

Preparation, characterization and theoretical study of metal complexes derived from N₅ acyclic ligand

Mahmoud Najim Al-jibouri¹, Omar Hamad Shehab AL-Obaidi^{2,*}

¹Chemistry Department, College of Science, Al-Mustansrya University

²Chemistry Department, Women Education College, Al-Anbar University

Email address:

Mahmoudnajim71@yahoo.com(M. N. Al-jibouri), dromaralobaidi@yahoo.com(O. H. S. Al-Obaidi)

To cite this article:

Mahmoud Najim Al-jibouri, Omar Hamad Shehab AL-Obaidi. Preparation, Characterization and Theoretical Study of Metal Complexes Derived from N₅ Acyclic Ligand. *American Journal of Applied Chemistry*. Vol. 1, No. 3, 2013, pp. 37-42.

doi: 10.11648/j.ajac.20130103.11

Abstract: The complexes of a new pentadentate acyclic ligand derived from 1,2-diamino benzen and 2,6-diacetylpyridine, with vanadium(IV), Mn(II) and Fe(III) have been synthesized and characterized on the bases of their elemental analysis, GS mass for ligand, conductivity, magnetic moments in addition to spectral data of IR and UV-Visible Spectra. Metal to ligand ratio in all complexes has been found to be (1:1). The polydentate ligand behaves as N₅ system upon linkage with Fe(III) and Mn(II) ions. All the complexes have been assigned as octahedral geometries of general formula [MnL]Cl, [FeLCl]Cl₂ and [VOL]SO. A theoretical treatment of the formation of complexes in the gas phase was studied; this was done using the HYPERCHEM-6 program for the Molecular mechanics and Semi-empirical calculations.

Keywords: Preparation, Characterization, Theoretical Study, Metal Complexes, Acyclic Ligand

1. Introduction

The coordination complexes of the Schiff bases have been widely investigated due to their manifestation of novel structural features, unusual magnetic properties and relevance to biological processes⁽¹⁻³⁾. The coordination compounds pent dentate Schiff bases have been reported to act as inhibitors for enzymes⁽⁴⁾. Considerable interest has been shown in the synthesis of transition metal complexes of pent dentate Schiff bases⁽⁵⁻⁶⁾. Pyran-2-one derivatives containing hydroxyl, acetyl and phenylazo substitutes have been employed as complexing agents⁽⁷⁻¹⁰⁾. Literatures survey reveals that very little work, however, have been reported on conduct metric studies of macro cyclic metal complexes involving pyridine moiety. In the present article we reported the synthesis and characterization of a new penta dentate ligand (L) derived from 2, 6-diacetylpyridine and 1, 2-diamino benzene and its complexes with oxovanadium (IV), Fe (III) and Mn(II).

2. Experimental

2.1. Physical Measurements and Analysis

Melting points were recorded on Gallen Kamp melting

point apparatus and were uncorrected. The FTIR spectra were recorded using FTIR – 8300 Shimadzo in the range (4000-400)cm⁻¹ and ?Samples of metal complexes were measured as CsI – disc, while the free ligand was done in KBr–disk The UV-Visible spectra of compounds were recorded on Shimadzu model spectrophotometer. Magnetic susceptibility of the sold complexes were done at room temperature using magnetic balance–model MS-BMK1 at AL-Nahrain University by Gouy method using mercury tetrathiocyanato cobalt(II) as calibrante. Metal estimations were carried out spectrophotometrically using atomic absorption Shimadzu AA-670 spectrophotometer.

Molar conductance of the solutions of the complexes in DMF (10⁻³M) were measured on PW9526 digital conductivity meter. The elemental analysis data of the ligand and complexes were obtained on a Carlo- Erba Model EA 1108 (C.H.N.) Elemental analyzer. The presents of metal complexes were estimated in Ibn-Cina center via Shimadzu AA680 G atomic absorption spectrophotometer.

