

Synthesis, Magneto-Spectral and Biological Studies of Manganese(II) Complexes with Heteroaroyl Hydrazones

SAYAJI RAO

Department of Chemistry, Osmania University Post Graduate College
Mirzapur-502 249, India
E-mail: s_rao8india@yahoo.com

Manganese(II) complexes of benzoic acid [(furan-2-yl)methylene]hydrazide, benzoic acid [1-(furan-2-yl)ethylidene]hydrazide, benzoic acid [(thiophen-2-yl)methylene]hydrazide and benzoic acid [1-(thiophen-2-yl)ethylidene]hydrazide have been synthesized and characterized by elemental analysis, conductivity, magnetic susceptibility, electronic and infrared spectral data. Magnetic and electronic data suggest dimeric tetrahedral with benzoic acid [(furan-2-yl)methylene]hydrazide, benzoic acid [(thiophen-2-yl)methylene]hydrazide and dodecahedral with benzoic acid [1-(furan-2-yl)ethylidene]hydrazide and benzoic acid [1-(thiophen-2-yl)ethylidene]hydrazide ligands. All the ligands and complexes have been screened for their antifungal and antibacterial activity against fungi and bacteria.

Key Words: Synthesis, Mn(II) complexes, 2-Furylmethyl ketone, Thiophene-2-carboxaldehyde.

INTRODUCTION

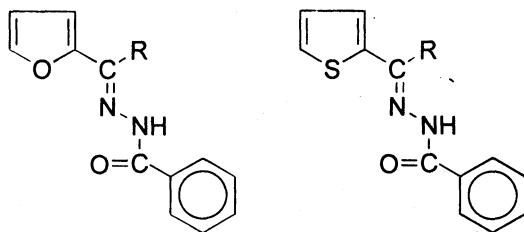
Heterocyclic aroylhydrazones are known to react with divalent transition metal ions forming both cationic and neutral metal chelates of the general formula $M(LH)_2X_2$ and ML_2 (where LH = heterocyclic aroylhydrazones) respectively with the heterocyclic aroylhydrazone acting as neutral or mono negative bidentate ligand. Metal complexes of aroylhydrazones have broad applications in biological processes such as in the treatment of leprosy¹, tuberculosis² and tumour^{3,4}. The present interest in the coordination chemistry of aroylhydrazones stems from their ligational behaviour⁵. Recently, complexes of hydrazones containing furan-2-carboxaldehyde residue have been reported^{6,7}. It should be of interest to study substituted hetero-donor ligands as these complexes are expected to show interesting structural and functional properties. So far no attempt has been made for the synthesis and characterization of transition metal complexes of benzoic acid [(furan-2-yl)methylene]hydrazide (BFMH), benzoic acid [1-(furan-2-yl)ethylidene]hydrazide (BFEH), benzoic acid [(thiophen-2-yl)methylene]hydrazide (BTMH) and benzoic acid [1-(thiophen-2-yl)ethylidene]hydrazide (BTEH).

In the present paper, the author incorporates the synthesis and spectral studies of heteroaroyl hydrazone ligands, *viz.*, BFMH, BFEH, BTMH, BTEH and their manganese complexes.

EXPERIMENTAL

$MnCl_2 \cdot 4H_2O$ was obtained from BDH. Reagent grade furfuraldehyde 2-furylmethylketone, thiophene-2-carboxaldehyde, 2-acetylthiophene and benzhydrazide were purchased from M/s. Fluka and were used as received. The elemental analyses were performed at RSIC, CDRI, Lucknow. Magnetic measurements were carried out in the polycrystalline state on a PAR model 155 vibrating sample magnetometer operating at a field strength of 2–8 kg. The molar conductances of the complexes in DMF (10^{-3} M) solutions were measured at $27 \pm 2^\circ C$ with Systronics model 303 direct reading conductivity bridge. The electronic spectra in nujol were recorded with Cary model 2390 spectrophotometer. The infrared spectra were recorded in the range $4000\text{--}180\text{ cm}^{-1}$ with a Perkin-Elmer 983 G spectrophotometer. The 1H NMR spectra were recorded on a Varian XL-300 MHz high resolution instrument in $CDCl_3$ solvent. The mass spectra were recorded using Fanning Mat 8230 mass spectrophotometer.

Synthesis of ligands BFMH, BFEH, BTMH and BTEH: Hot aqueous solutions of Benzhydrazide (6.8 g, 0.05 mol) were added to a boiling solution of carbonyl compound (0.05 mol) in 200 mL methanol. The reaction mixture was boiled for 1–2 h. On cooling, a pale yellow coloured product was formed, which was collected by filtration, washed several times with hot water and dried *in vacuo*. These ligands were also recrystallized from methanol.



