IJFANS INTERNATIONAL JOURNAL OF FOOD AND NUTRITIONAL SCIENCES
ISSN PRINT 2319 1775 Online 2320 7876
 Journal Volume 11, Iss 12, 2022

The Structural and Catalytic Activity Studies of some iron (III) complexes of the Schiff bases derived from 3-Hydroxy-quinoxaline-2-carboxaldehyde with various amines

Mayadevi S[1]*, Sudha George Valavi[2] Basil Baby[3], and K.K. Mohammed Yusuff[4]

1. **Dr. S.Mayadevi,** Dept of Chemistry, NSS College of Engineering, Palakkad-678008, Kerala, India,
2. **Dr. Sudha George Valavi**, Professor, Sahrdaya College of Engineering & Technology, College Road, PB NO 17, Kodakara, Kerala- 680684.
3. **Basil Baby**, Research scholar, Research and Development Center, Bharathiar University, Coimbatore-641046.
4. **Dr. K.K.Mohammed Yusuff**, Professor (Retd), Cochin University of Science and Technology, Harithakam, Unity road, Thrikkakara PO Kochi 682048, Kerala, India

Abstract

Iron (III) complexes of four Schiff base ligands of 3-hydroxy-quinoxaline-2-carboxaldehyde with the amines ethylenediamine (QED), o-phenylenediamine (QPD), hydrazine hydrate (QHD) and diethylenetriamine (QDT) were synthesized and the characterization of the complexes were done by spectral, magnetic and conductance measurements. The catalytic activity of the complexes incorporated on Seralite SRC 120 resin as support were screened in the oxidation of the biologically important substrate vitamin C. All the supported complexes were found to be catalytically active in this reaction and were stable during the reaction. Two of the complexes with flexible ligands QED and QDT were more active towards this reaction, than the other two complexes.

Keywords: 3-Hydroxy-quinoxaline-2-carboxaldehyde, Schiff base, Fe(III) complexes, ethylenediamine, *o*-phenylenediamine, hydrazone, diethylenetriamine, , ascorbic acid

Introduction

The design of Schiff base ligands containing heterocyclic ring systems draw special importance due to the scope of enhancing interesting properties in the resultant metal complexes (1,2). The electronic properties are modified by the presence of heterocyclic ring system. In this context we have designed and prepared certain Fe(III) Schiff base complexes having the quinoxaline ring system which is expected to induce interesting properties due to the tuning of the electronic structure. The complexes are expected to mimic the biological systems due to the structural resemblance which may lead to similarity in properties. Ascorbic acid can be used for screening the catalytic activity of the complexes prepared, as it is easily oxidized to dehydroascorbic acid and it is a vital biological reducing agent. Hexacyanoferrate (III) was proven to be a very effective catalyst in this reaction.(3-5)

Experimental

Synthesis of the aldehyde: A new procedure adopted consists of three synthetic steps as shown below

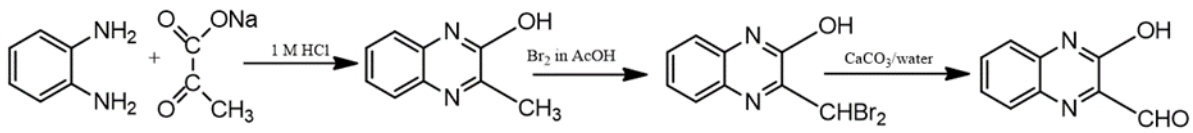

Fig. 1*: Scheme of Preparation of 3-hydroxy quinoxaline-2-carboxaldehyde*

Preparation of 3-Hydroxy-2-methylquinoxaline

o-Phenylenediamine was mixed and reacted with sodium pyruvate and excess HCl (conc) and stirred for 30 minutes. The separated product was obtained by filtration, purified by gentle flushing with water and stored over anhydrous $CaCl_2$. (Yield: 90 %, melting point 255°C, pale yellow colour).

The 3-Hydroxy-2-methylquinoxaline was dissolved in glacial acetic acid (0.1 mol/200mL) and Br_2 in acetic acid (10 % v/v,) was poured and the mixture was stirred. Then it was exposed to sunlight for 1 hour while stirring is done from time to time. 3-Hydroxy-2-dibromomethylquinoxaline was

ISSN PRINT 2319 1775 Online 2320 7876
, Journal Volume 11, Iss 12, 2022

precipitated on dilution of the solution to I litre and the compound was obtained in a pure form by flushing with water and recrystallised from 1:1 ethanol. (Yield : 95 % , melting point 246 ºC).

