“Studies on trivalent metal complexes with (*N*''-[(1*E*)-2-imino-1, 2-diphenylethylidene]thiocarbonohydrazide”

Santosh Kulkarni[1], Raj Badekar[1], Ganga Gore[2], and Pradeep Shimpi[3]
[1]Department of Chemistry, K.M. Agrawal College, Kalyan-421301, INDIA
[2]Dapoli Urban Bank Sr. Science College, Dapoli, Maharashtra 415712, NDIA.
[3]Dept of Chemistry, BNN College, Bhiwandi, Maharashtra 421305, NDIA.

Abstract:

The title ligand and its Ti(III), Mn(III), and Ni(III) transition metal complexes have been synthesized. The preparation of the ligand by condensation between α-Benzilmonoxime and thiocarbahydrazide in the presence of Conc. HCl and its trivalent metal complexes prepared by ML_3 (M = Metal and L = Ligand) Composition. The structures of the synthesized compounds were elucidated by electronic, FT(IR), PMR spectroscopic techniques and also physico-chemical techniques. The spectral data suggests octahedral geometries for Ti(III), Mn(III), complexes and Ni(III), is diamagnetic in nature.

Keywords: α-Benzilmonoxime, Thiocarbahydrazide, Ti(III), Mn(III), Ni(III)

1. Introduction:

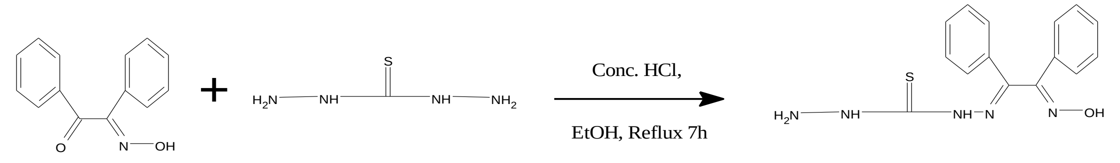
In coordination chemistry, Schiff bases have been used for over’s 150 years[1-2]. These ligands have played on important role in the development of coordination chemistry as they readily from stable complexes with most of the transition metals. Schiff base ligands with additional donor atoms appended to ring have attracted considerable interest because of their capacity to bind and transport metal ions, for the potential to prepare and study their mixed-valence forms and as models for metulloproteins[3]. The synthesis of transition metal complexes with Schiff base ligands are studied due to sensitivity, selectivity and synthetic flexibility[4]. They used as catalyst in medicine like antibiotics and anti-inflammatory agents and in the industry as anti-corrosion[5]. In view of this, we synthesized Schiff base α-Benzilmonoximethicarbahydrazide (HBMOTCH) ligand and its trivalent metal complexes. IUPAC name of the ligand is *N*''-[(1*E*)-2-imino-1, 2-diphenylethylidene]thiocarbonohydrazide. The α-Benzilmonoximehydrazone ligand and its various metal complexes also reported[6-7]. In this paper reports the synthesis and characterized of the title ligand and its Ti(III), Mn(III), and Ni(III) transition metal complexes. The spectral properties of the ligand and their metal complexes have been measured and the results are discussed in order to obtain information on the stereochemistry of the compound in the solid state.

2. Experimental Section:

All reagents were used without purification and supplied by Sigma-Aldrich. The metal contents were determined gravimetrically[23]. Melting point recorded on I-Therm AI-7782 instrument and uncorrected. Molecular Weight determined by Rast’s method[24]. The conductivity measurements carried out on a Toshcon CL54 conductivity bridge in nitrobenzene. Electronic spectra were recorded JASCO V60 spectrophotometer. FT(IR) spectra in KBr disc measured using Perkin-Elmer Spectrum100. PMR spectra in d_6 DMSO records on a Brucker AV300 NMR instrument with TMS as internal standard. The room temperature magnetic susceptibilities of all metal complexes reported in the present work were determined by the Gouys method using $Hg[Co(SCN)_4]$ and $[Ni(en)_3S_2O_3]$ as celebrants[25].

