

Synthesis and Characterization of Mixed Ligand Complexes of Transition

Archana Kumari* and Kiran Kumari Jha

*Research Scholar in Chemistry, L. N. Mithila University, Darbhanga-846004, India

Department of Chemistry, J. M. D. P. L. Mahila College Madhubani-847211, India

*Corresponding author's e-mail: archanakumari201984@gmail.com

Received: 22.06.2017

Accepted: 30.06.2017

ABSTRACT

Six mixed ligand complexers have been reported. In this paper, synthesis and characterization of mixed ligand complexes derived from 4-(Benzeneazo) salicylaldehyde and 2-amino-4-nitrophenol using transition metal ions such as Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) have been reported. The synthesized complexes have been characterized with the help of molar conductance, magnetic susceptibility measurements, and spectral techniques such as IR, ¹H-NMR and electronic spectra. The synthesized complexes are also screened for their antibacterial activities. The studies made on these complexes proposed a six coordinated octahedral geometry for all these complexes.

Keywords: Salicylaldehyde, Mixed ligand, 2-Amino-4-nitrophenol, Transition metal ions.

INTRODUCTION

Mixed ligand complexes differ from traditional complexes in the sense that they are having at least two different kinds of ligands associated with the same metal ion in a complex. The presence of more than one type of ligand in a complex increases chances of variation in properties expected for the complex. This makes the researcher interested in the synthesis of mixed ligand complexes with varying properties. Synthesis and characterization of mixed ligand complexes is gaining importance day by day. The increased interest in this research area has motivated many researchers to get involved in this field. In recent years many publications are devoted to synthesis and characterization of mixed ligand complexes.¹⁻⁶

Present work is continuation of our previous research work on synthesis and characterization of mixed ligand complexes^{7, 8}. In this paper, we report synthesis and characterization of a series of six mixed ligand complexes derived from 4-(Benzeneazo) salicylaldehyde and 2-amino-4-nitrophenol using transition metal ions such as Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II). These complexes are then characterized using molar conductance, magnetic measurements and spectral techniques such as IR, ¹H-NMR and electronic spectra.

MATERIALS AND METHODS

All the chemicals used in present study were of AR grade. 2-amino-4-nitrophenol and metal salts were procured from S. D. Fine Chemicals Limited and Spectrochem Private Limited, respectively. All the solvents used were distilled and dried using molecular sieves before use. The molar conductance of complexes was measured by preparing 10⁻³ M solutions in DMF solvent using Equiptronics conductivity meter with inbuilt magnetic stirrer Model (Eq-664) at room temperature. Magnetic susceptibilities were determined on the SES instrument's magnetic susceptibility Guoy's balance (Model EMU-50) at room temperature using copper (II) sulphate as a standard. These magnetic susceptibility values were utilized to

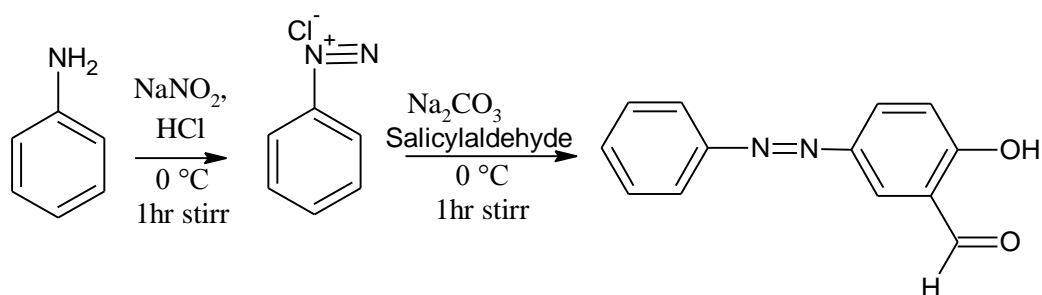
calculate magnetic moments using spin only formula $\mu_{\text{eff}} = (n(n+2))^{1/2}$ for all the synthesized complexes. IR spectra were recorded as KBr pellets in the region of 4000-400 cm^{-1} on a Perkin-Elmer Spectrophotometer. Electronic spectra were recorded in DMSO on a Shimadzu UV-1600 spectrophotometer. $^1\text{H-NMR}$ spectra were recorded on Bruker Avance II 400 NMR spectrometer using DMSO d_6 (spectroscopic grade) as a solvent⁹.

