washed with water and dry it. Now 1-ethoxy-2-arylhydrezo-2-butene-1, 3dione of (0.01mol) and thiourea (0.01mol) dissolved in (10ml) Sodium ethoxide mixture (freshly prepared) in a 1 liter round bottomed flask. Then fit a reflux condensers to the flask, introduced a few fragments of broken porcelain pieces for boiling the mixture for 30mins, few crystals are appear after 15 minutes and gradually increase in amount as the refluxing is continued. Cool the flask in ice and filter the solution and dry it.



Synthetic path way for and Metal Complex here R is O Nitro

Formation of the metal complexes can be represented by the general equations. $MX_2 + 2L \rightarrow [M(L)_2X] + X$. In this equation, M is Cu (II) and Fe (II), X is Cl and L is [6-Methyl-5-arylhydrazone-2-thio-4-oxo-Pyrimidine]. Both the complexes are stable at room temperature

3. Result and Discussion

3.1 XRD

The sample was characterized at room temperature by X-ray diffraction using Cu K α radiation. The X-ray diffraction patterns of the complexes are indicative of crystalline nature. The diffraction pattern of complexes recorded between 2 θ ranging from 10° to 75°. The crystalline size of the samples is estimated using the Scherrer's formula $D = k\lambda / \beta_{2\theta} \cos\theta$, here k is a constant taken to be 0.94, λ the wavelength of X-ray used ($\lambda = 0.154$ nm) and $\beta_{2\theta}$ full width at half maxima of all peaks of the XRD patterns θ is Bragg angle. The diffraction patterns have been successfully indexed.[3] The crystalline size was found for copper and iron complex 48.22 nm and 33.89 nm respectively. It is observed that crystalline size is different for both the complexes, due to change in the R position. The XRD patterns are shown in Figure 1.

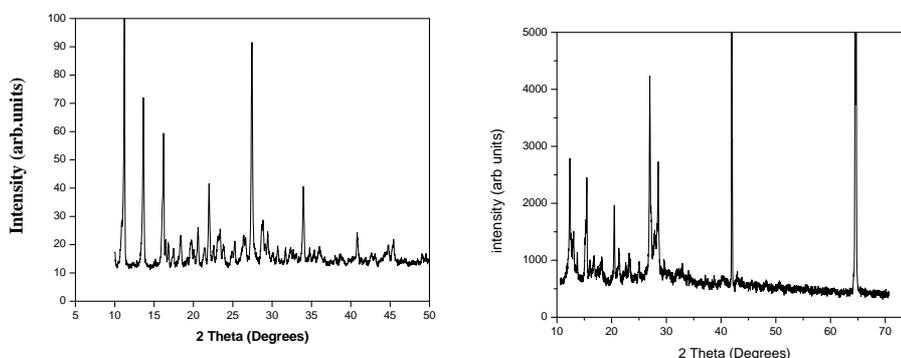


Figure 1. X-ray diffraction patterns of copper and Iron Metal complex

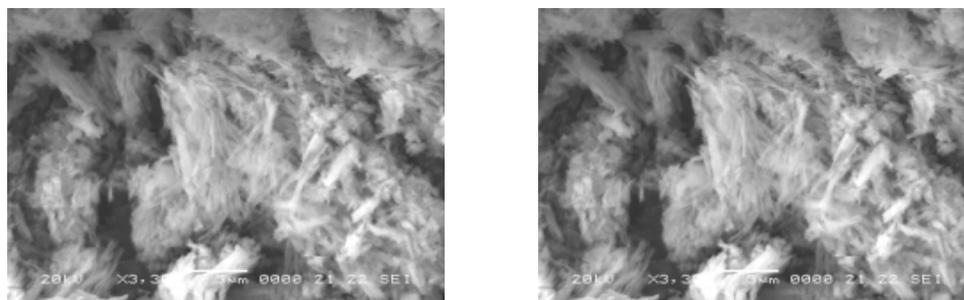


Figure 2. SEM images for copper and Iron complexes

3.2 SEM

The SEM images of the samples are shown in the figure 2. From the figure it can be seen that the average length of the crystals for the copper and Iron Metal Complex are 5 and 5.8 μm respectively. Also, it can be seen that there are some void spaces. The surface morphology changes with change in substituted anilines, both the images having large number of irregular shaped and some having regular crystals associated with the images shown in figure.2 It is quite clear from the results that the average grain size estimated by SEM is quite larger than the average grain size measured by XRD.