Precipitated calcium carbonate was intimately mixed with the dibromo derivative in (5g:20 g). This mixture was mixed with water (1500 mL) and the reaction was carried out over a water bath while shaking the mixture from time to time. The product which was stable in the aqueous medium could be obtained by filtering the hot reacting solution. The Schiff base syntheses were accomplished directly with the yellow aqueous solution obtained after cooling.

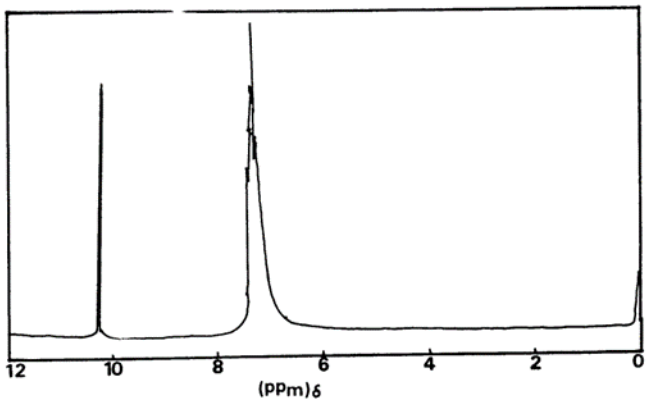

Fig. 2: NMR spectrum of 3-hydroxy quinoxaline-2-carboxaldehyde in d^6 DMSO

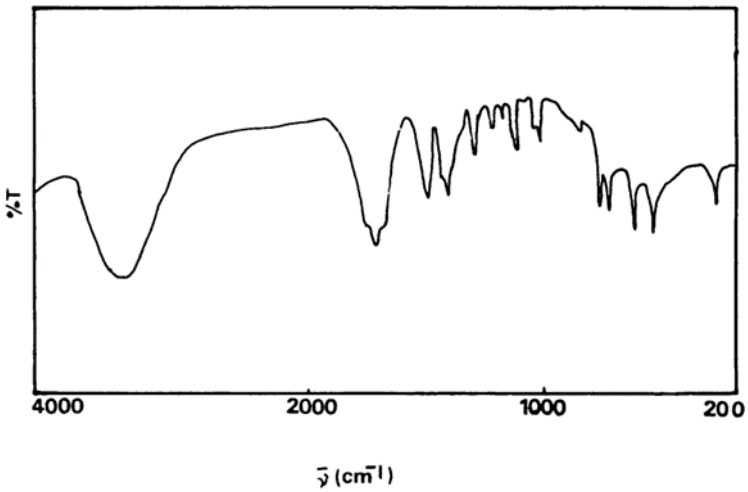

Figure 3: IR spectrum of 3-hydroxy quinoxaline-2-carboxaldehyde

Preparation of the Schiff bases

The Schiff bases N,N'-bis (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 the following procedure. An alcoholic solution of ethylenediamine (1:10 v/v ratio) was added drop by drop to a solution of aldehyde (0.025 molar in the case of QED and QPD, 0.05 molar for QHD and feebly acidic in the case of QDT with respect to HCl) with stirring. The Schiff bases precipitated were separated by filtration and further purified by washing with methanol and dried by keeping in vacuum over anhydrous calcium chloride. All the complexes were yellow compounds. (Yield: 50-70%, melting points 260 ºC, 225 ºC, 200 ºC and 200 ºC).