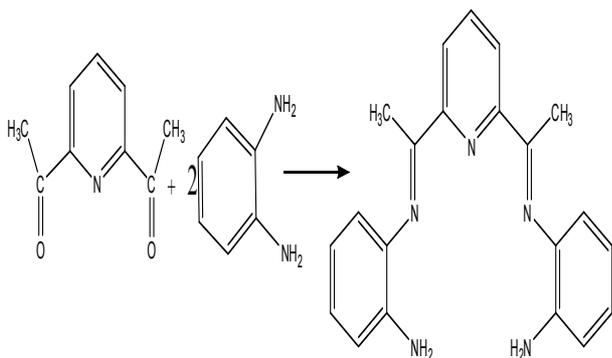
2.2. Materials and Preparations

2, 6-diacetylpyridine, starting material for synthesis of N₅ ligand (L) was purchased from Fluka Company. All the other chemicals used were of AR grade. The metal salt solutions were standraized by the recommended procedure

⁽¹¹⁾. Dilute solutions of the metal ions and ligand (N₅) under study of 2.5×10^{-6} M, 1×10^{-6} M, 2.5×10^{-5} M, 1×10^{-5} M and 1×10^{-4} M were prepared with accurate dilution.

2.2.1. Synthesis of the Schiff base (L)

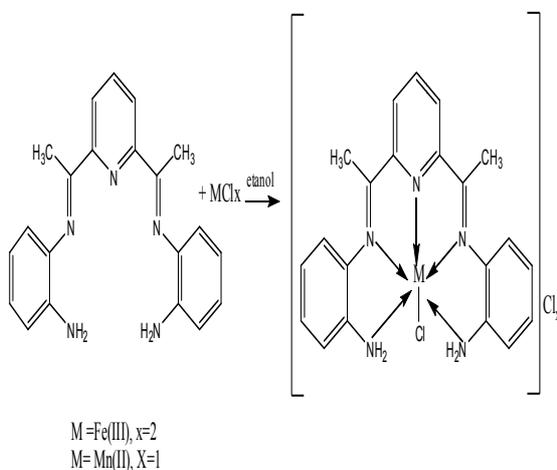
A methanolic solution of 2,6-diacetyl pyridine (1.56gm, 0.01 mole in 25ml) was added to a methanolic solution of 1,2-diamino benzene (0.523, 0.02 mole in 10ml), the mixture was refluxed on a water-bath for 2hr. The excess of solvent was partially evaporated under vacuum, and the separated yellow precipitate was filtered under reduced pressure, washed with ethanol and crystallized from ethanol. The compound was dried in vacuum at room temperature over silica gel as described in scheme (1). The physical properties of ligand shown in table (1)



Scheme (1). synthesis of acyclic ligand N₅ [L]

2.2.2. Preparation of the Complexes

The metal complexes were prepared by refluxing hot methanolic solutions of metal chloride (0.01 mol) [except in case of Fe (III) and vanadium (IV) complexes where DMF solutions were used] and the ligand (0.01mol) for 5hr, on a water bath. The complexes separated on adjusting the PH 6-8. were filtered, washed with methanol, diethylether and then left overnight to afford colored crystals of the metal complexes.



Scheme (2). synthesis of metal complexes

2.3. Study of Complex Formation in Solution

The complexes of the ligand (L) with the selected metal ions Fe(III), V(IV) and Mn(II) were studied in solution using ethanol as solvent, in order to determine (M:L) ratio in the prepared complexes, following molar ratio method⁽¹⁰⁾. Series of solutions were prepared having a constant concentration (C) 10^{-3} M of the hydrated metal chlorides or vanadyl sulfate VO (SO₄)₂.5H₂O, and the ligand (L).

The [M: L] ratio was determined from the relationship between the absorption of the absorbed light and the mole ratio of [M: L]. the result of complexes formation in solution was listed in table (2).

