

STUDIES ON SOME SCHIFF BASE COMPLEXES DERIVED FROM 3-HYDROXY-QUINOXALINE-2-CARBOXALDEHYDE AND VARIOUS AMINES WITH MANGANESE (II)

Mayadevi S^{1*}, Basil Baby², Sudha George Valavi³ and K.K. Mohammed Yusuff⁴

1. Dr. Mayadevi S., Dept of Chemistry, NSS College of Engineering, Palakkad-678008, Kerala, India
2. Basil Baby, Ahalia School of Engineering and Technology, Kerala
3. Sudha George Valavi, Professor, Sahrdaya College of Engineering and Technology, Thrissur, Kerala
4. Dr. K.K.Mohammed Yusuff, Professor (Retd), Cochin University of Science and Technology

Many of the manganese (II) complexes are reported to be highly efficient oxidation catalysts in the oxidation of a wide range of organic compounds including alkyl benzenes, alcohols, carboxylic acids, phenols and ethers [1]. Mn (II) SALEN complexes are widely known as epoxidation catalysts for many years [2-6]. The manganese (II) complexes of Schiff bases containing heterocyclic ring systems are interesting to understand the oxidation state accessibility of Mn (II) due to the deactivation caused by the heteroatom compared to the carbocyclic ring system.

1. Materials and Methods

3-Hydroxy-2-methylquinoxaline was obtained by mixing aqueous solutions of o-phenylene diamine to that of sodium pyruvate which is already acidified with conc. HCl slightly in excess than needed to convert sodium pyruvate to pyruvic acid in 1:1 molar ratio. The resultant solution was stirred for about half an hour and the product was separated by filtration.

3-Hydroxy-2-dibromomethylquinoxaline was obtained by adding a solution of bromine in glacial acetic acid (10 % v/v) to a solution of 3-Hydroxy-2-methylquinoxaline in glacial acetic acid (0.1 mol in 200 mL acetic acid). The precipitated dibromo compound was filtered and purified by recrystallization from 50 % alcohol (m.p. 246 °C). The dibromo compound (5 g) was intimately mixed with calcium carbonate (20 g) and the mixture was mixed with 1.5 L of water and heated on a water bath. The hot solution of the aldehyde was cooled to room temperature and the solution was employed as such for the synthesis of the complexes.

1 a Preparation of the Ligands

The Schiff base ligands (1-hydroxyquinoxaline-2-carboxalidene) ethylenediamine, (QED), N,N'-bis (3-hydroxyquinoxaline-2-carboxalidene)-o-phenylenediamine, (QPD), 3-Hydroxyquinoxaline-2-carboxaldehyde hydrazone, (QHD) and N,N'-bis (3-hydroxyquinoxaline-2-carboxalidene) diethylenetriamine (QDT) were prepared by mixing ethanolic solutions of the respective amines (2 g in 20 mL alcohol) in a drop wise manner to that of 3-hydroxy quinoxaline-2-carboxaldehyde (0.025 M with respect to HCl, in the case of QED and QPD, 0.05 M with respect to HCl in the case of QHD and slightly acidic with respect to HCl for QDT). All the Schiff bases were separated as yellow precipitates which were recovered by filtration and subsequent washing with methanol and kept over vacuum

for drying. The melting points of the complexes are determined to be 260 °C, 225 °C, 200 °C and 200 °C for QED, QPD, QHD and QDT respectively.

1 b Preparation of Complexes

0.01 M solution of the ligands (0.01 M) (QED, QPD, QHD and QDT) was added to a methanolic solution of NaOH and refluxed for 30 minutes. Solution of Mn(II) acetate in deoxygenated methanol 0.01M was mixed with the above ligand solution and stirred under nitrogen atmosphere for an hour. The complexes precipitated was filtered and washed with deoxygenated methanol. The complexes were non-hygroscopic and they were completely soluble in DMSO, DMF, nitrobenzene, pyridine and sparingly soluble in methanol and ethanol. All the complexes are non-electrolytes in pyridine and the metal ligand ratio is 1:1 and the empirical formulae is [MnL] where L= QED, QPD, QHD or QDT in all the complexes.

