



Schiff Base Complexes of Fe (III) Derived from Amino Acids

Al-Shaheen J. Amira Al-Mula A. Miaa

Department Chemistry, Education of College, University of Mosul, Mosul, IRAQ

Available online at: www.isca.in, www.isca.me

Received 28th May 2014, revised 7th June 2014, accepted 16th August 2014

Abstract

Schiff bases derived from vanillin and amino acids (glycine, L-serine, L-tyrosine and L-phenylalanine) and their complexes with Fe(III) have been prepared and characterized by many physicochemical methods such as elemental analysis (CHN), magnetic susceptibility, molar conductance as well as spectral studies such as IR and UV-Visible. The analytical data showed that the complexes having four and six coordination number with the following formulas $[Fe(VA)(H_2O)_2Cl]_2$, $[Fe_2(VA)(CH_3COO)(OH)_2]$, where A=serine or tyrosine $[Fe_2(Vg)(CH_3COO)(OH)_3]$, $[Fe_2(VA^*H_2)(H_2O)_2(NO_3)_2](NO_3)_4$ and $[Fe_2(VA^*)_2(H_2O)_2(NO_3)_2]$, A* =all the amino acids. The ligands behave as tetradentate coordinating through the atoms NOOO, or tridentate NOO; where V= vanillin, A= amino acids (glycine and phenylalanine).

Keywords: Schiffbase complexes, Fe (III) complexes, amino acid complexes.

Introduction

Recent years witness a growing interest in the chemistry of iron (III) complexes which serve as models for biological systems¹⁻³. Recently, considerable attention has been paid to the chemistry of metal complexes of amino acids of Schiff bases containing oxygen, nitrogen and other donors for their physiological reasons⁴⁻⁶, since amino acids are absorbed well from intestinal lumen by specific active transport mechanisms⁷, amino acids containing imines display significant biological⁸⁻¹⁰, they easily form stable complexes with most transition metal ions¹¹⁻¹³. According, we report herein synthesis and characterization of some new complexes of Fe(III) with N,O donor Schiff base derived from vanillin with some aminoacids, and they characterized by different chemical, physical and spectral methods.

Experimental: Chemicals: All chemicals and solvents used were of analytical grade. The metal salts were commercially available pure samples. They included iron (III) chloride, (Aldrich), iron (III) acetate (Fluka), iron(III) nitrate (Bisolve), vanillin (B.D.H).

Material and Methods

Melting point and decomposition temperature were determined using SMP30 melting point apparatus. IR spectra measurements were recorded using FTIR-Tensor 27-Burker co. Germany 2003 as KBr pellets in the range (400-4000 cm^{-1}). UV-visible spectral measurements were done on Shimaduz 1800 spectrophotometer for 10^{-3} M complexes in DMF solvent at room temp using 1cm quartz cell in range (190-1100) nm. microanalysis (C, H, N) were performed using Caltech instrumental elemental Combustion. Molar conductance of complexes were measured at room temp for 10^{-3} M in DMF using Multiline F-SET-2WTW Wissenschaft Technische Werkstattem 82362 Weicheim.

Magnetic susceptibility of the complexes was measured by Bruker -BM6. Iron contents were determined by apply inductively coupled plasma atomic absorption spectrometry (ICP-AAS) using sense AAGB Scientific Equip men, after the decomposition of the complexes with concentrated nitric acid.

Synthetic methods: 1-Preparation of the Schiff base salts(ligands), Sodium vanillin amino acids imine: Equal amounts of amino acids 0.01mol (1.05g of L- serine or 1.65g of L-phenylalanine or 0.77g of glycine or 1.81g of L-tyrosine) in 20ml (25% distilled water + 75% ethanol) was mixed with vanillin (1.5g, 0.01mol) in 20ml ethanol in presence of sodium acetate (0.82g,0.01mol).

The mixture was heated at 50°C in water bath for an hour, the mixture was cooled and measured the pH. Then the solution was evaporated about its half volume and left for overnight to complete precipitation, the precipitate was collected by filtration, washed with 1:1 ethanol -water mixture and diethylether and it was dried over anhydrous over anhydrous $CaCl_2$. The analytical data for C.H.N and % yield (table 1 and 2).