3.3 IR SPECTRA

The IR spectra for both complexes were performed at field between 4000–400 cm^{-1} , along with tentative assignments. The presence of a single medium band in the region 3,250–3,350 cm^{-1} in the spectra may be assigned due to N–H stretch. [4,5] The bands at 1580-1590 cm^{-1} due to the azomethine group of the ligand underwent a shift to lower frequency (1581-1495) cm^{-1} after complexation, indicating the coordination of hydrazono nitrogen to metal atom and this can be explained by the donation of electrons from nitrogen to the empty d-orbital of the metal atom.[6,7] In addition, the $\nu(\text{C}=\text{N})$ mode may be coupled with $\nu(\text{C}=\text{S})$ to give the intense band observed at 1270-1190 cm^{-1} . [8] The band corresponding to $(\text{C}=\text{O})$ at 1680-1690 cm^{-1} is shifted to lower frequency in the spectra for both the metal complexes. This is clear evidence for coordination by carbonyl oxygen. The vibrations absorption peaks of the $\nu(\text{M}-\text{N})$, $\nu(\text{M}-\text{Cl})$ and $\nu(\text{M}-\text{O})$, which should be at 559-300 cm^{-1} , as reported by other workers [9,10] could not be observed since it was beyond the extent of our measurement.

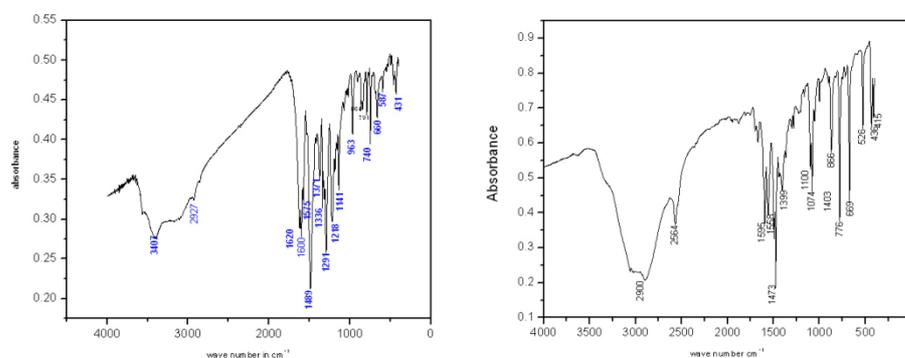


Figure 3. IR Spectra of Copper and Iron Metal Complexes

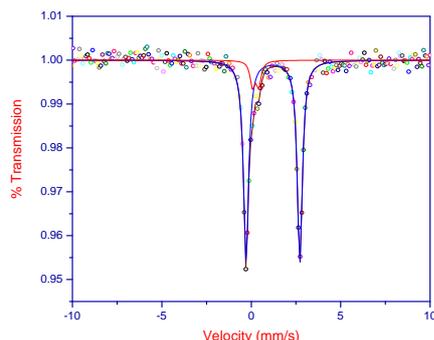


Figure 4. Mossbauer Spectra of Iron Metal Complex

3.4 MOSSBAUER SPECTRUM

The Mossbauer spectrum for iron complex is shown in figure 4. This spectrum was least-square fit with a superposition of two doublets and one singlet, all with Lorentzian line shape. According to the collected data the percentage of Fe (II) 88.9%. The isomer shift of 1.217 ± 0.005 mm/s (35.6%), 1.213 ± 0.006 (53.3%) corresponds to the expected value for octahedral Fe (II) complex, as previously described complex.[11] which exhibits distorted octahedral symmetry with an isomer shift of 1.212mm/s and quadrupole splitting of 3.01mm/s. From the obtained isomer shift values one can conclude that Fe exists in Fe²⁺ states with a relative fraction of 89.7 respectively.

Acknowledgment

The authors are sincerely thankful to UGC DAE Consortium for Scientific Research centre Indore.

References

- [1] Mishra. A, Awate Ruchita, 2009 *Taylor & Francis* **184** 2624.
- [2] Ramakrishnan S and Palaniandavar M, 2005 *J. Chem. Sci.* **117** 179.
- [3] B. D. Cullity Elements of X-ray Diffraction, Second Edition, Addison-Wesley Publishing Company, 1978.
- [4] Khan T A, Rather M A, Jahan N, Varkey S P and Shakir M, 1998 *Transition Met. Chem.* **23** 283.
- [5] Singh A K, Panwar A, Singh R and Beniwal S, 2003 *Transition Met. Chem* **28** 160.
- [6] Chandra S and Sharma S D 2002 *Transition Met. Chem.* **27** 732.
- [7] Lodeiro C, Basitida R, Bertolo E, Macias A and Rodriguez R 2003 *Transition Met. Chem.* **28** 388.
- [8] Offiong O E 1995 *Transition Met. Chem.*, **20** 126.
- [9] Satish M, Annigeri M P, Sathisha M P, and Revankar V K, 2007 *Transition Met. Chem.* **31** 81.
- [10] Chandra S and Kumar R, 2004 *Transition Met. Chem.* **29** 269.
- [11] Mishra A, Mishra N, Malviya P, Awate R, 2014 *international journal of Scientific Research in Physics and Applied Science* **02** 2348.