ISSN PRINT 2319 1775 Online 2320 7876
 Journal Volume 11, Iss 12, 2022

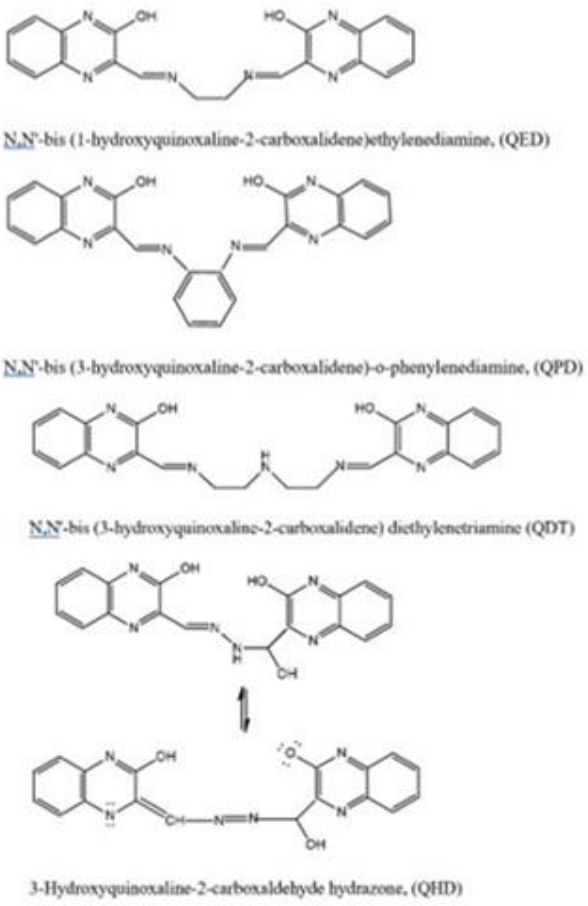

Figure 4. Proposed structures of the ligands

Preparation of complexes

0.01 mol of the respective ligand (3.72 g; QPD, 4.18 g; QHD, 3.44 9g QDT or 4.14 g QED) was made into a powder and dissolved in methylene dichloride (75 mL) and mixed with a solution of anhydrous ferric chloride (0.01 mol, 1.62 g) in methanol (25 mL) in an RB flask. The mixture was refluxed on a water bath for about an hour. The solution was filtered to remove any unreacted ligand species and the solution was then subjected to boiling till the resultant volume was reduced to half. The solution was cooled when the complexes crystallised out from the solution which could be obtained by filtration, The complexes were washed with ether and dried in vacuum over anhydrous $CaCl_2$. The yield was around 40-50 % for all the complexes and the melting points were above 250°C.

Heterogenization of complexes

The complexes were supported using the following procedure: The iron (III) complexes were heated under reflux with the resin in ethanol in the weight ratio for 2 hours. When the complex is taken up by the SRC 120 resin, there is a change in colour from an initial yellow to brown. The labile Fe-Cl bond is assumed to undergo rupturing and the complex gets supported on the resin during this process. The resin after incorporation of the complex was obtained by filtration. The chloride ion concentration of the filtrate was also estimated. The product of oxidation, dehydroascorbic acid, was estimated after each experiment by Roe's method (12).

Microanalyses for carbon, hydrogen and nitrogen were done on a Heraeus CHN elemental analyser.

The estimation of the metal was done in all the four cases after eliminating the organic content. This was done by digesting a known weight of the complexes (about 0.25 g) with conc. sulphuric acid (5 mL) and in turn by conc. nitric acid (20 mL) and when the vigorous reaction was completed 5 mL of 60 % perchloric acid was added and the boiling was continued for 3 hours on a sand bath. The mixture was then evaporated to dryness with subsequent addition of about 5 mL of nitric acid and again evaporated to dryness. The residue was dissolved in water and was used for the estimation of iron. Metal estimation was done by titrating against standard $K_2Cr_2O_7$ solution after reducing to $SnCl_2$.

Peroxide fusion of the sample and subsequent gravimetric precipitation as AgCl was the method used for the determination of halogen content of the complexes.

Magnetic susceptibility measurements were carried out at room temperature with $Co[H_g(SCN)_4$ as the (7) standard on a simple Gouy-type magnetic balance.. Molar conductance values were almost similar for all the complexes both in nitrobenzene and pyridine at using a conductivity bridge (Century CC 601) with a dip type cell and a platinised platinum electrode. All the complexes were appreciably soluble in nitrobenzene and pyridine but they remained stable only in pyridine. Electronic spectra were taken in solution or in the solid state by mull technique. The UV-Vis spectra of the complexes were recorded on a Shimadzu l60A spectrophotometer both in the solid and dissolved states. The FTIR spectra of the ligands and the complexes in the region, 4600-400 cm were taken as KBr discs and nujol mull on a Shimadzu 8101 FTIR spectrophotometer. NMR spectrum of 3-Hydroxy-quinoxaline-2-carboxaldehyde was recorded on Hitachi R 600 High Resolution NMR spectrometer.