Preparation of the complexes: i. Preparation of iron (III) chloride complexes: 0.01mol of Schiff base salt in 20 ml ethanol has been added to 0.01 mol iron (III) chloride in 10ml of hot ethanolic solution, followed by slow addition of aqueous solution of sodium acetate (0.02 mol). The mixture has been refluxed for half an hour at 50c with stirring, followed by cooling, and measuring the pH, then evaporated to half its volume, cooled, filtered, washed with ether and dried over $CaCl_2$. ii. Preparation of iron (III) acetate: By following above procedure in A expect without addition of sodium acetate and refluxing time 2 hours. iii. preparation of iron (III) nitrate: A general procedure has been adopted for the preparation of

complexes in neutral and basic medium. In neutral medium, a solution of 0.01mol of each of amino acids and vanillin in 20 ml (25% distilled water +75% ethanol) has been added to the solution of iron (III) nitrate (0.01mol), the mixture has been refluxed for an half hour at 50°C with stirring, followed by cooling and measuring the pH, The product has been filtered

off, washed with ether and dried over CaCl₂. In basic medium, complexes have been prepared by applying the same amount used in neutral medium, and after mixing the iron nitrate with ligands and heating on a water bath, sodium hydroxide solution (1M) has been added until pH (9-12), then followed above steps as in neutral medium.

Table-1
Names, Structures and Abbreviations of Schiff Base Ligands

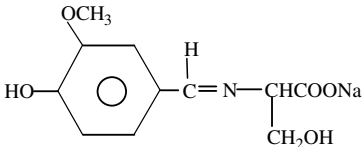
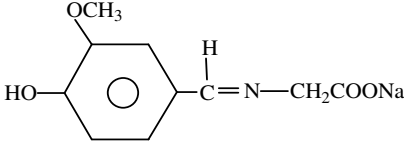
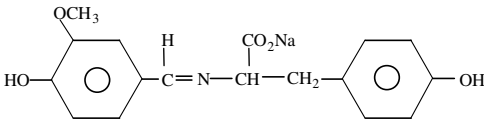
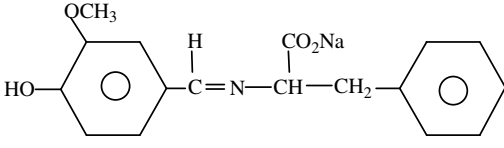
Schiff base compound	Structure	Abbreviation
Sodiumvanillinserine imine		NaVs
Sodiumvanillinglycine imine		NaVg
Sodiumvanillintyrosine imine		NaVt
Sodiumvanillinphenylalanineimine		NaVphe

Table-2
Some physical properties of Schiff Base Ligands

No.	Abbrev.	Chemical formula	Color	C ^o m.p or d	Yield (%)	% Analysis, Calc. (Observ.)		
						C	H	N
1	NaVs	C ₁₁ H ₁₂ NO ₅ Na	yellow	83	80	50.57 (50.41)	4.59 (4.45)	5.36 (5.22)
2	NaVg	C ₁₀ H ₁₀ NO ₄ Na	Yellow	75	85	51.94 (51.82)	4.32 (4.19)	6.06 (5.90)
3	NaVt	C ₁₇ H ₁₆ NO ₅ Na	Pale yellow	197	75	60.53 (60.47)	4.74 (4.80)	4..15 (4.02)
4	NaVphe	C ₁₇ H ₁₆ NO ₄ Na	Dark yellow	112	69	63.35 (63.20)	4.98 (4.80)	4.36 (4.25)