2. Results and Discussion

The complexes were found to be non-hygroscopic in nature and the solubility tests indicated its soluble nature in pyridine, nitrobenzene, DMF, DMSO and they exhibited very poor solubility in methanol and ethanol.

2a Chemical Analysis

The analytical data are presented in Table 1 and it is agreeable to a ligand to metal ratio of 1:1.

Table 1 Analytical data of the complexes Found (Calculated)

| Compound | % Carbon | % Hydrogen | % Nitrogen | % Manganese |
|------------------------|---------------|-------------|---------------|---------------|
| [Mn(QED)] ₂ | 56.38 (56.47) | 3.74 (3.76) | 19.81(19.76) | 13.04 (12.92) |
| [Mn(QPD)] ₂ | 60.75 (60.89) | 3.35(3.38) | 17.81(17.76) | 11.83 (11.6) |
| [Mn(QHD)] | 51.98 (52.05) | 3.25 (3.32) | 20.33 (20.24) | 13.34 (13.24) |
| [Mn(QDT)] ₂ | 56.20 (56.4) | 4.37 (4.48) | 21.10 (20.94) | 11.85 (11.74) |

2b Magnetic and conductivity studies

All the four complexes shows magnetic moment values close to the spin-only value of a high-spin d⁵ system [7,8]. In the [Mn(QED)]₂, [Mn(QHD)]₂ and [Mn(QDT)]₂ complexes, the slightly lower values of the magnetic moment than the spin only value suggests the existence of antiferromagnetic coupling propagating due to the metal - metal bridging interaction. The magnetic moment values are presented in Table 2. In the [Mn(QPD)] complex the magnetic moment value is not deviated from the spin only value ruling out any dimerization or distortion which may be attributed to the rigid nature of the QPD ligand.

Table 2 Magnetic and Conductance data of the complexes

| Compound | Colour | Magnetic moment (BM) | Conductance Ohm ⁻¹ cm ² mol ⁻¹ |
|------------------------|--------|----------------------|---|
| [Mn(QED)] ₂ | Yellow | 4.6 | 1.4 |
| [Mn(QPD)] | Yellow | 5.7 | 1.2 |

| | | | |
|------------------------|--------|-----|-----|
| [Mn(QHD)] ₂ | Yellow | 4.5 | 1.1 |
| [Mn(QDT)] ₂ | Yellow | 4.8 | 1.4 |

2c Infrared Spectra

The coordination of the azomethine nitrogen is indicated from the shift of the IR stretching frequency of the C=N bond to lower frequencies [9]. The deprotonation and the coordination of the phenolic O-H group is shown by the absence of $\nu_{\text{O-H}}$ in all the complexes except that of [Mn(QHD)]₂. In the case of [Mn(QHD)]₂ complex, the coordination of phenolic oxygen does not occur as evidenced from the retention of the $\nu_{\text{O-H}}$ band at 3350 cm⁻¹. The $\nu_{\text{C=O}}$ stretching band at 1282 cm⁻¹ in the IR spectrum of the ligand is undergoing a blue shift to 1300 cm⁻¹ in the IR spectra of the three complexes except [Mn(QHD)]₂ [10]. This substantiates the coordination of the ligands via the azomethine nitrogen and the two phenolic oxygen atoms to the metal ion. In [Mn(QHD)]₂ the coordination of the ligand through the azomethine group along with the phenolic group is not possible due to the stereochemistry of the ligand QHD. The red shift of the N-H stretching frequency in this complex evidences the coordination of the N-H nitrogen to the metal. In the [Mn(QHD)]₂ complex, the square planar geometry arises probably due to the coordination of azomethine nitrogen of one molecule to the metal centre of the neighbouring molecule and vice versa which leads to dimerization. The super exchange mechanism propagating through two 2-atom bridges gives rise to antiferromagnetism. In the ligand QDT, in addition to the azomethine nitrogen and the phenolic oxygen, the amino nitrogen is also coordinating which enables the ligand to bind the metal ion in a pentadentate manner [11].

2d Electronic spectra

There are no characteristic d-d transitions in the spectra of the complexes and this is due to the fact that in a d5 system the electronic transitions are spin forbidden [12].