3. Results and Discussion

The free tetra dentate ligand (L) has been prepared by condensation reaction of two moles of dactyl pyridine and tow moles of 1, 2-diamino propane scheme (1). The ligand was stable in atmosphere, and insoluble in common organic solvents except DMF and DMSO.

3.1. Elemental Analysis

The physical and analytical data of the pent dentate legend (L), and its metal complexes are given in table (1), which are in a satisfactory agreement with the calculated values. The electron impact mass spectrum of ligand, as shown in fig. 1, confirms the proposed formula by showing a peak at 341 amu corresponding to acyclic moiety [(C₂₁H₂₁N₅) atomic mass 343.18]. It also shows a series of peaks, i.e. 39, 90, 131, 145 and 250 amu, etc. corresponding to various fragments. Their intensity gives an idea of stability of fragments. The suggested molecular formulas for all complexes are supported by the subsequent spectral, and molar ratio, as well as magnetic moment and molar conductivity in 10^{-3} M solution of DMF. The Values of Λ_m (table 2) show that Mn(II) complexes are electrolytes in ratio 1:1, whereas VO(IV) and Fe(III) complex is conductive in 2:1⁽¹⁴⁾.

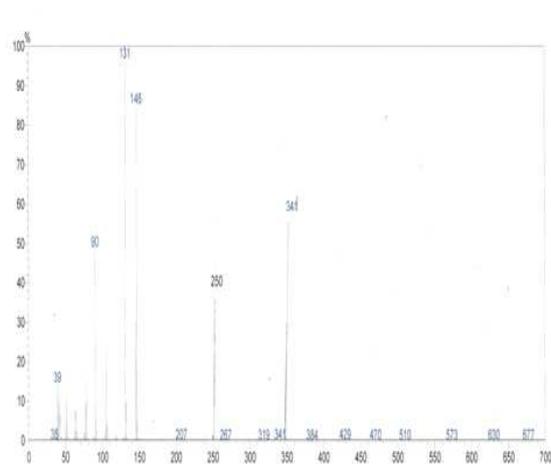


Fig. 1. Electron impact mass spectrum of ligand (L)

Table (1). physical and analytical data for the ligand and their complexes

Compound	Color	Yield (%)	M.P. C°	Elemental analysis Calc.(found)			
				C%	H%	N%	%M*
Ligand	Yellow	88	133– 135	74.79 (73.44)	6.02 (5.77)	7.43 (6.66)	-
[VO (L)]SO ₄	Olive	77	288d	54.98 (53.13)	4.26 (3.66)	4.97 (5.00)	11.33 (10.00)
[Fe(L) Cl]Cl ₂	Pale green	76	300	52.02 (51.44)	5.06 (56.71)	5.68 (6.71)	12.01 (13.87)
[Mn(L) Cl]Cl	Cream	65	312d	55.87 (54.88)	4.65 (4.00)	14.17 (13.00)	11.43 (12.00)

d = decomposed,*=analysis of metal content via flame atomic absorption

3.2. Infra- Red Spectra

Table (2) lists the most useful infrared assignments for those bands most diagnostic of the mode of coordination of ligand (L). The infrared spectra of all metal complexes a decrease in the frequency by (15-20)cm⁻¹ on complication for $\nu(\text{C}=\text{N})$ and $\nu(\text{NH}_2)$ and are constant with coordination carbonyl oxygen and azomethan nitrogen atoms, moreover

the presence of bands at range. 415 – 610 and 395 – 415cm⁻¹ are assigned to $\nu(\text{M}-\text{N})$ ⁽¹⁵⁻¹⁶⁾ and $\nu(\text{M}-\text{O})$ respectively. The infrared spectra of chloro complexes show one new band at 295 – 350cm⁻¹ as assigned to $\nu(\text{M}-\text{Cl})$ of trans - isomer ⁽¹⁷⁾. A strong band in the oxovanadium(IV) complex was observed at 990cm⁻¹ which is assigned to $\nu(\text{V}=\text{O})$ ⁽¹⁸⁾.