IR Spectra: The coordination sites of the ligands involved in the bonding with metal ions had been determined by careful comparison of the (table 4 and 5) infrared spectra of those compounds with that of the parent ligands. The ligands basically composed of different groups of potent ability to coordinate with the metal ions. The IR spectra of the Schiff bases showed a strong band in the region (1672-1650) cm^{-1} , which is characteristic of the azomethane (stretching frequency C=N) group. In all complexes, this band is slightly shifted to lower frequency indicating coordination of the Schiff bases through azomethine nitrogen atom^{15,16}. The IR spectrum of the ligands exhibit a broad band of stretching frequency of phenolic(OH) group at (3369-3443) cm^{-1} (the broadness due to the presence of hydrogen bonding) and a second band at (1371-1300) cm^{-1} due to bending phenolic OH group, these two bands are absent in the complexes due to deprotonation on coordination to the metal ion, and shifted toward a lower frequency on coordination for complexes that have been prepared in neutral medium. Also, two new bands were observed in region 3240-3245 and 1235-1342 cm^{-1} due to the stretching and bending respectively, of hydroxyl group for complexes 3-5. In addition, the stretching vibration of C-O single band split in to two peaks support the above suggested coordination of the hydroxyl group of the amino acid moiety without deprotonation¹⁷. Another important strong band observed in the spectrum of the free ligand ascribed to phenolic stretching (C-O) group at (1245-1267) cm^{-1} is shifted to lower frequency in all complexes. This is usually indicates that the (C-O) group of the ligand involved in coordination with the metal ion through the deprotonated oxygen of phenolic group¹⁸. The ligands exhibit other two intense bands at (1411-1334), (1590-1585) cm^{-1} corresponding to symmetric and asymmetric stretching frequencies of (COOH) group, respectively of the organic ligand and of the acetate group. On complexation symmetric bands were shifted to a higher frequencies or remained unaltered in the position of the ligands, while asymmetric bands were shifted to ward a lower frequencies respectively¹⁹. The difference between the symmetry and asymmetry stretching vibration of COO group ($\Delta\nu$ which is equal to 150-160 cm^{-1}) gave indication about the manner of coordination of carboxylic group, this value showed that amino acid Schiff bases coordinated through COO group which was acted as monodentate²⁰. The acetate complexes exhibited bands differences as bidentate chelating acetate group and confirmed by electronic spectra of the complexes¹⁹. The presence of (COO) group makes the coordination phenomenon is more complicated due to presence of acetate group belongs to metal. The C-O stretching vibration of the free acetate ion was observed at 1600 cm^{-1} and shifted to lower frequency that is conformity with many authors²⁰. The IR spectra of nitrate complexes display three (N-O) stretching bands. The infrared data indicated the occurrence of two strong absorption bands in 1470-1424 cm^{-1} , 1290-1234 cm^{-1} and 950 cm^{-1} regions, which were attributed to (ν_5, ν_1 and ν_2) modes of vibrations of the covalently bonded nitrate groups, respectively¹⁵. The (ν_5, ν_1) is taken as an approximate measure of the covalency of nitrate group¹⁵, a value of $\sim 220 \text{ cm}^{-1}$ for the complexes suggested strong

covalence for the metal-nitrate bonding. Authors have shown that the number and relative energies measure of the covalence of nitrate combination frequencies (ν_5, ν_1) in the infrared spectrum and may be used as an aid to distinguish the various coordination modes of the nitrate group and have suggested that bidentate coordination of the nitrate group involves a greater distortion from D_{3h} symmetry than unidentate coordination, therefore, bidentate nitrate groups should show a larger separation of (ν_5, ν_1). After an investigation of the spectra of a number of compounds showed that the separation for monodentate nitrate groups appeared to be 115 cm^{-1} and that for bidentate groups 220 cm^{-1} . In the present complexes, a separation of 190-180 cm^{-1} , and the nitro groups seem to be bidentate. On the other hand, the spectra of 10-13 complexes showed the presence of additional band at (1380-1385) cm^{-1} due to ionic nature of nitrate group¹⁵. The aqua complexes contain weak to medium a broad band at (3451-3205) cm^{-1} due to stretching vibration OH of water¹⁹ and a sharp shoulder at (1513-1540) cm^{-1} may be assigned to bending vibration of water. Water molecules are coordinated, confirmed by occurrence of additional strong and sharp band at (813-876) cm^{-1} due to OH rocking vibrations²¹. For all complexes new bands were observed at (410-518) and (524-590) cm^{-1} , these bands assigned to the stretching modes of M-N and M-O, respectively²². The presence of these bands support the formation of the complexes under investigation figures.