2e EPR Spectra

The EPR spectra of all the complexes were recorded in DMSO at liquid nitrogen temperature. The g values of all the complexes were found to be 2 and this is in accordance with the results of manganese (II) systems in the literature [13].

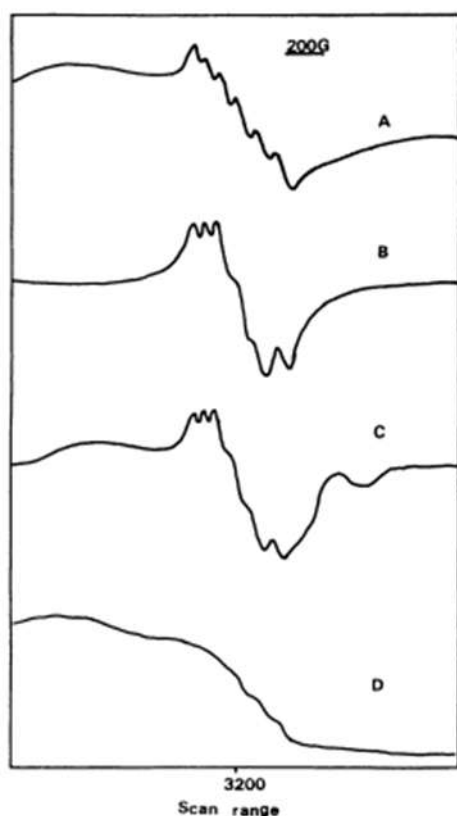


Fig. 1 EPR spectra of the complexes in DMSO at LNT

Table 3. EPR spectral data of the complexes

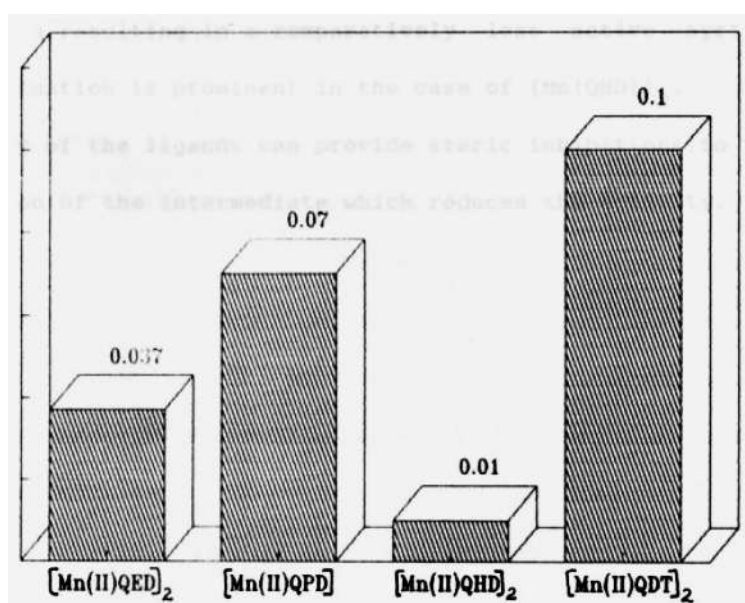
| Compound | G_{av} | A_{av} |
|------------------------|----------|----------|
| [Mn(QED)] ₂ | 2.0 | 87 |
| [Mn(QPD)] | 2.0 | 62 |
| [Mn(QHD)] ₂ | 2.0 | 75 |
| [Mn(QDT)] ₂ | 2.0 | 80 |

2f Catalytic Activity Studies in the oxidation of hydrogen peroxide

The disproportionation of H_2O_2 by the metal chelates therefore draws immense importance in bioinorganic chemistry. The catalytic efficiency of the synthesised Mn(II) complexes in the oxidation of H_2O_2 , have been investigated. The commercially obtained H_2O_2 solution was diluted to a concentration of 0.5 % with deionized water and its concentration was determined by potassium permanganate method. 2.5×10^{-5} mol of the complexes were used as the catalyst each time. 50 mL of 0.5 % H_2O_2 solution was mixed with the catalyst in the reaction vessel and the potassium permanganate taken in a U tube apparatus. After making the levels of the solution equal in the two arms readings were noted at an interval of 300seconds. The rate of the reaction was followed by a computerised technique [14].

