Asian Journal of Chemistry; Vol. 29, No. 4 (2017), 843-845

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2017.20329

Synthesis and Characterization of Mn(II), Fe(II), Co(II) and Ni(II) Complexes of Salicyloylpyrazole Oxime

N.T. DHOKALE[1], B.K. KARALE[2] and A.V. NAGAWADE[1,*]

[1]Department of Chemistry, Ahmednagar College, Ahmednagar-414 001, India
[2]Department of Chemistry, Radhabai Kale Mahila Mahavidyalaya, Ahmednagar-414 001, India

*Corresponding author: E-mail: avnagawade@gmail.com

Received: 6 October 2016; *Accepted*: 20 December 2016; *Published online*: 31 January 2017; AJC-18256

In the present investigation, a simple and efficient synthesis of Mn(II), Fe(II), Co(II) and Ni(II) complexes containing salicyloylpyrazole oxime moiety is reported. The synthesized complexes were characterized by elemental analysis and spectral techniques such as IR, NMR and UV-visible. The formation of complexes were also confirmed by thermal studies and molar conductance. The analytical data supports 1:2 stoichiometry for metal:ligand. The molar conductivity data indicated the non-electrolytic nature of complexes. The electronic absorption spectra suggested the square planar geometry for metal complexes.

Keywords: Synthesis, Transition metal(II) complexes, Salicyloylpyrazole Oxime.

INTRODUCTION

A Schiffs base with 2-hydroxyoxime behaves as flexidentate ligand and commonly coordinate through O atom of phenolic group and the N atom of oxime group. The lone pair of electron present on nitrogen atom of oxime group is having considerable interest of chemical importance. It provides an excellent chelating ability when used with one or more donor atoms near to oxime group. This chelating ability of C=N group makes it an interesting ligand in coordination chemistry.

Oximes are versatile ligands and can easily forms complexes with transition metal ions [1]. Several transition metal complexes with 2-hydroxyoximes have been reported previously. The coordination chemistry of transition metal ion with 2-hydroxyoximes have shown considerable interest due to many applications in various fields [2,3]. Oxime complexes have been used as cerebral and myocardial perfusion image agent [4,5]. The metal complexes of oximes have structural features due to formation of intramolecular hydrogen bonds and a packing configuration which gives rise to important applications as biochemical model [6,7] and semiconducting materials [8,9]. Schiff base and their metal complexes show wide range of applications in agriculture, pharmaceutical and industrial chemistry. Oxime containing Schiff base copper complex shows good catalytic activity in degrading various organic dyes [10]. The oxime containing Schiff base complexes also shows antimicrobial [11], anticancer [12] activity. The complexes derived from pyrazole and their derivatives are widely used as herbicides, fungicides [13] and anti-inflammatory [14] agents.

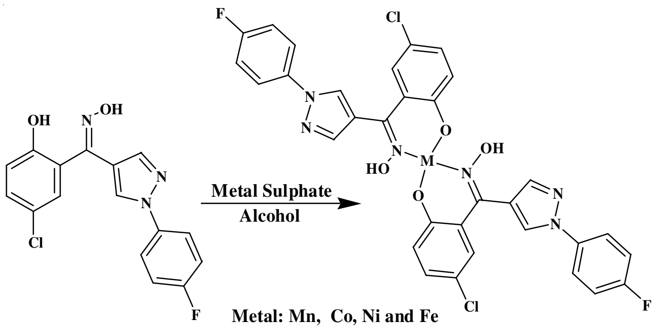
The wide biological applications of pyrazoleoximes and emergence of new fungal pathogens 1-(3,4-difluorophenyl-4-(2-hydroxybenzoyl)-1*H*-pyrazole) [15], prompted us to work on the synthesis of salicyloylpyrazole oxime and its transition metal complexes. The properties of all newly synthesized complexes investigated by physical and spectroscopic methods.

EXPERIMENTAL

All the chemicals used were commercially available, solvents were research grade and used after purification. Both water and ethyl alcohol were distilled before use. Melting points were recorded on open capillary method and uncorrected. Electrical conductivity data were recorded in 1×10^{-3} M solution in DMF on Elico digital conductivity meter model (CM-180). The elemental and FTIR spectra (4000-350 cm^{-1}) recorded at SAIF, Punjab University, Chandigarh. The UV-visible spectra were recorded on Shimadzu double beam spectrophotometer (UV-1800) in range 700-190 nm. The thermal analysis was recorded on Shimadzu thermometric analyzer (TGA-50). Standard volumetric methods were used to find the concentration of metal ions [16]. The ligand salicyloylpyrazoleoxime was prepared using the method reported in our previous investigation [17].