2.1. Preparation of α-benzilmonoximethiocarbahydrazide Ligand:

α-Benzilmonoxime[24] and Thiocarbahydrazide[25] were prepared by reported method. HBMOTCH was prepared by mixing hot aqueous solution of 20.000 g of thiocarbohydrazide (0.188 mol) with ethanolic solution of 10.000 g of α-benzilmonoxime (0.044 mol) in presence of sodium acetate (20.000 g), the mixture was refluxed for 7h on a water bath and kept overnight, a colorless solid was obtained. This was filtered and washed by hot water and dried at 100 ºC. [The yield of a product was 10.165 g, 73.80% of the theoretical. Melting point is 168 ºC]. ; UV-vis (MeOH) λ_{max}: 239nm, 290, (0.1N NaOH) λ_{max}: 222nm, 271nm; ^{1}H NMR (d_6 DMSO, 300MHz) δ12.53(s, 1H), δ8.00(d, 2H), δ8.67(s, 1H), δ7.44-7.95(m, 10H);FT(IR)(KBr); 3288, 3300, 2345, 1600, 1693, 1589, 1000, 1072 cm^{-1}; Anal Calcd for $C_{15}H_{15}N_5OS$: C: 57.51, H 4.89, N 22.36, O 5.11, S: 10.22; found C :57.11, H 4.42, N 22.48, O 5.29, S: 10.00.



α-benzilmonoxime thiocarbohydrazide α-Benzilmonoximethicarbahydrazide

Scheme-I: One step preparation of α-benzilmonoximethiocarbahydrazide

2.2. Synthesis of metal complexes:

All metal complexes prepared by under nitrogen atmosphere and they were prepared by following methods:

2.2.1. Tris(α-benzilmonoximethiocarbahydrazide)Titanium(III), [Ti(BMOTCH)₃]:

The ligand 0.717g (3mmol) was dissolved in ethanol (20mL) by heating at 80° C, to this hot solution added alcoholic Titanium trichloride (0.154g, 1mmol) solution drop by drop with constant stirring and the reaction mixture was refluxed for 3 hrs. The solid product obtained on cooling was filtered, wash thoroughly with hot ethanoland recrystallized from chloroform to yield 81.29%; m.p.199ºC; UV-vis ($CHCl_3$) λ_{max}: 550nm; ^{1}H NMR (d_6 DMSO, 300MHz) δ7.45-7.90 (m, 30H), δ7.80 (d, 6H), δ8.66(s, 2H); FT(IR)(KBr) ν: 3220, 2350, 1667, 1728, 1582, 1022, 1091, 580, 523cm^{-1}; Anal Calcd for $C_{45}H_{42}N_{15}O_3S_3Ti$: C 54.88, H 4.28, N 21.38, O:4.87, S:9.56, Ti:4.86; found C 53.00, H 4.21, N 21.07, O:4.81, S:9.13, Ti:4.71.

2.2.2. Tris(α-benzilmonoximethiocarbahydrazide)Manganese(III), [Mn(BMOTCH)₃]:

Manganese (III) Acetate dihydrate (0.268g, 1mmol) was added alcoholic solution (20mL) of ligand (0.717g,3mmol) and refluxed for 3hrs. afterword's the dark brown solution obtained was evaporated to half of its original volume and allowed to crystallize, dark brown complex that separated was filtered, washed with hot ethanol and recrystallized from chloroform to yield 88.00%; m.p.196ºC; UV-vis ($CHCl_3$) λ_{max}: 761, 585, 503, 361nm; ^{1}H NMR (d_6 DMSO, 300MHz) δ7.40-7.85 (m, 30H), δ7.82 (d, 6H), δ8.60(s, 3H); FT(IR)(KBr) ν: 3222, 2358, 1666, 1730, 1588, 1026, 1085, 570, 511cm^{-1}; Anal Calcd for $C_{45}H_{42}N_{15}O_3S_3Mn$: C 54.45, H 4.24, N 21.19, O:4.84, S:9.69, Mn:5.54; found C 53.00, H 4.21, N 21.07, O:4.81, S:9.13, Mn:5.71.