Synthesis of mixed ligand complexes:

The synthesis of mixed ligand complexes was carried out in two steps. In the first step the ligand 4-(Benzeneazo)salicylaldehyde was prepared and it was then utilized in the second step to prepare the complexes using 2-amino-4-nitrophenol.

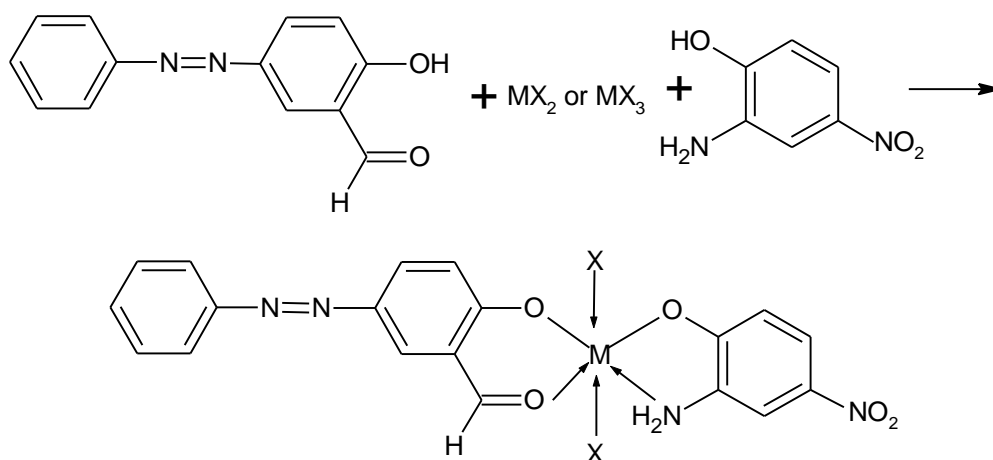
(a) Preparation of 4-(Benzeneazo) salicylaldehyde:

4-(Benzeneazo) salicylaldehyde was prepared as per the procedure reported earlier by Liu *et al.*¹⁰



(b) General procedure for the synthesis of mixed ligand complexes:

Synthesis of mixed ligand complexes was carried out using template method. A hot methanolic solution (10 mL) of respective transition metal salt (1 mmol) was mixed with a hot solution (1 mmol) of 2-amino-4-nitro phenol and 4-(benzeneazo) salicylaldehyde (1 mmol). Few drops of Conc. HCl were added to the mixture. The resulting mixture was then left under reflux for 4 hours. After refluxing for 4 hrs appropriate complexes were precipitated out on cooling the reaction mixture. Those were then filtered, washed with methanol and recrystallized from ethanol. The purity of the complexes was checked by taking TLC [solvent system (9:1) $\text{CHCl}_3 + \text{MeOH}$]. The synthesized complexes were obtained in 60-70% yield. The general scheme for the synthesis of mixed ligand complexes is given as below.



Where $\text{M} = \text{Mn (II)}, \text{Fe (III)}, \text{Co(II)}, \text{Ni (II)}, \text{Cu (II)}$ and Zn (II)
 $\text{X} = \text{Cl}^-$

RESULTS AND DISCUSSION

The general composition of the synthesized mixed ligand complexes can be represented as $[M(C_{19}H_{13}N_4O_5)X_2]$ (where $M = Mn(II), Co(II), Ni(II), Cu(II)$ and $Zn(II)$) and $[M(C_{19}H_{13}N_4O_5)X_2]X$ [where $M = Fe(III)$]. All the synthesized complexes were thermally stable and colored. Observations such as colour, melting point, % yield, solubility behavior for all the complexes were recorded.