- | | | | |
|-------------------------|------|-------------------------|------|
| I. R = H | BFMH | III. R = H | BTMH |
| II. R = CH ₃ | BFEH | IV. R = CH ₃ | BTEH |

Synthesis of complexes: The complexes were prepared by mixing hot aqueous solution of $MnCl_2 \cdot 4H_2O$ and ligands in the molar ratio of 1 : 2.

To the boiling solution of the ligands (0.01 mol) in methanol (100 mL) was added $MnCl_2 \cdot 4H_2O$ (0.05 mol) dissolved in minimum quantity of water and heated under reflux for 2–6 h. Crystalline complexes which separated out were collected by filtration, washed with hot water, small quantity of methanol and hexane and dried *in vacuo*. Analytical data of the ligands and their complexes are given Table-1.

RESULTS AND DISCUSSION

The analytical and IR data for all the ligands and their manganese complexes are summarized in Table-1. The absorption spectra of 2×10^{-5} M solution of hydrazones at various pH values were recorded. The pKa values for the deprotonation of BFMH, BFEH, BTMH and BTEH, respectively are 3.0, 4.7, 3.7 and 5.6 calculated from variation of absorbance with pH by Philips and Merit's method⁸.

TABLE-1
ANALYTICAL DATA AND SELECTED IR (cm^{-1}) SPECTRAL BANDS OF LIGANDS AND THEIR MANGANESE(II) COMPLEXES

Compound	Colour (m.p., °C)	Found (Calcd) %			IR (cm^{-1})				
		C	H	N	$\nu(\text{N—H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{N—N})$	$\nu(\text{OH})$ of H_2O
BFMH	Light yellow (151–152)	67.4 (67.3)	4.6 (4.6)	13.2 (13.1)	3246 m	1665 m	1642 m	1013 m	
[Mn(BFM)Cl] ₂	Brown (162–163)	47.1 (47.46)	3.0 (2.96)	9.0 (9.22)	3144 m	—	1625	1029 w	
BFEH	Dark brown (143–145)	67.8 (68.4)	5.4 (5.3)	12.5 (12.3)	3229 m	1660 s	1630 m	1020 s	
[Mn(BFE) ₂ (H ₂ O) ₂]	Brown (151–153)	58.9 (57.25)	4.4 (4.77)	10.3 (10.27)			1630 m	1025 w	3414 s
BTMH	Dark yellow (192–194)	63.3 (62.6)	4.1 (4.3)	12.2 (12.2)	3254 s	1660 s	1638 s	1041 m	
[Mn(BTM)Cl] ₂					3086 s		1620 m	1058 s	
BTEH	Yellow (197–199)	64.5 (63.9)	4.8 (4.9)	11.5 (11.4)	3329 m	1650 s	1638 s	1023 m	
[Mn(BTE) ₂ (H ₂ O) ₂]	Red (200–202)	54.5 (54.02)	4.6 (4.5)	9.9 (9.69)	3067 s		1614 s	1035	3440

The proton NMR spectra of BFMH, BFEH, BTMH and BTEH in CDCl_3 show low field signals respectively at 11.23, 11.35, 9.07 and 8.91 ppm for the imino proton⁹ present in ligands. In the spectra of BFMH and BTMH, $>\text{CH}=\text{N}$ peak is observed respectively at 8.60 and 8.80 ppm. Signals due to aromatic protons occur as multiplets between δ 6.4–7.4 ppm. The resonance signals due to CH_3 protons present in BFEH and BTEH occur at 2.38 and 2.30 ppm respectively.

The mass spectra of BFMH, BFEH, BTMH and BTEH show molecular ion peaks. The important peaks observed in the mass spectra of these ligands are m/z 67, 77, 105, 125, 139 and 161, respectively corresponding to $\text{C}_4\text{H}_3\text{O}$, C_6H_5 , $\text{C}_6\text{H}_5\text{CO}$, $\text{C}_4\text{H}_3\text{O}(\text{CH}_3)\text{—C:N—NH}_2$ (BFEH), $\text{C}_4\text{H}_3\text{S}(\text{CH}_3)\text{—C:N—NH}_2$ (BTEH), $\text{C}_6\text{H}_5\text{CONH}$; N—C—CH_3 (BTEH).

All the complexes are crystalline solids, stable at room temperature, non-hygroscopic, soluble in DMF and DMSO, but insoluble in water, methanol and

ethanol. The molar conductivities of *ca.* 10^{-3} M solution of the complex in DMF were found in the range $8-15 \Omega \text{ cm}^{-2} \text{ mol}^{-1}$ indicating their non-electrolytic nature¹⁰.