A Varian E-l12 X/Q band spectrometer was used to take X-band EPR spectra of the complexes. Quartz tubes were employed to obtain the solid state spectra of the complexes.

Mossbauer spectra were taken at room temperature and at liquid nitrogen temperature (magnetic field = 0) on a polycrystalline sample using a Canberra 8100 Mossbauer spectrometer with a ^{57}Co source blended to a cryostat. The standard used was sodium nitroprusside spectrum collected at room temperature.

Procedure adopted for the oxidation of ascorbic acid

The ascorbic acid solution (2.5 X 10- 4 M, 50 mL), was prepared afresh and mixed with the SRC 120 resin (500 mg). The absorbance values of the resultant solution were recorded at 250 nm at intervals of 10 minutes. From the concentration versus time data, rates of the reactions could be evaluated.

Results and Discussion

The complexes were crystalline in nature and stable in air. The complexes exhibited high solubility in DMSO, DMF, nitrobenzene, pyridine and only partial solubility in ethanol and methanol. From the elemental analyses (Table I) the complexes were formulated as [FeLCI], where L is QED, QPD, QHD or QDT. The molar conductance values (Table 2) of the complexes suggest. that $[Fe(QED)CI]_2$, [Fe(QPD)CI] and $[Fe(QHD)CI]_2$ are non-electrolytes in pyridine i.e., the chlorine atom is directly attached to the metal. The complex of QDT showed a molar conductance value normally given by a 1:1 electrolyte. In this case, the chloride ion was thought (8) to be out of the coordination sphere and the complex might be formulated as [Fe(QDT)]CI and probably as a dimer, $[Fe(QDT)]_2CI_2$ (91).

Analytical Data

Table 1

Complex	% C	% H Found (Calculated)	% N	% Cl	% F
$[Fe(QED)CI]_2$	51.96	3.38	18.31	7.64e	12.22

ISSN PRINT 2319 1775 Online 2320 7876
 Journal Volume 11, Iss 12, 2022

	(52.02)	(3.46)	(18.20)	(7.68)	(12.10)
[Fe(QPD)CI]	56.47 (56.54)	3.09 (3.14)	16.53 (16.49)	7.12 (6.96)	10.85 (10.96)
$[Fe(QHD)CI]_2$	47.79 (47.86)	3.06 (3.10)	18.74 (18.60)	7.81 (7.86)	10.52 (10.63)
$[Fe(QDT)]_2CI_2$	52.28 (52.34)	4.05 (4.10)	19.52 (19.43)	17.20 (17.03)	11.00 11.07

The slightly low values of the magnetic moments of the compounds $[Fe(QED)CI]_2$ and $[Fe(QHD)CI]_2$ indicate a dimeric structure which might cause antiferromagnetic coupling as reported before (9-13). [Fe(QPD)Cl] has a magnetic moment value of 5.87 BM. No orbital contribution can be present in this case and rules out any metal-metal interaction. The significantly lower magnetic moment value of the $[Fe(QDT)]_2CI_2$ complex when compared to a spin free complex may be due to the spin cross over in the Fe (III) centre at ambient temperature. The system is supposed to be a combination of low-spin and high-spin Fe(III) ions. Spin cross over phenomena is observed only in octahedral geometries in iron (III) complexes. The role of antiferromagnetic coupling is also expected due to possibility of a dimeric structure for the complex. Spin transitions in the solid state are reported to be cooperative in nature in which an interplay of the spin crossover vs antiferromagnetic coupling may be expected which is thought to have a vital role here (10-12).

Table 2

Magnetic and Conductance data of the complexes

Compound	Colour	Magnetic moment (BM)	Conductance $Ohm^{-1}cm^2mol^{-1}$
$Fe(QED)Cl_2$	Brown	5.27	5
$Fe(QPD)Cl_2$	Brown	5.87	6
$Fe(QHD)Cl_2$	Brown	5.52	4
$Fe(QDT)Cl_2$	Yellowish red	4.55	113