Electronic Spectra and magnetic moment: The spectrum of the ligands exhibited two bands in the UV intervals at (40650-40535) cm^{-1} and (30864 -30756) cm^{-1} , assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively. The electronic spectral bands observed for the Fe(III) complexes (1-5) at 14880-14925 cm^{-1} and 16339-16501 cm^{-1} (table-6) may be attributed to the ${}^6A_1 \rightarrow {}^4T_1(G)$ and to the ${}^6A_1 \rightarrow {}^4E(G), {}^6A_1 \rightarrow {}^4A_1(G)$ double transition respectively. The band at 18484-18691 cm^{-1} may be due to the ${}^6A_1 \rightarrow {}^4E$ transitions while the remaining one at 21551-21786 cm^{-1} may be due to ${}^6A_1 \rightarrow {}^4F$ transition, and (30303-33333) cm^{-1} (C.T). These bands are in conformity with a tetrahedral coordination for the iron (III) complexes²². The values of the magnetic moments of these complexes are in the range (5.7-6.0) B.M. which are comparable with the values reported for other tetrahedral iron(III) complexes^{22,23}. In the case of iron (III) complexes (6-13), only sextet term of the d^5 configuration octahedral geometry is the term ${}^6A_{1g}$ and does not split by the ligand field. Consequently, all the excited states have different spin multiplicity from the ground term and transition to them is forbidden. Many weak bands were observed and assigned as due to transition from ${}^6A_{1g}$ to ${}^4T_{1g}(G), {}^4T_{2g}(G)$ and ${}^4E_g(G)$. and these three bands are observed in the region (9328-9900, 10204-1103 and 12106-14084) cm^{-1} assignable to above mentioned transitions respectively. All these complexes also exhibit charge transfer bands at (30303-39525) cm^{-1} (C.T). The complexes (6-13) show magnetic moments at room temperature calculated from the corrected magnetic susceptibilities are in the range (4.1-5.0) B.M revealing the presence of five unpaired electrons are present

in the complex molecule and indicating high spin octahedral iron (III) complexes^{24,25}.

Conclusion

From the above discussion of various physicochemical and spectral studies, we conclude that the Schiff base ligands of glycine and phenyl alanine coordinated as tridentate through phenoxy oxygen, carboxy oxygen and azomethine nitrogen atoms, while the Schiff base ligands of serine and tyrosine

coordinated as tetradentate through phenoxy oxygen, carboxy oxygen, azomethine nitrogen and alcoholic or phenoxy oxygen atoms. The ligands are used as stabilizer for dinuclearmetal complexes and according to the measurements and theoretical calculations the Fe(III)chloride or acetate complexes have tetrahedral geometries, while Fe(III)nitrate complexes have octahedral geometries around central metal ion, figure 1 and 2.

Table-4
Important IR spectra bands cm⁻¹ of the ligands

Comp.No	$\nu_{C=N}$	ν_{C-O}	ν_{sCOO}	ν_{asCOO}	ν_{M-N}	ν_{M-O}	$\nu_{OH_2 R(H_2O)}$	Others
1	1606	1216	1339	1502	534	587	3426, 866	-
2	1561	1225	1410	1502	469	524	3441, 848	-
3	1596	1200	1430	1512	420	550	-	ν_{OH} 3240 δ_{O-H} 1342
4	1562	1206	1409	1500	468	525	-	ν_{OH} 3245 δ_{O-H} 1335-
5	1608	1212	1411	1512	522	588	-	ν_{OH} 3243 δ_{O-H} 1339
6	1601	1220	1421	1508	432	528	3410, 860	1470, 1290, 950, 1380
7	1582	1242	1389	1510	480	525	3400, 875	1424, 1234, 950, 1385
8	1590	1200	1431	1500	420	590	3480, 838	1463, 1270, 950, 1380
9	1593	1200	1403	1508	424	528	3446, 820	1455, 1245, 950, 1385
10	1570	1234	1420	1509	434	586	3214, 810	$\nu_{ionic} NO_3$, 1385
11	1585	1233	1410	1510	502	543	3220, 865	$\nu_{ionic} NO_3$, 1380
12	1582	1235	1425	1500	474	543	3300, 835	$\nu_{ionic} NO_3$, 1380
13	1582	1224	1445	1502	524	529	3442, 814	$\nu_{ionic} NO_3$, 1385

Table-5
Important IR spectral bands (cm⁻¹) of the complexes

Ligand	$\nu_{C=N}$	ν_{C-O}	δ_{O-H}	$\nu_{s(COO)^-}$	$\nu_{as(COO)^-}$	ν_{O-H}
NaVg	1665	1266	1371	1430	1588	3377
NaVphe	1672	1246	1339	1411	1579	3443
NaVS	1650	1245	1300	1434	1590	3369
NaVT	1665	1267	1338	1429	1585	3440

