SYNTHESIS AND SPECTRAL STUDIES OF MN(II) COMPLEX WITH TRIDENTATE NNN FUNCTIONALIZED LIGAND

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ABSTRACT

In this study (hydroxyimino) (2-phenyl 1, 2, 3, 4-tetrahydroquinazolin-2-yl) methane which is tridentate ligand was synthesized by reacting 2-(hydroxyimino)-1-phenylethan-1-one with 2-aminobenzylamine. This ligand further reacted with Manganese Chloride [MnCl2.2H2O] to synthesize Manganese complex [MnL(HL)].H2O. The ligand and the complex were characterized on the basis of elemental analysis and structure of the complex was elucidated by FT-IR-1H, Mass spectra, NMR spectra and TEM.

Keywords: 1, 2, 3, 4-tetrahydroquinazoline, 2-aminobenzylamine,Manganese Chloride

1. Introduction: Quinazoline is an organic compound which is aromatic heterocyclic with a bicyclic structure consisting of two fused six-membered aromatic ring i.e. a benzene ring and a pyrimidine ring [1]. Quinazolines possessing wide spectrum of biological properties like antibacterial, antifungal, anticonvulsant, anti-inflammatory, anti-HIV, anticancer and analgesic activities. A Schiff base is a compound with the general structure $R_2C=NR^1$, considered a sub-class of imines [2]. A series of quinazolinone derived Schiff base derivatives were synthesized and characterized as novel antioxidants and anti-inflammatory agents. Many types of Schiff base ligands are known and the properties of their metal chelates have been investigated [3]. A cyclic ligands which contains nitrogen, oxygen and sulphur as donor atoms in their structures was proved to be effective chelating agents for transition and non-transition metal ions [4].

Oximes are important class of chelating agents have found numerous application. Synthesis of Schiff bases have been extensively studied because of their biological and structural importance arising from their specific and selective reactions with metal ions. Various schiff base derivatives which contain oxime or substituted oxime have been synthesized, characterized and then complexed with different transition metal ions [3-4].

Because of so many uses of these quinazoline derivative, oxime ligand and its complex with Mn was synthesized and the ligand and its manganese complex was characterized by elemental analysis, mass spectroscopy, FT-IR and NMR. Size of ligand is also determined by TEM.

2. Materials and Methods:

All the chemicals required for the synthesis of ligand and complex were purchased from Merck and Sigma (99.99% pure) and used without further purification. Melting points were determined on a BUCHI - B - 540 digital melting point apparatus and are uncorrected. The IR spectra was recorded on FTIR - 8101 by using KBr pallets in the range 400 - 4000 cm^{-1}. ^{1}H-NMR solution spectra in DMSO-D6 was recorded at 295.3 K on a Bruker avance II 400 NMR spectrometer with TMS as references. Elemental analysis (C, H, N, O) was carried out on Eassuperuser elemental analyser system, GmbH, Access, Vario EL Super User, NEERI. As well as mass spectroscopy and TEM were also carried out at SAIF, Punjab University, Chandigarh.

3. Experimental

3.1 Synthesis of Ligand –

(Hydroxyimino) (2-phenyl (1, 2, 3, 4-tetrahydroquinazolin-2-yl) methane was synthesized by condensation method. In 30 ml absolute ethanol 2-aminobenzylamine (1.222g) was dissolved and then added to alcoholic solution of 2(Hydroxyimino - 1 - phenylethan - 1- one) (1.4930 g). The reaction mixture was stirred well and kept for 48 hrs at room temperature. The product obtained was filtered and recrystalised with ethanol. (Hydroxyimino) (2-phenyl (1, 2, 3, 4-tetrahydroquinazolin-2-yl) methane is soluble in acetone, THF, DMSO, DMF and pyridine and slightly soluble in $CHCl_3$, EtOH and MeOH [5]. Yield of ligand obtained was 1.87 g while melting point of ligand is 142^0C (Decomposition point)