Magnetic moments: The magnetic moments of $[\text{Mn}(\text{BFM})\text{Cl}]_2$ and $[\text{Mn}(\text{BTM})\text{Cl}]_2$ are found to be 3.8 and 4.2 BM, respectively. These moments are sub-normal to the spin value of 5.9 BM. The magnetic moment values for these complexes suggest magnetic exchange between two manganese centres.

The magnetic moment of $[\text{Mn}(\text{BFE})_2(\text{H}_2\text{O})_2]$ and $[\text{Mn}(\text{BTE})_2(\text{H}_2\text{O})_2]$ complexes are found to be 5.8 and 5.7 BM, respectively. These moments are very close to spin only value¹¹.

Electronic spectra: The electronic spectra of $[\text{Mn}(\text{BFM})\text{Cl}]_2$ and $[\text{Mn}(\text{BTM})\text{Cl}]_2$ show absorbance bands at 22000 and 28000 cm^{-1} . The magnetic moment values together with electronic spectral data suggest a dimeric¹² tetrahedral structure for these complexes. The electronic spectra of $[\text{Mn}(\text{BFE})_2(\text{H}_2\text{O})_2]$ and $[\text{Mn}(\text{BTE})_2(\text{H}_2\text{O})_2]$ complexes exhibit weak spectral bands in the region 22000–23800, 28000–28500 and 31000–32000 cm^{-1} . The positions of electronic spectral bands suggest an octahedral geometry^{13, 14}.

Infrared spectra: Some important bands are observed (Table-1) in infrared spectra of BFMH, BFEH and BTEH and their complexes are considered for identification of donor sites of the ligands. The IR spectra of free ligands exhibit $\nu(\text{NH})$ absorbance bands at *ca.* 3250 cm^{-1} and $\nu(\text{C}=\text{N})$ bands at *ca.* 1640 cm^{-1} indicating that the ligands exist in keto form in the solid state. However, in solution, the ligands probably exist in equilibrium with tautomeric enol form. By the loss of proton, the enolic form may act as a uninegative ligand. The bands appearing in the spectra of ligands *ca.* 1660, 1640, 1535, 1015 cm^{-1} are attributed to amide-I [$\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N})$], amide-II [$\beta(\text{NH}) + (\text{CN})$] modes, respectively. The two strong bands observed at 710–690 and 610–605 cm^{-1} regions are due to furan/thiophene ring deformation modes.

Manganese complexes of BFMH and BTMH: The presence of $\nu(\text{NH})$ in the spectra of these complexes suggests that BFMH and BTMH remain protonated in chelation. Amide-I and amide-II bands shift to lower frequencies in the spectra of these complexes. The strong band observed in the spectra of these ligands at 1640 cm^{-1} is shifted to a lower wavenumber suggesting the participation of azomethine nitrogen in coordination¹⁵. On the other hand, $\nu(\text{N}-\text{N})$ band is shifted to higher frequencies¹⁶ in the spectra of both complexes supporting the coordination of azomethine nitrogen atom. Similarly, the highest frequency band observed due to $\nu(\text{C}=\text{O})$ is shifted to lower wavenumber suggesting the participation of carbonyl oxygen in coordination. The non-ligand bands occurring in the regions 532–500, 410–350 and *ca.* 290 cm^{-1} are tentatively assigned to $\nu(\text{M}-\text{O})$, $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{Cl})$ vibrational modes, respectively¹⁷. The molecular weights of $[\text{Mn}(\text{BFM})\text{Cl}]_2$ and $[\text{Mn}(\text{BTM})\text{Cl}]_2$ were found to be 607 and 639 as required for dimeric complex.

Complexes of BTMH and BTEH: Absorption bands due to $\nu(\text{N}-\text{H})$ and $\nu(\text{C}=\text{O})$ stretching vibrations are not observed in the IR spectra of these complexes. Instead, they show new bands characteristic¹⁸ of $\nu(\text{NCO})$ in the spectra of these complexes suggesting the presence of $\text{>C}=\text{N}-\text{N}=\text{C}<$ res-

ides of the stoichiometry and the destruction of keto group presumably *via* enolization and bonding of the ligand through the resulting enolate oxygen. The red shift of the ring deformation vibrations in the IR spectra of these complexes suggests the participation of furan oxygen and thiophene sulphur in complex formation. The bands observed in the 500–595, 475–495 cm^{-1} regions, which are absent in the spectra of ligands may tentatively be assigned $\nu(\text{M—O})$ and $\nu(\text{N—N})$ vibration modes¹⁹ respectively. The highest energy bands in the IR spectra of $[\text{Mn}(\text{BFE})_2(\text{H}_2\text{O})_2]$ and $[\text{Mn}(\text{BTE})_2(\text{H}_2\text{O})_2]$ complexes observed at 3440 and 3414 cm^{-1} respectively are assigned to the presence of coordinated water molecules.