Solubility behaviour

Solubility behaviour of all the synthesized complexes was checked using different solvents such as water, methanol, ethanol, chloroform, acetone, acetonitrile, DMSO and DMF. All the synthesized complexes were found to be insoluble in water and partially soluble in methanol, ethanol, acetone and ethyl acetate. All the complexes were found to be soluble in DMF and DMSO. In acetonitrile three of the complexes of $Mn(II)$, $Fe(III)$ and $Cu(II)$ were soluble and the remaining were found to be partially soluble.

Molar conductance

Molar conductance for all the complexes was measured by preparing their 10^{-3} M solutions in DMF as a solvent. Low values ($13-27 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ mol}^{-1}$) for complexes with divalent metal ions such as $Mn(II)$, $Co(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$ and high value i.e. $82 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ mol}^{-1}$ for $Fe(III)$ complex was recorded. The low values recorded for divalent metal ion complexes indicate towards nonelectrolytic behavior of these complexes whereas that for $Fe(III)$ complexes indicate towards its 1:1 electrolytic nature^{11,12}.

Magnetic properties

The observed magnetic moment values for $Mn(II)$ and $Fe(III)$ complexes are 5.84 and 5.38 B. M., respectively indicating towards d^5 configuration and five unpaired electrons present in these complexes. This means these complexes are having an octahedral geometry. Magnetic moment of $Co(II)$ complex is 4.29 B. M. corresponding to three unpaired electrons in an octahedral environment. The observed magnetic moment value for $Ni(II)$ and $Cu(II)$ complexes are 2.81 and 1.85 B.M., respectively corresponding to two and one unpaired electrons in these complexes. $Zn(II)$ complex has been found to be diamagnetic¹³. The magnetic moment values of all the synthesized complexes have been reported.

IR Spectra

IR spectra of all the synthesized complexes have been recorded in the range $4000-400 \text{ cm}^{-1}$. The spectra are interpreted considering few main peaks observed. The presence of peaks in the region around 3400 cm^{-1} indicates towards the presence of $-NH_2$ group in the complexes. The bands observed around $1440-1450 \text{ cm}^{-1}$ and $2854-3100 \text{ cm}^{-1}$ were assigned to $\nu(C=C)$ and $\nu(C-H)$ aromatic stretching, respectively⁶. The peaks observed in the region $1600-1650 \text{ cm}^{-1}$ for all the complexes are due to $>C=O$ group present in complexes. The peaks observed around $1515-1535 \text{ cm}^{-1}$ can be assigned due to $-N=N-$ group present in the complexes. Similar observation was reported by Rao and Shaw¹⁴. In their paper, they have reported a peak at $1535-1560 \text{ cm}^{-1}$ for $-N=N-$ group in complexes. Identification of peaks for $\nu(M-O)$ and $\nu(M-N)$ is difficult as these can be observed at any value between $400-800 \text{ cm}^{-1}$. Many authors have defined peaks at different values for these signals¹⁵⁻¹⁸. In the present case, the peaks of weak intensity observed in the region $500-650 \text{ cm}^{-1}$ can be assigned to $\nu(M-O)$ and $\nu(M-N)$ present in the complexes. The $\nu(M-Cl)$ band is usually reported to be observed below 400 cm^{-1} region^{19,20}. Due to instrument limitation, the said region was not scanned for present investigation. The results obtained from the IR spectra are listed in Table 1.