General procedure for synthesis of metal complexes: One equivalent of the corresponding metal sulphate ($MnSO_4$,

$FeSO_4$, $CoSO_4$ and $NiSO_4$) solutions were prepared in distilled water and acidified by concentrated hydrochloric acid. The resulting acidic solution was made warm using hot water bath. It was further treated with 2 equivalents of alcoholic ligand solution. The addition of ligand solution was made slowly drop by drop. Slight excess of ligand solution was added to ensure the complete complexation. The resulting mixed solution was then treated with alcoholic solution of ammonia to make it alkaline.The solution was then digested on boiling water bath where coloured complex precipitated out. The product was filtered,washed first with little hot distilled water and then by ethyl alcohol to remove excess of ligand. It was dried under ambient conditions (**Scheme-I**).



Scheme-I: Synthetic route for synthesis of metal complexes of salicyloyl-pyrazole oxime

RESULTS AND DISCUSSION

The metal complexes were synthesized by simple and efficient method. All the complexes were soluble in DMF and DMSO but insoluble in water and other polar and non polar solvents. The complexes were formed of different colour which is different than free ligand suggesting formation of complex. The metal complexes were found to decompose only at high temperatures suggesting that they are thermally stable. The elemental analysis data is in agreement with the molecular formula for the metal complexes. The analytical data for ligand and its metal complexes are reported in Table-1. The analytical data suggest the metal:ligand stoichiometry is 1:2 for all the metal complexes.

FTIR spectra of ligand and corresponding metal complexes have been examined in the region 4000-350 cm^{-1}. The significant bands in IR spectra of ligand salicyloylpyrazole oxime as well as metal complexes are shown in Table-2. To study the binding mode of ligand and metal, IR spectra of free ligand and corresponding metal complexes have been compared. A broad band near region 3391 cm^{-1} assigned for OH group which is disappeared in the spectra of complexes indicating deprotonation of OH group and involved in formation of metal oxygen bond.The band at 3131 cm^{-1} has been assigned to intramolecularly hydrogen bonded OH group oxime in ligand [18,19]. It also showed characteristic bands at 1563, 1232, 1097 cm^{-1} which are due to ν(C=N) oxime, ν(N-O) oxime and ν(C-O) of the phenolic functional groups respectively. The shifting in frequencies ν(C=N), ν(C-O) and ν(N-O) in the complexes indicating chelation of phenolic oxygen atom to metal and oximes nitrogen atom to metal [20,21]. The oxygen and nitrogen coordination to the metal ion is proved by the bands that appears in the range 546-538 and 464-409 cm^{-1} assigned to ν(M-O) and ν(M-N) respectively [22,23].

Thermal behaviours of complexes have been studied using TGA. Thermogravimetric analysis of metal complexes was carried out from 30 to 1000 °C at heating rate of 10 °C per min. According to thermogravimetric data of complexes **I-IV** they were found to exhibit high stability. Thermogram of complexes **I-IV** do not show any significant weight loss up to 200 °C indicating that there is no lattice or coordinated water molecules. Further increase in temperature the metal complexes were found to decompose slowly in the temperature range 200 to 650 °C giving residue of corresponding oxides. The final decomposition products of the metal complexes were Mn_2O_3, CoO, NiO and Fe_2O_3. The residue obtained in metal complexes **I-IV** were 10.63 % (calcd. 11.03 %), 10.11 % (calcd. 10.41 %), 9.87 % (calcd. 10.27 %) and 11.01 % (calcd. 11.20), respectively. The TG curves are shown in the Fig. 1.

The solution of known concentration (1×10^{-4} M) of ligand and its corresponding metal complexes prepared in DMF and their UV-visible spectra were recorded in the region 190-700 nm. The ligand shows absorption band at 329 and 283 nm which is assigned to π→π* and n→π* transitions. In metal complexes exhibits two bands in the region 20,704-17,271