Table 4 The catalytic activity of the complexes [Mn(QED)]₂, [Mn(QPD)], [Mn(QHD)]₂, [Mn(QDT)]₂ in the disproportionation reaction of H₂O₂

| | Complex | Rate of O ₂ evolved per second in mL |
|---|------------------------|---|
| 1 | [Mn(QED)] ₂ | 3.7 x 10 ⁻² |
| 2 | [Mn(QPD)] | 7.3 x 10 ⁻² |
| 3 | [Mn(QHD)] ₂ | 1.0 x 10 ⁻² |
| 5 | [Mn(QDT)] ₂ | 12.8 x 10 ⁻² |

**Fig.2** Hydrogen Peroxide Decomposition Catalysis by Mn(II) complexes.

The catalytic efficiency of the complexes are found to be decreasing in the order [Mn(QDT)]₂ > [Mn(QPD)] > [Mn(QED)]₂ > [Mn(QHD)]₂. The physical state of the catalyst is found to influence its catalytic effectiveness in the reaction as it is a heterogeneous system and the complexes are having a hydrophobic nature. The formation of a vacant coordination site during the oxidative dissociation of the dimeric complex and the preferential formation of an H₂O₂ adduct with the penta coordinate [Mn(QDT)]₂ is a possible explanation for the very high activity exhibited by the complex. The catalytic behaviour which is arising from such vacancy in the coordination sphere with labile ligand systems are powerful biomimetic models of metalloproteins [15, 16]. The high catalytic activity of the [Mn(QPD)] complex may be the result of the square planar structure of the complex which enables enhanced interaction with the H₂O₂ reactant [17]. The stability of the dimeric structure may be the reason for the low activity shown by the complexes [Mn(QED)]₂ and [Mn(QHD)]₂ towards the oxidation of H₂O₂. The steric hindrance offered to the approach of the H₂O₂ molecule by the ligand environment is blocking the intermediate formation in these cases.