2.2.3. Tris(α-benzilmonoximethiocarbahydrazide)Ni(III) [Ni(BMOTCH)₃]:

A solution containing ligand (0.717g, 3mmol) in 20mL ethanol and Ni(III)Cl_3(0.165g, 1mmol) were refluxed for 3hrs on oil bath, on cooling green colored solid product was collected by filtrationand recrystallized from chloroform to yield 78.96%; m.p.195ºC; UV-vis ($CHCl_3$) λ_{max}: 290nm; ^{1}H NMR (d_6 DMSO, 300MHz) δ7.40-7.80 (m, 30H), δ7.82 (d, 6H), δ8.60(s, 3H); FT(IR)(KBr) ν: 3233, 2346, 1660, 1728, 1580, 1020, 1091, 592, 529cm^{-1}; Anal Calcd for $C_{45}H_{42}N_{15}O_3S_3Ni$: C 54.32, H 4.32, N 21.11, O:4.83, S:9.65, Ni:5.90; found C 53.87, H 4.19, N 20.98, O:4.69, S:9.13, Ni:5.78.

3. Results and Discussions:

All metal complexes are stable for 5-6 days at room temperature in open atmosphere, hygroscopic, sparingly soluble in methanol and fairly soluble in $CHCl_3$, DMF, DMSO, ACN, Nitrobenzene etc. The analytical data for ligand and their metal complexes are consistent with their proposed molecular formulae. The molar conductivity data (**Table-1**) of metal chelates indicates that all the metal complexes are non-electrolyte. The metal complexes are insoluble in dilute alkali solution, suggested their formation by replacement of the ligand.

Table-1: Physical and Analytical data of the HBMOTCH ligand and its metal complexes

Compound	D.P.(°C)	% Yield	% of expected (found)						Conductance	Magnetic moments (BM)
			C	H	N	O	S	M	10^{-3} M Nitrobenzene mhos	
HBMTCH	168	73.80	57.51 (57.11)	4.89 (4.42)	22.36 (22.48)	5.11 (5.29)	10.22 (10.00)	-	-	-
$[Ti(BMTCH)_3]$	199	81.29	54.88 (53.00)	4.28 (4.21)	21.38 (21.07)	4.87 (4.81)	9.56 (9.13)	4.86 (4.71)	0.12	1.72
$[Mn(BMTCH)_3]$	196	88.00	54.45 (53.00)	4.24 (4.21)	21.19 (21.07)	4.84 (4.81)	9.69 (9.13)	5.54 (5.71)	1.38	4.80
$[Ni(BMTCH)_3]$	195	78.96	54.32 (53.87)	4.32 (4.19)	21.11 (20.98)	4.83 (4.69)	9.65 (9.13)	5.902 (5.78)	0.90	Dia

3.1. Magnetic moments:

The room temperature magnetic moment of the $[Ti(BMOTCH)_3]$ complex is 1.72BM, indicate the octahedral geometry for this complex. The complex of $[Mn(BMOTCH)_3]$ have magnetic moment is 4.80BM at room temperature. This value is in the range expected for four unpaired electron and its octahedral geometry. The $[Ni(BMOTCH)_3]$ complex is diamagnetic in nature.

3.2. Electronic Spectra:

The electronic spectrum of HBMOTCH in methanol for the UV region reveals two high intensity bands at 239nm and 290nm respectively (**Table-2**), be due to $\pi \rightarrow \pi^*$ transitions possible from the oximino and azomethine environments in the molecules. The UV spectrum of HBMOTCH in dilute alkali (0.1N NaOH) solution shows that, the band at 239nm methanolic solution spectrum has suffered along with a bathochromic shift to 222nm,. It means that this band could have its origin in the oximino linkage in the molecules as such; the band at 271nm in the dilute alkali solution spectrum could be assigned to the azomethine linkage. This band is suffered as bathochromic shift compared to methanolic solution[8].