TABLE-1
PHYSICAL, ANALYTICAL AND MOLAR CONDUCTANCE DATA OF LIGAND AND ITS METAL COMPLEXES

Compd.	Colour	m.p. (°C)	Yield (%)	Elemental analysis (%): Found (calcd.)				Λ_M
				M	C	H	N	
Ligand (LH)	White	174-176	69	–	58.12 (57.93)	3.64 (3.34)	12.89 (12.67)	28.6
$[MnL_2]$ (**I**)	Shiny brown	> 300	90	7.49 (7.67)	54.04 (53.65)	3.11 (2.81)	11.98 (11.75)	17.3
$[CoL_2]$ (**II**)	Gray	264-266	71	8.84 (8.18)	52.84 (53.35)	3.09 (2.80)	11.46 (11.67)	62.7
$[NiL_2]$ (**III**)	Green	276-278	78	7.86 (8.15)	52.97 (53.37)	2.99 (2.80)	11.51 (11.67)	56.8
$[FeL_2]$ (**IV**)	Brown	> 300	93	7.07 (7.79)	53.88 (53.58)	2.71 (2.81)	11.54 (11.72)	60.6

TABLE-2
KEY IR FREQUENCIES (cm^{-1}) OF FREE LIGAND AND ITS METAL COMPLEXES

Compound	ν(O-H)	ν(C=N)	ν(N-O)	ν(C-O)	ν(M-O)	ν(M-N)
Ligand (LH)	3391, 3131	1563	1232	1097	–	–
$[MnL_2]$ (**I**)	3165	1541	1232	1053	540	464
$[CoL_2]$ (**II**)	3140	1543	1228	1031	543	468
$[NiL_2]$ (**III**)	3145	1560	1228	1057	538	409
$[FeL_2]$ (**IV**)	3162	1545	1233	1057	546	461

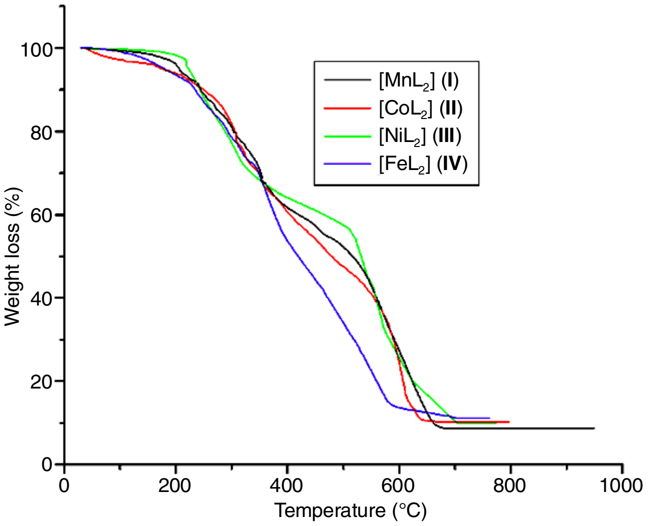


Fig. 1. TG spectra of [MnL_2] (**I**), [CoL_2] (**II**), [NiL_2] (**III**) and [FeL_2] (**IV**) complexes

and 15,924-15,948 cm^{-1}) attributed to $d \rightarrow d$ transitions. This is probable indicative of four coordinate square planer geometry [24].

^1H NMR spectra of all synthesized complexes recorded in DMSO as solvent and TMS as internal standard. However due to presence of metal ion, proton resonance was not effected and gave broad peaks indicating the formation of metal complexes.

XRD pattern of metal complexes were obtained in solid form. The X-ray diffractogram of all metal complexes showed broad peak, which indicate polycrystalline nature [25]. Though polycrystalline nature of complexes was observed they were generally not soluble in non polar solvents. The electrical conductivity of complexes measured in DMF, 0.001 M at room temperature. The low molar conductance values of the metal complexes suggest that they are non-electrolytic in nature [26].

Conclusion

In the present report synthesis of salicyloylpyrazoleoxime and its four new metal complexes **I-IV** is reported. The newly synthesized metal complexes were characterized by spectral and elemental analysis. The formations of metal complexes were also confirmed by thermal methods of analysis. The available physical and spectroscopic data revealed that the oxygen atom of phenol group and nitrogen atom of oxime group are involved in the coordination with the metal ion. The complexes have good solubility in DMF and DMSO but were found to be insoluble in water and other organic solvents. Thermal analysis data suggested that the metal complexes have high stability below 200 °C and decomposes slowly after 200 °C giving formation of corresponding metal oxides. The electronic absorption spectra reveled probably square planer geometry for the complexes. The XRD data suggested polycrystalline nature of metal complexes. The magnitudes of molar conductance of these complexes suggested that complexes are non electrolytic in nature.