Infrared spectra: The important spectral bands and their assignments are given in Table.3. The C=N stretching frequency of the azomethine group do not undergo any appreciable shift in the metal complexes. A broadening of this band was actually observed which may be due to the keto-amine tautomeric structure possible for the ligand of these types. The interaction with a hard Lewis acid like Fe(III) ion can cause a change in hybridisation at the SP^2 hybridised azomethine nitrogen by generating a partial sp^3 character in it (13,14). The band around 1282 cm^{-1} in the free ligands which may be assigned to the C-O stretching frequency of the phenolic group was shifted to higher frequencies 1300 cm^{-1} in the complexes. The ligand coordination through the phenolic oxygen atoms was indicated by the blue shift of ν_{C-O} band and the retention of the O-H stretching frequency at 3350 cm^{-1} in the spectrum of the QHD complexes (15). The coordination of amino group of the ligand to the metal is suggested by a change in C-N stretching frequency in $[Fe(QDT)]_2C1_2$ (16).

In the electronic spectra of the complexes, no characteristic d-d bands are observed indicating that electronic transitions are spin forbidden. But a band at 18200 cm^{-1} observed in the electronic spectrum of $[Fe(QDT)]_2CI_2$ complex is assigned to be due to the ^2T_g--> E_g transition, characteristic of low spin Fe(III) species. The existence of high-spin - low-spin equilibrium in this system further supported by this observation.

ISSN PRINT 2319 1775 Online 2320 7876
 Journal Volume 11, Iss 12, 2022

Figure 5 shows powder EPR spectra of $[(Fe(QDT)_2]C1_2$ at three different temperatures. In this complex, several effects like relaxation, spin-orbit coupling, zero field splitting and strong antiferromagnetic exchange interaction are expected to operate in the solid state. The EPR spectra of this complex cannot be fully explained on the basis of simple high-spin and low-spin mixtures. The EPR spectrum at 133 K evidences the presence of low-spin Fe(III) ion. This is expected from a probable transition from high-spin to low-spin state, the system can encounter at lower temperatures which can be accompanied by a geometrical change. The Kramers doublets of the rhombic Fe(III) ion in this spectrum are occurring as absorptions at g = 9.8, g = 5 and g = 0.75. The rhombic nature is also confirmed by the fine splitting on the high field signal. There is a decrease in the intensity of the signals of the high-spin Fe(III) at higher fields.

The low-spin signal at g = 2 is also weakened at this temperature. In a distorted geometry, low-spin Fe(III) centres suffer large zero field splitting and eventually makes the ground state orbitally and electronically non-degenerate and therefore it would be difficult to observe an EPR spectrum. Furthermore, strongly antiferromagnetically coupled low-spin Fe(III) centres can have an S = 0 ground state. This also causes the loss of intensity of the low-spin signal.