The electronic spectrum of $[Ti(BMOTCH)_3]$ complex shows broad band at 550nm due to $^2T_{2g}\rightarrow{}^2E_g$ transition which indicate octahedral geometry around the metal ion[9]. The electronic spectrum of $[Mn(BMOTCH)_3]$ complex exhibits an intense band at 361nm which due ligand to metal charge transfer transition. In the second region three *d-d* bands are observed at 761, 585, 503nm which may be due to $^5B_1\rightarrow{}^5B_2$, $^5B_1\rightarrow{}^5A_1$ and $^5B_1\rightarrow{}^5E$ transitions respectively.

The spectra of the $[Ni(BMOTCH)_3]$ complex shows band at 290nm, assigned metal to ligand charge transfer transition. The spectrum of the $[Au(BMOTCH)_3]$ complex shows bands at 300nm, and 370nm assigned to the $^1A_{1g}\rightarrow{}^1A_{1u}$ and $^1A_{1g}\rightarrow{}^1E_{1u}$ transition respectively[13].

Table-2: Electronic spectral data of the HBMOTCH ligand and its metal complexes

Compound	Solvent	Bands in nm	Transitions
HBMOTCH	Methanol	239	Oximino$\pi\rightarrow\pi^*$
		290	Azomethine $\pi\rightarrow\pi^*$
	0.1M NaOH	222	Oximino $\pi\rightarrow\pi^*$
		271	Azomethine $\pi\rightarrow\pi^*$
[Ti(BMOTCH)$_3$]	Chloroform	550	$^2T_{2g}\rightarrow{}^2E_g$
[Mn(BMOTCH)$_3$]	Chloroform	761	$^5B_1\rightarrow{}^5B_2$
		585	$^5B_1\rightarrow{}^5A_1$
		503	$^5B_1\rightarrow{}^5E$
		361	M→LCT
[Ni(BMOTCH)$_3$]	Chloroform	290	M→LCT

3.3. ^{1}H NMR Spectra:

The spectrum of ^{1}H NMR in d_6 DMSO solvent was recorded and reported in **Table-3**. In ligand showed sharp peak at δ12.53 (*s, 1H)* due to oximino –OH group, but in the metal complexes case which has been disappeared, indicating the involvement of oximino (>C=N-OH) group in the coordination via deprotonation[14]. The peak appeared at δ8.00 (*d, 2H)* due to azomethine (>C=N-NH_2) group in the ligand and this is unshifted to metal complexes indicating non-involvement of this for complexation and also the ten aromatic proton due to two phenyl rings have resonated in region δ7.44-7.95 (*m, 10H)* as a multiplet is unchanged in all metal complexes. Suggests this group also non-involve in coordination[15]. The ^{1}H NMR spectral data indicated that, only oximino proton is deprotonated and rast's of the groups are unchangeable or unshifted during formation of complex.

Table-3: ^{1}HNMR data of the HBMOTCH ligand and its metal complexes

Compound	>C=N-OH(δ)	>C=N-NH_2(δ)	-NH-	-C_6H_5(δ)
HBMOTCH	12.53 (*S, 1H)*	8.00 (*d, 2H)*	*8.66(s,2H)*	7.44-7.95 *(m, 10H)*
[Ti(BMOTCH)$_3$]	-	7.80 (*d, 6H)*	*8.66(s,6H)*	7.45-7.90 *(m, 30H)*
[Mn(BMOTCH)$_3$]	-	7.82 (*d, 6H)*	*8.60(s,6H)*	7.40-7.85 *(m, 30H)*
[Ni(BMOTCH)$_3$]	-	7.82 (*d, 6H)*	*8.60(s,6H)*	7.40-7.80 *(m, 30H)*