Table 1

IR spectroscopic data (cm⁻¹) of the synthesized mixed ligand metal complexes

| S. No. | Molecular formula | N-H str | C=O str | M-O str | M-N str |
|--------|---|---------|---------|---------|---------|
| 1 | C ₁₉ H ₁₃ Cl ₂ MnN ₄ O ₅ | 3433 | 1631 | 632 | 505 |
| 2 | C ₁₉ H ₁₃ Cl ₂ FeN ₄ O ₅ | 3421 | 1604 | 648 | 509 |
| 3 | C ₁₉ H ₁₃ Cl ₂ CoN ₄ O ₅ | 3429 | 1604 | 651 | 524 |
| 4 | C ₁₉ H ₁₃ Cl ₂ NiN ₄ O ₅ | 3444 | 1627 | 636 | 509 |
| 5 | C ₁₉ H ₁₃ Cl ₂ CuN ₄ O ₅ | 3433 | 1612 | 648 | 532 |
| 6 | C ₁₉ H ₁₃ Cl ₂ ZnN ₄ O ₅ | 3433 | 1627 | 632 | 509 |

1H-NMR Spectra

1H-NMR spectrum for Ni(II) complex was recorded as a sample study to confirm the skeleton of metal complex. The spectrum shows three peaks out of which a peak observed in the region 2.5-2.6 ppm was due to the residual protons of the solvent DMSO-d-6²¹. The well resolved multiplet at δ 7.20-7.7 ppm corresponding to aromatic protons in mixed ligand complexes and the singlet broad peak observed at δ 4.5 ppm corresponds to NH protons.

Electronic spectra

An electronic spectrum for all the synthesized complexes was recorded in DMSO solvent. Normally two to three bands are reported for azo compounds by different workers²²⁻²⁴. Out of these, the first band expected around 220 nm is assigned to $\pi \rightarrow \pi^*$ of the benzenoid moiety and the second one expected around 425 nm is assigned to $n \rightarrow \pi^*$ electronic transition of -N=N- group. A shift in positions of these bands is observed when these azo compounds are engaged in complex formation with metals through -N=N- group.

In the present case, these two bands are observed in the same region and they are almost undisturbed as the -N=N- group is not taking part in bond formation with the metal ion. Apart from these bands some specific bands are also observed in case of metal complexes which are listed as below in Table 2.

Table 2

Electronic spectral data (in nm) of the synthesized mixed ligand metal complexes

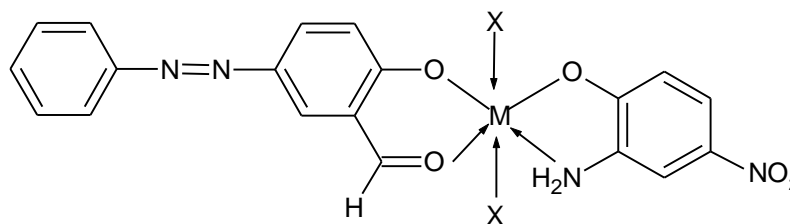
| S. No. | Molecular formula | Wavelength (nm) | Transition |
|--------|---|-------------------|--|
| 1 | C ₁₉ H ₁₃ Cl ₂ MnN ₄ O ₅ | 650 | ⁶ A _{1g} → ⁴ E _g |
| 2 | C ₁₉ H ₁₃ Cl ₂ FeN ₄ O ₅ | 660 | ⁶ A _{1g} → ⁴ T _{2g} |
| 3 | C ₁₉ H ₁₃ Cl ₂ CoN ₄ O ₅ | 560 nm and 680 nm | ⁴ T _{1g} (F) → ⁴ T _{1g} (P) and ⁴ T _{1g} (F) → ⁴ A _{2g} (F) |
| 4 | C ₁₉ H ₁₃ Cl ₂ NiN ₄ O ₅ | 580 nm | ³ A _{2g} (F) → ³ T _{1g} (F) |
| 5 | C ₁₉ H ₁₃ Cl ₂ CuN ₄ O ₅ | 580 nm | ² E _g → ² T _{2g} |

CONCLUSION

In present paper, we have reported a series of six mixed ligand complexes synthesized by reacting 4-(Benzeneazo)salicylaldehyde and 2-Amino-4-nitrophenol with respective metal chlorides in methanolic medium. These synthesized complexes have been characterized with the help of molar conductance, magnetic susceptibility measurements and spectral techniques such as IR, 1H-NMR and electronic spectra.