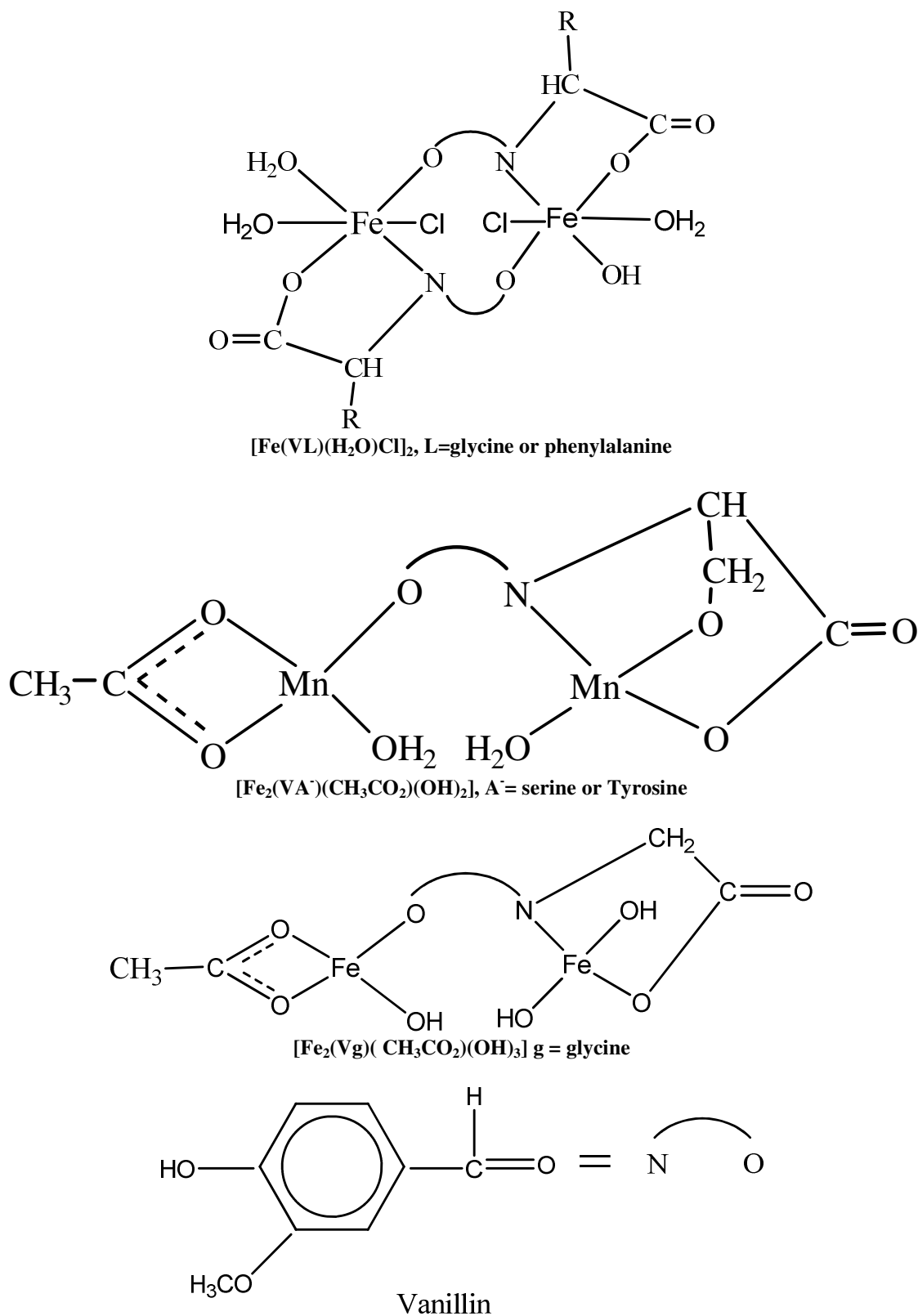


Figure-1

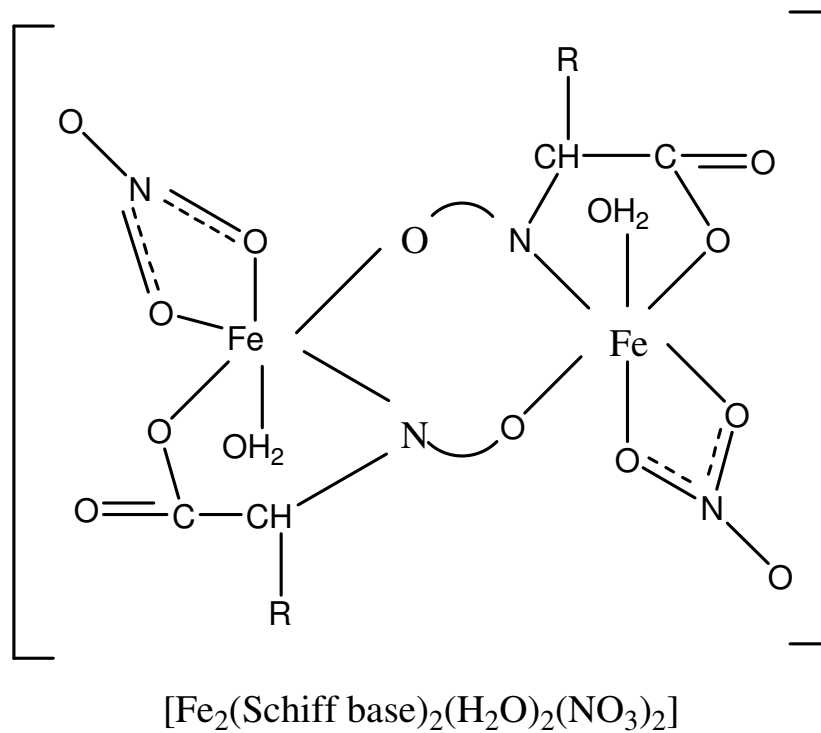