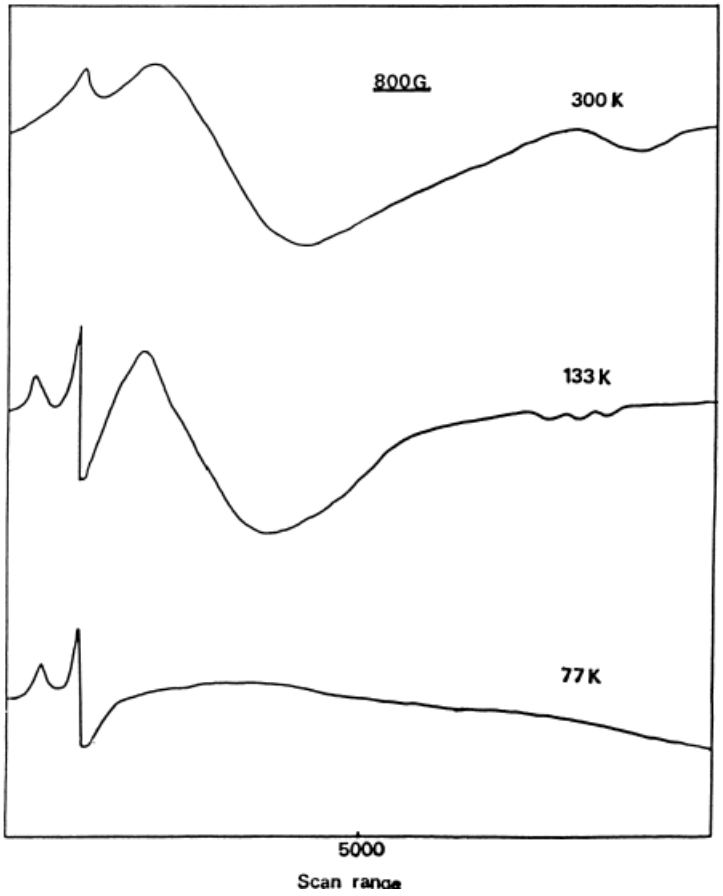

Figure 5 EPR spectra of $[Fe(QDT)_2]Cl_2$ at different temperatures

Only high-spin signals at g = 9.8 and g = 4.8 are observed at 77 K in the spectrum of this complex. At this temperature low spin Fe (III) centres are assumed to be severely distorted and strongly coupled and were not able to give the signals.

Mössbauer spectroscopy: Figure 6 represents the Mossbauer spectra of $[Fe(QDT)Cl_2]$ at two different temperatures which sheds light into the antiferromagnetic coupling present in the complex. A quadrupole split doublet with a centre shift of 0.62 mm/s was observed at room temperature. Compared to the Larmour period of ^{57}Fe, (10^{-9} s) the relaxation between electronic spin states is quite fast and the low spin and the high spin Fe (III) species could not be distinguished from the spectrum.

ISSN PRINT 2319 1775 Online 2320 7876
 Journal Volume 11, Iss 12, 2022

(17,18). The complex exhibits dominant low-spin nature at 77 K and the low centre shift value unlike the room temperature spectrum. The spectrum has a large central peak with narrow peak at the left. The magnetic hyperfine splitting exhibited by the Mössbauer spectrum of [Fe(QDT)]$_2$C1$_2$ at 77 K endorse that the system is strongly antiferromagnetically coupled at this temperature which is capable of slow relaxation between the spin states (19-24).

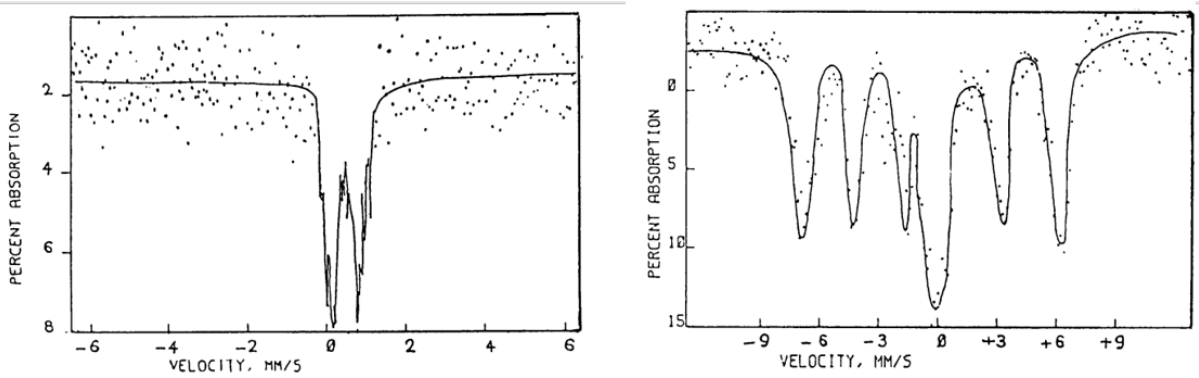

Figure 6 Mössbaur spectra of [Fe(QDT)$_2$Cl$_2$] at RT and LNT

Based on the above arguments, a dimeric structure with two chloride ions in the outer sphere has been proposed for [Fe(QDT)]$_2$C1$_2$. In [Fe(QHD)Cl]$_2$ the dimerisation is expected to take place by the mutual coordination of the azomethine within the dimer, whereas in [Fe(QED)Cl]$_2$ the dimerisation is through phenolic oxygen atoms. [Fe(QPD)Cl] may be a monomer with a square pyramidal structure. The schematic diagram of the complexes are given in Fig. 4.3.