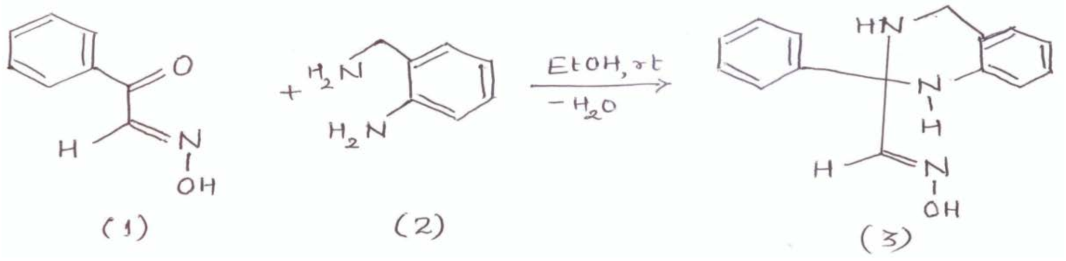

Figure 1: Synthesis of Ligand

Where, 1) 2-(Hydroxyimino) -1- phenylethan -1-one
2) 2-aminobenzylamine
3) (Hydroxyimino) (2-phenyl (1, 2, 3, 4 - tetrahydroquinazolin-2-yl) methane.

3.2 Synthesis of $[MnL(HL)].H_2O$ Complex

As ligand is tridentate for synthesizing the complex metal and ligand was taken in 1:2 ratio. $MnCl_2.2H_2O$ was dissolved in minimum quantity of distilled water and ligand was dissolved in minimum quantity of DMF separately. Both solutions were warmed and then mixed. The solution was warmed in waterbath, solid portion obtained was filtered and washed with distilled water to wash out the excess of metal ions present. The complex obtained was soluble in chloroform, DMSO and DMF but slightly soluble in acetone and alcohol. Decomposition point for the complex was 167^0C while the yield obtained was 2.329 gm.

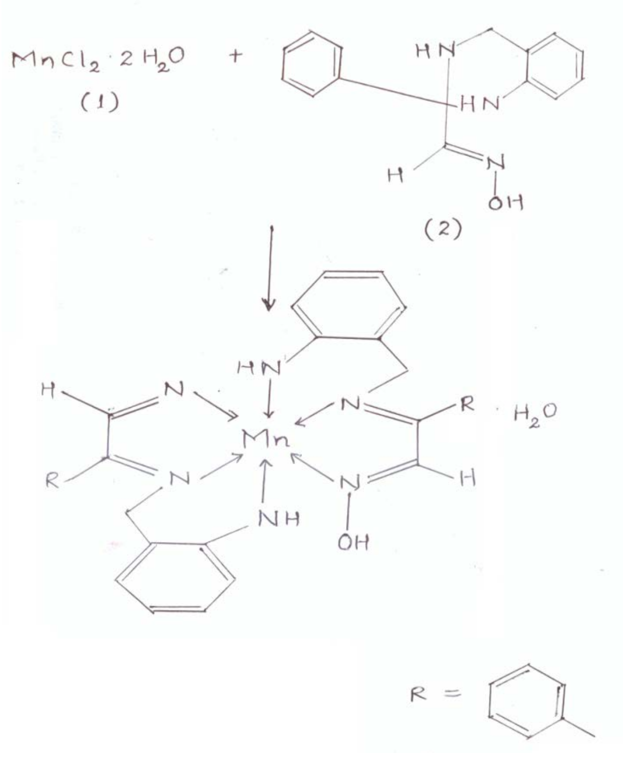

Figure 2: Synthesis of Complex $[MnL(HL)].H_2O$

Where 1) Manganese chloride dihydrate
2) (Hydroxyimino) (2-phenyl (1, 2, 3, 4 - tetrahydroquinazolin-2-yl)
3) [MnL(HL)].H_2O

4. Result and Discussion

Table-1

4.1 Elemental analysis of ligand Manganese complex

Molecular formula	Colour	Mol. Wt.	Found (Calculated)			
			C	H	N	M
H_2L $C_{15}H_{15}N_3O$	Pale yellow	253.31	70.89 (71.12)	6.09 (5.97)	16.56 (16.59)	-
[MnL(HL)].H_2O $C_{30}H_{29}N_6O_3Mn$	Lemon yellow	576.55	65.14 (64.17)	4.84 (5.04)	14.48 (14.88)	9.07 (10.05)

4.2 Mass spectral studies

Mass spectra of ligand and Mn complex were analyzed to determine the molecular mass of ligand and the complex [MnL(HL)].H_2O. In the ligand the molecular ion peak was observed at m/e 253.8

While in the spectra of complex [MnL(HL)].H_2O, the strong base peak at m/e 576.5 was observed.