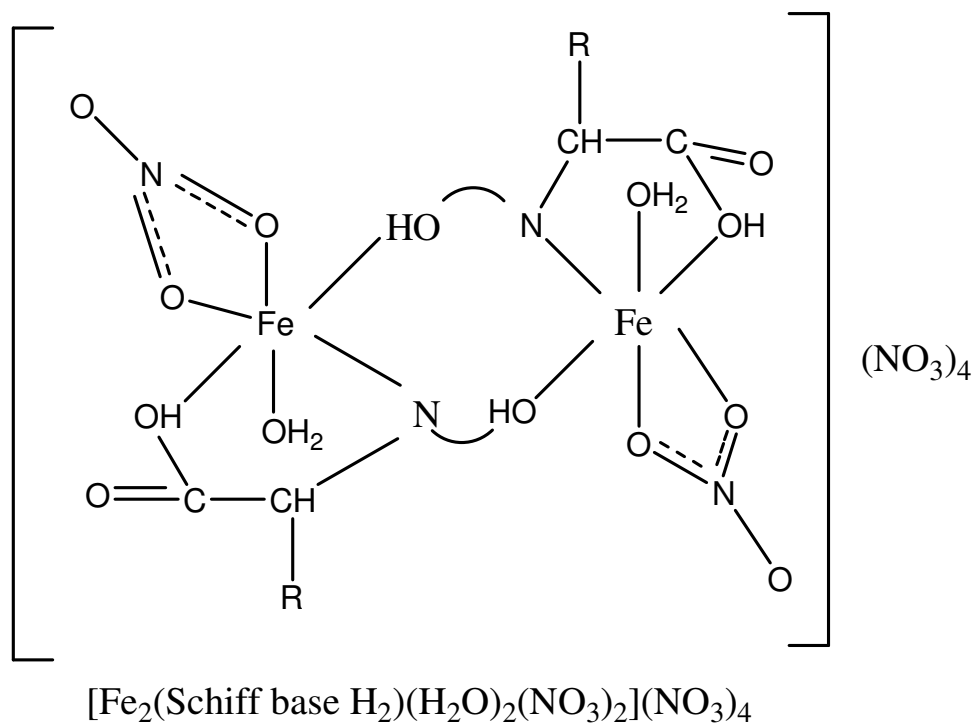


Figure-2

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