3.4. FT(IR) Spectra:

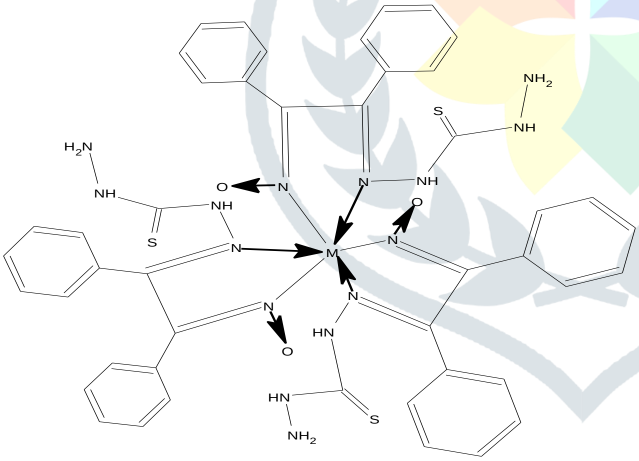
The Inorganic complexes derived from organic chelating groups have a tendency to absorb in the IR region 400-660cm^{-1} which is of greatest practical values in the study of metal complexes[16]. A strong and broad band is observed at 3288cm^{-1} for the free ligand due to N-OH which is absent in metal complexes, suggests the deprotonation of the hydroxyl group of the oxime in the process of formation of the complexes. The ligand shows the IR stretch in the region of 1600cm^{-1} for azomethine (>C=NN) group and 1493cm^{-1} for oxomino (>C=NO) group, which are in agreement with literature values[17], they are shifted by higher frequencies in the complexes indicating that the nitrogen atom of both the group is coordinated to the metal[18]. A non-ligand band that appears in the complexes in the region 511-590cm^{-1} has been assigned to ν(M-N)[20]. Thus, it may be concluded that the ligand acts towards the metal studies in a neutral, bidentate manner, coordinating through the nitrogen of azomethine and oximino groups (M-N$_4$) type.

Table-4: FT(IR) spectral data for HBMOTCH and its metal complexes in cm^{-1}

Compound	υ(O-H)	υ(N-H)	ν(C-S-H)	C=NN	C=NO	υ(N-H)	N - O	N-N	M-N
HBMOTCH	3288	3300	2345	1600	1493	1693	1000	1072	-
[Ti(BMOTCH)$_3$]	-	3220	2350	1667	1582	1698	1022	1091	580, 523
[Mn(BMOTCH)$_3$]	-	3222	2358	1666	1588	1699	1026	1085	570, 511
[Ni(BMOTCH)$_3$]	-	3233	2346	1660	1580	1696	1020	1091	592, 529

4. Conclusion:

Ti(III), Mn(III) and Ni(III) complexes of the title ligand are non-electrolytes. Schiff base behave as a neutral bidentate ligand is coordinated to the central metal ion through the azomethine and oximino nitrogen atoms. The elemental analysis, magnetic susceptibility, electronic spectra, FT(IR) and ^{1}H NMR spectra observations the following structure for these complexes were Ti(III), Mn(III) and Ni(III) exhibit coordination number of six. On the basis of magnetic and spectral data, structure of all metal complexes tentatively assigned as;



Where; M = Ti(III), Mn(III) and Ni(III)

Acknowledgements:

The authors are thankful to the Dr. R. G. Deshmukh, principal of K.G.K.C. college of ASC, Karjat-Raigad for providing the facilities.

References:

1. Ilhan, S.; Temel, H.; Yilmaz, I. and Sekerci, M.; *J. Org. Chem.***2007,** 692, 3855**.**
2. Parvez, A. and Meshram, J.; *Synth. React. In Inorg. Met. and Nano Met. Chem.* **2010,** 40, 633.
3. Kumar, D.S. and Alexander, V.; *Polyhedron.***1999,** 18, 156.
4. Spinu, C. and Kriza, A.; *Acta ChimSolv.***2000,** 47, 179.
5. Sun, B.; Chen, J.; Huj, Y. and Lix, J.; *J Chin. Chem. Letter.***2001,** 12(11), 1043.