4.3 Infrared-Spectral Studies

IR bands of H_2L is presented in table 2. In this ligand the functional groups ≡N-H, -OH, C=N and N-O are readily determined from IR spectra.

Ligand shows sharp, peaks at 3261 cm^{-1} and 3399 cm^{-1} attributed to the ν (N-H) vibration. The ν (N-H) band assigned to the stretching hydrogen motions in the intramolecular O-H…N hydrogen bond appears broadened with a maximum in the range of 2760.34 cm^{-1}. The bands for the oxime ν (C=N) and ν (N-O) groups due to stretching vibrations were observed at 1605 cm^{-1} and 943.50 cm^{-1} respectively. These absorptions are in good agreement with the values reported for similar compounds [6,7,8].

In IR spectra of Manganese complex, band at 3057 cm^{-1} observed for ν (O-H) band due to presence of water molecule. The band is very broad which prohibit the appearance of other bands in the region. Complex shows weak and sharp ν (C=N) stretching bands in the range of 1453-1613 cm^{-1} which is due to ν (C=N) of the azomethine of imine. But this IR band is not appear in case of ligand, so this band is further evidence for tetrahydroquinazoline ring formation. After complexation the appearance of this new ν (C=N) stretching band, the shift of the ν (N-O) bands to upper frequency region and the shift of ν (C=N) of oxime bonds to the lower frequency region in the IR spectrum of Manganese complex may be attributed to N, N-chelation. These observed stretching bands indicate the involvement of both the nitrogen atoms of the azomethine ν (C=N) of imine group and the azomethine ν (C=N) of oxime group in coordination with the metal. In addition non-ligand band at 465 cm^{-1} are tentatively assigned to ν (C=N) stretching vibrations.

In IR spectrum of Manganese complex ν (C=N) bands due to water molecules was assigned at 3399 cm^{-1} strong and sharp stretching bands in the range of 1471 to 1603 cm^{-1} of complex shows ν (C=N) stretching while non-lingand band at 488 cm^{-1} may be tentatively assigned to ν (C=N) stretching vibrations [9-10].

Table-2

Characteristic infrared bands (cm^{-1}) of the ligand and complex (KBr pallets)

Compound Molecular Formula	NH/NH_2	H_2O/O-H	C=N			
			Oxime	Imine	N-O	M-N
H_2L	3261 m, sh 3319 m, sh	(2760.34) b	1605.61 sh	-	943.5 sh	-
[MnL(HL)].H_2O	3399 s, sh	3260 s, sh	1471 s, sh	1595 m, sh	943 s, sh	488 w

w : weak; m : medium; s : strong; b : broad ; sh : sharp

4.4 NMR Analysis and Structure Determination

The ^{1}H-NMR spectra (400 MHz) of the ligand is recorded in deuterated dimethylsulfoxide (DMSO) as presented in Table 1 C.

The ligand H_2L shows signals corresponding to D_2O exchangeable - NOH (Oxime, 1H) - NH (tetrahydroquinazoline ring nitrogen - 3, 1H) protons at δ 10.81 - 10.91 ppm(s), 6.64 - 6.71 ppm(s) and 2.50 ppm respectively. Signals observed in the range of 7.44 - 7.45 ppm region for HC = N proton. Interpretation of the ^{1}H-NMR spectrum suggests the presence of a range of proton resonances between 6.45 and 7.57 ppm because of the resonance of 9-phenyl proton of H_2L. [9]

The chain form is easy to differentiate from the ring form based on the proton and carbon signal of sp^2 hybridized C=N carbon and proton attached to it [10-11]. In addition to this the ring can be easily identified from magnetically non-equivalent methylene proton. Tetrahydroquinazoline derivative H_2L has an AB system centre at δ 3.57 ppm, J = 17.0 Hz.

These observed signals are in good agreement with values reported for similar compound [12, 13] and more evidence for tetrahydroquinazoline ring formation [14-15]

Table - 3

^{1}H-NMR spectral data (δ ppm) and the coupling constants (Hz) of H_2L in DMSO D_6

Compound Molecular Formula	$-CH_2$	-OH	$-NH_2$	NHf	Phenyl	H-C=N
H_2L	3.57 AB system J=17.0, 2H	10.81S, 1H	-	2.99-3.17b, w, 1H, 6.60 s, sh, 1H	6.45 td, J=7.6, 1H 6.72t, J = 7.0, 2H 6.90 td J = 7.2, 1.6, 1H 7.23 t, J = 7.6, 1H, 7.31t, J = 7.6, 2H, 7.57 d, J = 7.2, 2H	7.42 s, 1H
$[MnL(HL)].H_2O$ $C_{30}H_{29}N_6O_3Mn$	3.76 - 3.57 m, 4H	10.94 s, 1H	-	8.07 - 8.00, 1H	7.62 m, 18H	6.92 - 6.08, s 2H