ACKNOWLEDGEMENTS

The authors are indebted to SAIF, Punjab University, Chandigarh for providing spectral analysis facilities.

REFERENCES

1. A.M. Whyte, B. Roach, D.K. Henderson, P.A. Tasker, M.M. Matsushita, K. Awaga, F.J. White, P. Richardson and N. Robertson, *Inorg. Chem.*, **50**, 12867 (2011); https://doi.org/10.1021/ic2020644.
2. A.W. Ashbrook, *Coord. Chem. Rev.*, **16**, 285 (1975); https://doi.org/10.1016/S0010-8545(00)80438-5.
3. S. Kumar, D.N. Dhar and P. N. Saxena, *J. Sci. Ind. Res.*, **68**, 181 (2009).
4. S.S. Jurisson and J.D. Lydon, *Chem. Rev.*, **99**, 2205 (1999); https://doi.org/10.1021/cr980435t.
5. W.A. Volkert and T.J. Hoffman, *Chem. Rev.*, **99**, 2269 (1999); https://doi.org/10.1021/cr9804386.
6. D.G. Brown, *Inorg. Chem.*, **18**, 177 (1973).
7. G.N. Schrauzer and H. Prakash, *Inorg. Chem.*, **14**, 1200 (1975); https://doi.org/10.1021/ic50147a046.
8. T.W. Thomas and A.E. Underhill, *Chem. Soc. Rev.*, **1**, 99 (1972); https://doi.org/10.1039/CS9720100099.
9. A.E. Underhill, D.M. Watkins and R. Pethig, *J. Inorg. Nucl. Chem.*, **9**, 1269 (1973); https://doi.org/10.1016/0020-1650(73)80009-1.
10. X.-J. Hong, X. Liu, J.-B. Zhang, C.-L. Lin, X. Wu, Y.-J. Ou, J. Yang, H.-G. Jin and Y.-P. Cai, *CrystEngComm*, **16**, 7926 (2014); https://doi.org/10.1039/C4CE01207K.
11. A. Ugur, B. Mercimek, M.A. Özler and N. Sahin, *Transition Met. Chem.*, **25**, 421 (2000); https://doi.org/10.1023/A:1007064819271.
12. D. Jayaraju and A.K. Kondapi, *Curr. Sci.*, **81**, 787 (2001).
13. S. Trofimenko, *Prog. Inorg. Chem.*, **34**, 115 (1986); https://doi.org/10.1002/9780470166352.ch3.
14. M.S. Alam, J.H. Choi and D.U. Lee, *Bioorg. Med. Chem.*, **20**, 4103 (2012); https://doi.org/10.1016/j.bmc.2012.04.058.
15. A.V. Gadakh, C. Pandit, S.S. Rindhe and B.K. Karale, *Bioorg. Med. Chem. Lett.*, **20**, 5572 (2010); https://doi.org/10.1016/j.bmcl.2010.07.019.
16. Vogel's, Text book of Practical Organic Chemistry, John Wiley, New York, edn 5 (1989).
17. N.T. Dhokale, B.K. Karale and A.V. Nagawade, *Res. J. Chem. Sci.*, **1**, 100 (2014).
18. R.M. Silverstein and G.C. Bassler, Spectroscopic Identification of Organic Compounds, John Wiley, New York, edn 2 (1963).
19. A. Bigotto, *J. Mol. Struct.*, **175**, 377 (1988); https://doi.org/10.1016/S0022-2860(98)80106-3.
20. I.H. Bukhari, M. Arif, J. Akbar and A.H. Khan, *Pak. J. Biol. Sci.*, **8**, 614 (2005); https://doi.org/10.3923/pjbs.2005.614.617.
21. B. Basavaraju, H.S.B. Naik and M.C. Prabhakara, *E-J. Chem.*, **4**, 39 (2007); https://doi.org/10.1155/2007/836582.
22. S.S. Black and G.B. Young, *Polyhedron*, **8**, 585 (1989); https://doi.org/10.1016/S0277-5387(00)83820-6.
23. B.B. Mohapatra and S.K. Saraf, *J. Indian Chem. Soc.*, **8**, 696 (2003).
24. B.H. Mehta and Y.A. Swar, *Asian J. Chem.*, **13**, 928 (2001).
25. R. Hussain and H.D. Juneja, *Int. J. Chem. Sci.*, **7**, 632 (2009).
26. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971); https://doi.org/10.1016/S0010-8545(00)80009-0.