Kumari & Jha

On the basis of studies made a six coordinated octahedral geometry has been proposed for all these complexes. The general structure of the complexes as:



Where M = Mn (II), Fe (III), Co(II), Ni (II), Cu (II) and Zn (II)
X = Cl⁻

REFERENCES

1. Sanap, S. V. and Patil, R. M. 2013. *Res. J. Pharma. Sci.* 2(1):35-40.
2. Mrinalini, L. and Manihar Singh, A. K. 2012. *Res. J. Chem. Sci.* 2(1):45-48.
3. Malghe, Y. S., Prabhu, R. C. and Raut, R. W. 2010. *Acta Polo. Pharma. Drug Res.*, 66(1):45-52.
4. Ndosiri, N. B., Agwara, M. O., Paboudam, A. G., Ndifon, P. T., Yufanyi, D. M. and Amah, C. 2009. *Res. J. Pharma. Bio. Chem. Sci.* 4(1):386-388.
5. Shaker, S. A., Farina, Y. and Salleh, A. A. 2009. *Europ. J. Sci. Res.*, 33(4):702.
6. Fayad, N. K., Al-Noor Taghreed, H, and Ghanim, F. H. 2012. *Chem. and Mat. Res.*, 2(5): 18.
7. Wankhede, D. S., Kulkarni, P. A., Jadhav, N. S., Gurle, M. D., Wagh, P. B. and Omkar Shankarrao. 2013. *Asian J. Res. Chem.*, 6(6): 525.
8. Wankhede, D. S., Hussain, S., Jadhav, N., Wagh, P. B., Chaudhari, M. D., Murke, A. G. and Omkar Shankarrao, *Der Chem. Sinica*, 4(5):79.
9. Aneja, K. R., 2003. *Experiments in Microbiology Plant Pathology and Biotechnology*, 4th Edition, New Age International Publishers, India.
10. Liu, J., Wu, B., Zhang, B. and Liu, Y. 2006. *Turk J. Chem.*, 30:41.
11. Chandra, S. and Verma, S. *Spectrochim. Acta Part A*, 71:458.
12. Rafat, F. and Siddiqui, K. S. 2011. *J. Korean Chem. Soc.*, 55(6):912.
13. Cotton, F. A. and Wilkinson, G. 1988. *Advanced Inorganic Chemistry*, 5th Edition, John Wiley, Singapore.
14. Rao, T. V. R. K. and Shaw, A. K. 1995. *Asian J. Chem.*, 7(4):731.
15. Abdussalam, A. M., Faten, S. A., El-Ajaily, M. M. and Abdunnaser, M. E. 2014. *Green and Sustain. Chem.*, 4:103.
16. Gaber, M., El-Hefnawy, G. B., El-Borai, M. A. and Mohamed, N. F. 2012. *J. Therm. Ana. Calori.*, 109:1397.
17. Thakur, G. A. and Shaikh, M. M. 2006. *Acta Polo. Pharma. Drug Res.*, 63(2):95.
18. Patel, K. B., Kharadi, G. J., Vyas, K. B. and Nimavat, K. S. 2012. *Int. J. Pharma. Res. Scholars*, 1(2):474.
19. Chandra, S. and Kumar, R. 2004. *Trans. Met. Chem.*, 29:269.
20. Prasad, S., Jyaseelan, P. and Rajavel, R. 2011. *Int. J. Chem. Sci.*, 9(4):1711.
21. Prasad, R. N. and Gupta, S. 2002. *J. Serb. Chem. Soc.*, 67(7):523.
22. Anitha, K. R., Venugopala Reddy, K. and Vittala Rao, S. 2011. *J. Chem. Pharm. Res.*, 3(3): 511.
23. Jber, N. R., Abood, R. S. and Al-Dhaief, Y. A. 2011. *J. Al-Nahrain Univ.*, 14(4):50.
24. Anitha, K. R., Venugopala Reddy, K., Vittala Rao, S., Fasiulla, A., Sridhara, M. and Shobha, K. S. 2011. *Der Pharma Chem.*, 3(2):118.