Antifungal and antibacterial activity: All the complexes and ligands were screened for their antifungal activities against *Aspergillus niger*, *Aspergillus flavus*, *Aspergillus nidulans* and *Aspergillus pterius* by spore suspension²⁰ method at concentrations 100, 200 and 300 $\mu\text{g/d}$ using potato dextrose agar medium (PDA). It is observed from the data that the metal complex of $[\text{Mn}(\text{BFM})\text{Cl}]_2$ only showed inhibition zone at 200 and 300 $\mu\text{g/d}$ respectively towards *Aspergillus pterius*. At the same time the other fungi are found to be tolerant to the other complexes and ligands or do not have inhibition activity against the above fungi.

All the complexes and ligands were screened for antibacterial activity against *Staphylococcus aureus*, *Bacillus subtilis*, *Pseudomonas aeruginosa* and *Escherichia coli*. The testing was carried out by disc diffusion method²¹ using 100, 200 and 300 $\mu\text{g/d}$ in DMF. The zones of inhibition are recorded after incubation for 18 h. It is observed that the ligand BTEH showed inhibition towards two bacteria, *viz.*, *Staphylococcus aureus* and *Escherichia coli* and 200 $\mu\text{g/d}$ and 300 $\mu\text{g/d}$ respectively. This might be due to the influence of inductive effects of methyl group and the presence of sulphur atom in the heterocyclic ring of the ligand.

Conclusion

Chemical composition, conductivity measurements, magnetic moments and electronic together with infrared spectral data suggest a dimeric structure for $[\text{Mn}(\text{BFM})\text{Cl}]_2$ and $[\text{Mn}(\text{BTM})\text{Cl}]_2$ and dodecahedral structure for $[\text{Mn}(\text{BFE})_2(\text{H}_2\text{O})_2]$ and $[\text{Mn}(\text{BTE})_2(\text{H}_2\text{O})_2]$ respectively.

ACKNOWLEDGEMENT

The author thanks CDRI, Lucknow and RSIC, Bombay and Madras for providing elemental analysis and spectral data, respectively.

REFERENCES

1. N.P. Bau-Hri, M.D. Xuong, F. Binyon and F. Roger, *J. Chem. Soc.*, 1358 (1953).
2. T.S. Ma and T.M. Tein, *Antibiotics and Chemotherapy*, **3**, 491 (1953).
3. M. Mesubi, D. Adediran and B. Ugo, *Synth. React Inorg. Met-org. Chem.*, **23**, 435 (1993).
4. M. Mohan, A. Kumar, M. Kumar and N.K. Jha, *Inorg. Chim. Acta.*, **136**, 63 (1987).
5. K.L. Dutta and M.M. Hussain, *J. Sci. Ind. Res.*, **44**, 635 (1985).

6. B. Singh, R.N. Singh and R.C. Aggarwal, *Synth. React. Inorg. Met-Org. Chem.*, **14**, 815 (1984).
7. K.H. Ibrahim, T.H. Rakha, A.M. Abdalla and M. Hussain, *Indian J. Chem.*, **31A**, 58 (1992).
8. J.P. Phillips and L.L. Merrit, *J. Am. Chem. Soc.*, **70**, 410 (1948).
9. J. Goffart, J.P. Mevriar and G. Duyckaerto, *Inorg. Nucl. Chem. Lett.*, **14**, 233 (1980).
10. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1977).
11. S. Sugden, *J. Chem. Soc.*, 328 (1943).
12. D.K. Rastogi, S.K. Sahani, V.B. Rana and S.K. Dua, *Transition Met. Chem.*, **3**, 56 (1978).
13. J. Lewis, P.P. Mabbs and A. Richards, *J. Chem. Soc. (A)*, 1014 (1967).
14. E.K. Barefield, D.H. Busch and S.M. Nelson, *Q. Rev.*, **22**, 457 (1968).
15. R.C. Agarwal and K.K. Narang, *Inorg. Chim. Acta*, **1**, 65 (1973).
16. M. Rosatzur, *Spectrochim. Act.*, **19**, 1107 (1963).
17. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd Edn., Wiley-interscience, New York (1978).
18. N.K. Singh and R. Tripathi, *Transition Met. Chem.*, **13**, 346 (1988).
19. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York (1963).
20. R.S. Gordec, T.R. Mathews, *Antimicrob. Ag. Chemo. Ther.*, 378 (1967).
21. *Indian Pharmacopoeia*, Controller of Publications, Delhi, Vol. II, p. 105 (1996).

(Received: 25 January 2005; Accepted: 25 July 2005)

AJC-4307