(s : singlet, d : doublet, t : triplet, m : multiplet, b : broad, w : weak, sh : sharp, C : $COCl_2$ F : D_2O exchange)

Manganese complex shows signals corresponding to D_2O exchangeable – NOH (oxime, ^{1}H), -NH(^{1}H) proton at 7.13 - 7.41 ppm region [16,17,18]. The presence of a range of proton peak at 7.61 ppm, integrate the ^{1}H-NMR spectrum due to resonance of phenyl proton of H_2L.

5. Conclusion

The complex $[MnL(HL)].H_2O$ is lemon yellow in colour and are soluble in DMSO and DMF while insoluble in acetone and ethanol. Decomposition temperature is 167^{0}C. The complex is crystalline in nature. By using elemental analysis study, IR spectra, NMR spectra and TEM of complex structural elucidation of the complex was done, according to which the Mn complex was found to have octahedral geometry. Spectral studies of the complex also shows presence of secondary bonding in complex such as hydrogen bonding – TEM study shows small size of complex i.e.105nm.

6. References

[1] International Journal of Medicinal Chemistry, Volume 2014, Article ID 395637, 27 pages (http://dx.doi.org/10.1155/2014/395637) Mohammad Asif.

[2] Biological activity of Quinazoline - A Review Sukriti Srivastava Sujiti

Shrivastava [International Journal of Pharma Sciences and Research (IJPSR)]

[3] Quinazoline and quinazolinone as important medicinal scaffolds, a comparative patent review (2011-2016) Abdul Hameed, Mariya Al Rashida, Malina Uroos, Syed Abid Ali, Asshia, Marium Ishtiaq and Khalid M. Khan. Pages 281-297, 25th Jan. 2018 (Journal Expert Opinion on Therapeutic Patents) Volume 28, 2018

[4] Schiffs bases of quinazoline derivatives: Synthesis and SAR Studies of a novel series of potential anti-inflammatory and antioxidants. Rakesh KP, et al – Bio-org Med Chem Lett 2015

[5] Hasene Mutlv; Gazi irez.; Turk J. Chem 32(2008), 731-734.

[6] Harris, C. S.; Kettle, J. G. Williams, E. J. Tetrahedron Lett. 2005, 45, 7381-7384.

[7] Mizuno, T.; Twai; Ishino, Y. Tetrahedron Lett. 2004, 45, 7073-7075.

[8] Reddy, P. S.; Reddy, K. H. Polyhedron, 2000. 19(14), 1687-1692.

[9] Daveci, M.A.; Trex, G. Synth, Reac. Inorg. Me-org, Chem. 1995, 25(8), 1295-1307.

[10] Ucan, S. Y.; Ucan, M.; Mercimek, B. Synth. React. Inorg. Met-Org. Nano-Me. Chem. 2005 35(3), 197-201.

[11] Alexander, F: Berecibar, A.; Wrigglesworth, R.; Besson, T. Tetrahedron let. 2003, 44, 4455-4458.

[12] Ucan, S. Y.; Mercimek, B. Synth. React Inorg. Met. Org. Nano-Met. Chem 2005, 29. 409-415

[13] Canpolat, E.; Kaya, M. Turk. J. Chem 2005, 29. 409-415.

[14] Demir, I.; Pekacar, A. I. Synth. React. Inorg. Met-Org. Nano-Met Chem 2005. 35(10), 825-828.

[15] Sinkkonen. J.; Zelenine, K. N.; Potapov, A. A. Lagoda, I. V.; Alekseyev, V. V.; Pinlaja, K. Tetrahedron 2003, 59, 1939-1950.

[16] Wei, Y.; Wang F. Synth. React. Inorg. Met. Org. Nano-Met. Chem 2006, 36(10), 723-727.

[17] Coskun, N.; Cetin, M. Tetrahedron Lett. 2004, 45, 8973-8975.

[18] Goblos, A.; Lazar, L.; Fulop, F. Tetrahedron 2002, 58, 1011-1016.