The IR spectrum of the complex supported on the resin shows C-N stretching frequency at 1670 cm^{-1}, which supports the presence of the complex in the resin. The occurring of the anchoring of the complex through the displacement of the chlorine atom is evidenced from the presence of chloride ions in the solution collected after the filtration of the resin supported complex. Ascorbic acid is a potential reducing agent in biochemical systems and is easily oxidised to dehydroascorbic acid by many transition metal centres. The rate of the oxidation reaction is expected to depend on the stability of the complexes due to the probable dissociative mechanism of the process. The exact pathway of the catalytic process and assessing the key factors influencing it will be complex as the metal complexes are supported on ion-exchange resins. But the displacement of one or more groups of the coordinated ligand occurs during the formation of the transition state. This is in accordance with an inner sphere oxidation process where the displacement is accompanied by significant steric factor and variation of this effect for a given complex is strongly dependent upon the nature of the ligand.

During the experiment any leaching out of the metal chelates from the resin was found to be absent. The rate of oxidation of ascorbic acid obtained for each resin supported complex are given in Table 3. The [Fe(QED)Cl]$_2$ and [(Fe(QDT)$_2$]C1$_2$ shows more activity towards the oxidation. The higher activity of the complexes with flexible ligands [Fe(QED)Cl$_2$] and [Fe(QDT)]$_2$Cl$_2$ compared to those with rigid ligands is a unique observation. In [Fe(QPD)Cl] the rigidity of the ligand may be the reason for the lower catalytic activity, whereas the steric inhibition to the reducing agent offered due to the dimeric nature of [Fe(QHD)Cl]$_2$ may be the reason for its lower activity. The complexes are not undergoing any type of degradation during the catalytic process which may be due to the stability acquired from its incorporation in the Seralite SRC 120 resin.

ISSN PRINT 2319 1775 Online 2320 7876
 Journal Volume 11, Iss 12, 2022

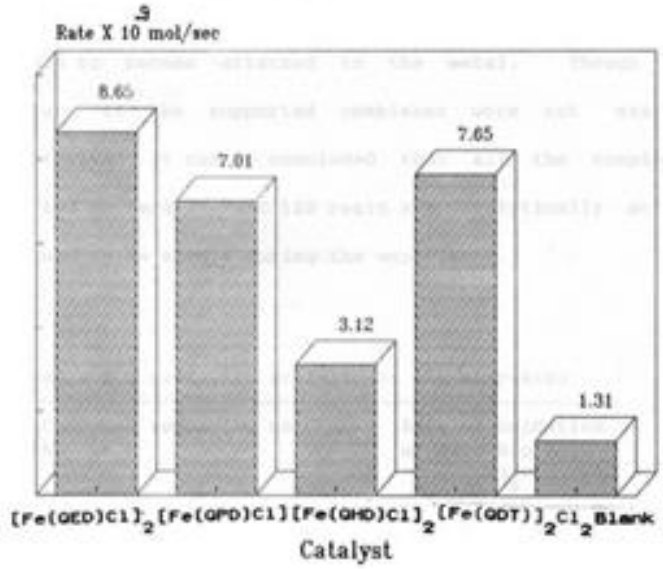

Table 3

Complex supported on Seralite SRC 120 resin	Rate of oxidation of ascorbic acid (mol $dm^{-3}s^{-1}$)
$Fe(QED)Cl_2$	8.654×10^{-9}
$Fe(QPD)Cl_2$	2.014×10^{-9}
$Fe(QHD)Cl_2$	3.125×10^{-9}
$Fe(QDT)Cl_2$	7.653×10^{-9}
Blank	1.315×10^{-9}

Conclusion

In the present study we have synthesised Fe(III) complexes of 3-hydroxy-quinoxaline-2-carboxaldehyde with the amines ethylenediamine (QED), o-phenylenediamine (QPD), hydrazine hydrate (QHD) and diethylenetriamine (QDT) and these complexes were characterised by analytical, magnetic and spectral studies. The complexes exhibit interesting electronic properties due to the presence of quinoxaline ring. The complexes were formulated as $Fe(QED)Cl_2$, $Fe(QPD)Cl_2$, $Fe(QHD)Cl_2$ and $Fe(QDT)Cl_2$.. The antiferromagnetic coupling in $Fe(QDT)Cl_2$ was well established from the mössbauer spectrum. The catalytic activity of the complexes were studied after immobilisation of the complexes in the SRC 120 resin and the catalytic activity of the supported complexes were studied in the oxidation of ascorbic acid to dehydroascorbic acid. The activity of the complexes were found to increase with the flexibility of the ligand moiety and leaching out of the metal complexes was not observed. This also rules out any type of degradation of the complex during the reaction after its incorporation into the resin.