6. Badekar, R. R.; Lokhande, R. S.;Kulkarni, S. W. and Patil, R. M; *Intern. J. Adv. Res.***2016,**4, 7.

7. Badekar, R. R.; Lokhande, R. S.;Kulkarni, S. W. and Patil, R. M; *Intern. J. Adv. Res.***2016,**4, 8.

8. Badekar, R. R.; M.Sc. Dissertation, University of Mumbai, Mumbai, **2012,** pp78-81.

9. Yaw, A. R.; Aswar, A. S.; Dhande, V. V. and Suryawanshi, N. J.; *Polish J Chem.* **2009,** 29, 556.

10. Jorgensen, C. K.; *Abs Spectra and Chem Band in Complexes, Pergamen Press, London.* **1964.**

11. Chandra, S.; Kumar, S. and Rani, S.; *Ind J Chem.* 27, 417-420

12. Chandra, S.; Kumar, S. and Rani, S.; *SpectrchimicaActa.* A78, 1507-1514.

13. Bayoumi, H. A.; Shoukry, E. M. and Mostafa, M.; *Synthetic React Inorg Met Org Chem.***2001,**31, 579.

14. Dayer, J. R.; *Applications of AAS of Org Comp, Prentice Hall of India pvt ltd* **1996.**

15. Singh, N. K. and Singh, S. B.; *Ind J Chem.***2001,**40A, 1047.

16. Barbucci, R. et al; *J ChemSoc.***1969,** 1775(A).

17. Mayuri, R. C. et al; *Polyhedron.***1992,**11, 2837-2840.

18. Sharma, P. K. et al; *J Ind Chem Soc.***1997,** 74, 446-447.

19. Rao CNR; *Chem Appl of IR Spectrum, Acad press, NewYork,* **1963.**

20. Symal, A.; Kumar, D. and Ahmad; *Ind J Chem.***1982,**216, 634.

21. Arima, H.;Ashida, H. and Danno, G.; *Biosci, Biotechol, Biochem.*I**(2002)**66, 1014.

22. Jeongmok, K.; Maurice, R. M. and Chen, I. W.;*J Agric Food Chem;* **1995,**45, 2834.

23. Vogel, A.I. “*A text book of quantitative Inorganic Analysis* ” *Longmans Green and Co. Ltd.*, 3rd Ed., London, **1964**

24. Vogel, A.I.;*Vogel Textbook of Quantitative chemical analysis*” – 5th Ed. Revised *Longman publication*, **1996**

25. Audrieth L.F., Scott E.S. and Kippur P.S., *Chem. Abstr.*, 10857e (1955).

26. Dutta R.L.and Syamal A.; ‘*Elements of Magnetochemistry*’ S. Chand and company Ltd., **1982.**

27. Badekar, R. R.; Lokhande, R. S.;Kulkarni, S. W. and Patil, R. M; *Intern. J. Adv. Res.***2016,**4, 8

28. Nishina, C.; Enolci, N.; Tawata, S.; Mori, A.;Kobryashi, K. and Fukushima, M.;*Agric. Bio. Chem.***1987,** 51, 139.

29. Grover, R. K. and Moore, J. B.; *Phytopathology.***1962,** 52, 879.

30. Migh, Mat.; Ahmad, H. O.; Sharma, N. A.; Ali, A. and Miah, S. A.; *Bangladesh J Bot.* **1990,** 195.

31. Badekar R. R.; *PhD. Thesis; Jaipur National University;* **2017.**

32. Badekar R. R., Kulkarni S. W., Lokhande R. S. and Thawkar B. S.; *Int. J. of App. Res.;* **2016**, 2(9), 175-179.

33. Badekar R. R., Badekar V. R., Kulkarni S. W. and Lokhande R. S; *Make in India: a Myth or Reality;* **2017**, 1037-1049.

34. Badekar R. R., Thube A., Kulkarni S. W. and Lokhande R. S; IJRASET, Vol.6, Issue-VI (2018), 716-719.

35. Chaugule S., Badekar R., Shimpi P., and Lokhande R.; IJRASET; Volume 6 Issue VI, June 2018;1233-1237.