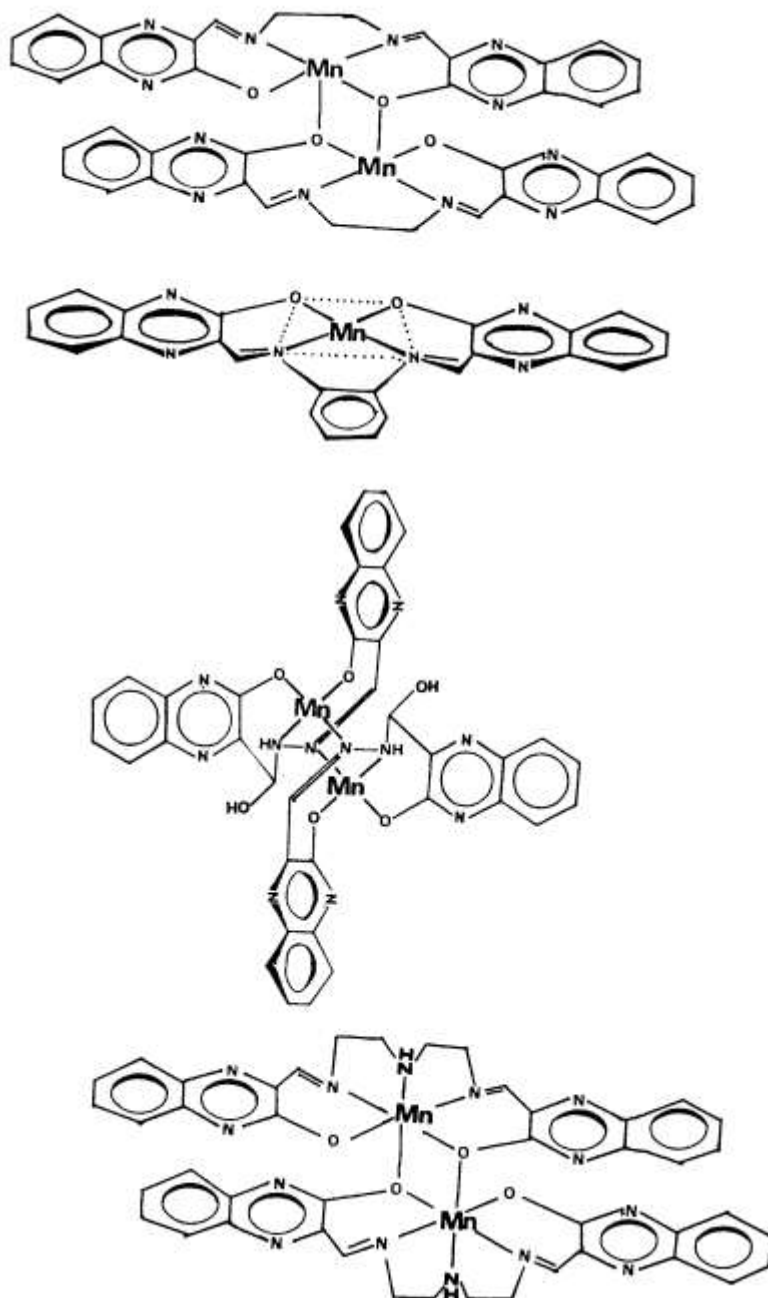


Fig. 3 The structures proposed for the complexes

A. $[Mn(QED)]_2$, B. $[Mn(QPD)]$, C. $[Mn(QHD)]_2$ and D. $[Mn(QDT)]_2$

REFERENCES

1. Benzon, D.; "Mechanism of Oxidation of Metal Ions", Elsevier, New York (1976).
2. Djebbar-Sid, S.; Benali-Baitich, Q.; Transition Met. Chem., 23, 443±447 (1998).
3. Pérez-Otero, Y.; Fernández-García, M. I.; Gómez-Fórneas, E.; González-Riopedre,,; Gland Maneiro, M., Hindawi, 2015 <https://doi.org/10.1155/2015/963152>.

4. Kumar, G.; Johari, R.; Devi, S., *E-Journal of Chemistry*, 2012, 9, no. 4, pp. 2119–2127.
5. López-Torres, E.; Mendiola, M. A., *Inorganica Chimica Acta*, 2010, 363, no. 6, 1275–1283.
6. González-Riopedre, G.; Fernández-García, M.I.; González-Noya, A. M.; Vázquez-Fernández, M. Á.; Bermejo, M. R.; Maneiro, M., *Physical Chemistry Chemical Physics*, 2011, 13, no. 40, 18069–18077.
7. B. N. Figgis and J. Lewis, "Progress in Inorganic Chemistry", F. A. Cotton, Ed, Interscience, New York, 4 (1964) .
8. A. Earnshaw, "Introduction to Magnetochemistry", Academic Press, New York (1968)
9. Ohtani, S.; Nakamura, M.; Gon, M.; Tanaka, K.; Chujoa, Y., *Chem. Commun.*, 2020, 56, 6575–6578, (<https://doi.org/10.1039/D0CC02301A>)
10. Smith, B. C., *Spectroscopy*, 2017, 32, Issue 3, 14–21.
11. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", John Wiley & Sons 4 New York, 4th Edn. (1986).
12. Wegeberg, C.; Wenger, O. S., *Am. Chem. Soc.*, 2021, 1, 11, 1860–1876, (<https://doi.org/10.1021/jacsau.1c00353>).
13. R. D. Dowsing, J. F. Gibson, D. M. L. Goodgame, M. Goodgame and P. J. Hayward, *Nature*, 219 (1968) 1037.
14. N. Sreedevi, "Some Kinetic and Mechanistic Studies on the Oxidation of Selenium(IV)" Ph.D. Thesis, Andhra University, Visakhapatnam, India, 1991.
15. Young, K. J.; Takase, M. K.; Brugvig, G. W., *Inorg Chem.* 2013, 52(13): 7615–7622 (doi: 10.1021/ic400691e).
16. Bermejo, M. R.; Fernández, M. I.; A. M. González-Noya A. M. *Journal of Inorganic Biochemistry*, , 2006, 100, 1470–1478.
17. Sun, W.; Sun, Q., *Acc. Chem. Res.* 2019, 52, 8, 2370–2381 (<https://doi.org/10.1021/acs.accounts.9b00285>)