Conflicts of Interest

There are no conflicts of interest to declare.

Acknowledgement

The authors express gratitude for availing the facilities of SAIF, IIT, Madras.

References

76 B. N. Figgis and R. s. Nyho1m**, J** Chem. Soc. , (1958) 4190

91 W. J. Geary, Coord. Chem. Rev., 7 (1971) 96.

ISSN PRINT 2319 1775 Online 2320 7876
 Journal Volume 11, Iss 12, 2022

S. Mayadevi, S., P. G, Prasad, K. K. M. Yusuff, K. Synth. React. Inorg. Met-Org. Chem. in Inorganic, Metal-Organic Chem., 33 (2003) 3, 481-496.
3. . S. Mehrotre, M. C. Agrawal and S.P. Hushran, J. Phys. Chero., 73 (1969) 96.
4. P. Martlnez, J. Zuluaga, D. Uribe and R. Van Eldik, Inorg. Chiro. Acta, 136 (1987) 11.
5. Laxmi, N. J, Kirthi, S. B, Noorjahan, M. S, Sharanappa, T. N, Shivamurti, A. C; J. Chem. Pharm. Res., 2013, 5(4):290-300
6. J. H. Roe, "Methods of Biochemical Analysis", 245. Interscience Publishers, New York, 1 1981.
5. W. M.Reiff, G. J. Long and W. A. Baker, Jr, J. Am. Chem. Soc., 90 (1968) 6347.
6. w. Klemm and K. H. Raddatz, Z. Anorg. Chem., 250 (1942) 207.

7. M. Gerloch, J. Lewis, F. E. Mabbs and A. Richards, J. Chem. Soc. A, (1968) 112.

8. W. M. Reiff, W. A. Baker,Jr. and W. E. Erickson, J. Am. Chem. Soc., 90 (1968) 6347.
9. R. De. Isasi, S. L. Holt and B. Post, Inorg. Chem., 10 (1971) 1598.
10. M. Thomman, O. Kahn, J. Guilhem and F. Varret, Inorg. Chem. 33 (1994) 6027.
11. J. A. Gonzalez and L. J. Wilson, Inorg. Chem., 33 (1994) 1543.
12. S. W. Taylor, J. D. Cashion, L. J. Brown, C. J. Hawkins and G. R. Hanson, Inorg. Chem., 34 (1995) 1487.
13. J. J. L. Garriga, G. T. Babcock and J. F. Harrison, J. Am. Chem. Soc., 108 (1986) 7241, 8173.
14. M. Gulliotti, L. Casella, A. Pasini and R. Ugo, J. Chem. Soc., Ddl ton. Trdns., (1977) 339.
15. K. K. M. Yusuff and R. Sreekala, Thermochim. Acta, 179 (1991) 313.
16. L. J. Bel1amy, "The Infrared Spectra of Molecules", Chapman and Hall, London (1978).
17. R. Aasa and T. Vanngard, Arkiv. Kemi., 24 (1965) 331.
18. P. Gutlich, in "Mössbauer Spectroscopy in Chemistry", Mossbauer Spectroscopy, Topics in Applied Physics, U. Gonser, (Ed), Vol-5, Springer-Verlag, New York, (1975).
19. R. W. Grant in "Mössbauer Spectroscopy in Chemistry.Mössbauer Spectroscopy, Physics, U. Gonser, (Ed), Vol-5, York, (1975). Topics in Applied Springer-Verlag. New
20. G. R. Hoy and M. R. Corson, in "Relaxation Effects Associated with Magnetic Phase Transitions", Mössbauer Spectroscopy and its Chemical Applications, J. G. Stevens and G. K. Shenoy, (Ed), Advances in Chemistry Series, 194, Washington D.C, (1981).
21. P. Gutlich, "Recent Investigations of Advances in Chemistry Series, 194, 405(1981) . Spin Crossover", Washington D.C,
22. N. N. Greenwood, T. C. Gibb, "Mössbauer Spectroscopy", Chapman and Hall Ltd, London (1971).
23. E. Konig, Struct. Bonding, 76 (1991) 51.
24. D. Petridis, A. Simpoulos and A. Kosticas, Phys. Rev. Let., 27 (1971) 1171.