Table (2). U.V. - visible, I.R. spectra and other physical properties of the prepared compounds

Compound	Electronic absorption bands	Assignment	IR frequency peaks(cm ⁻¹)	Assignment (stretching)	μ_e ff (BM)	Λ_m Ohm ⁻¹ .cm ² .mol ⁻¹ (DMF)
L	293	$\Pi \rightarrow \Pi^*$	1660,3400, 1615	C = N,-C=C, NH ₂	-	-
Fe(III)	220	$\Pi \rightarrow \Pi^*$	3370,1578	NH, C = N	3.35	189
	285	$n \rightarrow \Pi^*$				
	541	$A_2g^4 \rightarrow T_2g^4$	350,415	Cr – Cl,Cr – N		
	392	$A_2g^4 \rightarrow T_1g^4$	515	Cr–O		
VO(IV)	278	$A_2g^4 \rightarrow T_1g^4(p)$	3380,1588	NH,C=N	1.5	95
	330	$\Pi \rightarrow \Pi^*$				
	499	$B_2 \rightarrow E_2$	400,600	V–N,V=O		
Mn(II)	655	$B_2g \rightarrow B_1g^2$	990		4.4	76
	265	$n \rightarrow \Pi^*$	3400,1585	NH,C = N		
	362	$\Pi \rightarrow \Pi^*$	400,470	Mn-Cl, Mn-N		
	415	$A_1g^6 \rightarrow E_g^4$	410	Mn-O		

3.3. Electronic Spectra and Magnetic Moment Studies

The UV-visible spectra of the ligand and their metal complexes were recorded for their solutions in ethanol and DMSO as solvents in the range (200 – 1000) nm . The vanadyl complex show a weak peak in the visible region 365, 560 and 750nm which are assigned to ${}^2B_2 \rightarrow {}^2E$, ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2A_1$ transitions respectively⁽¹⁷⁾ which are consistent with octahedral environment of V(IV) complexes. The magnetic moment of oxovanadium complex is consistent with presence of one unpaired electron⁽¹⁸⁾. The electronic spectra of green solution of Fe (III) complex exhibits two bands in the 624

and 455 nm region which are assignable to ${}^4A_2g \rightarrow {}^4T_2g$ (ν_1) and ${}^4A_2g \rightarrow {}^4T_1g$ ($f\nu_1$) transitions. The (ν_2/ν_1) ratio is 1.22 which is very close the value of 1.42 obtained for octahedral d³ complexes ⁽²¹⁾. The Mn(II) complexes shows a slightly low value magnetic moment as compared to spin-only value (5.92 B.M). The low value may be investigated on the basis of presence spin – exchange in the solid phase ⁽²²⁾.

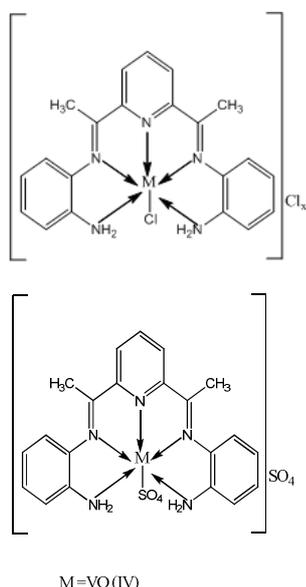
The results shown in table(2), indicate that the molar ratio of(1:1) for complexes yielded high stability. Furthermore the molar absorptivities for all complexes is rather high, this probably was investigated on the presence of pent dentate ligand of N₅ system which was stable

kinetically due to the formation of six-membered ring with the central metal ion⁽²³⁾. On the bases of magnetic data and spectral studies, oxovanadium(IV), Fe(III) and Mn(II) complexes According to previous data reported by Fengetal have been assigned octahedral. ⁽²⁴⁾

Molar Conductance of complex:

By using the relation $\Lambda_m = K/C$ the molar conductance of the complex (Λ_m) can be calculated where is the molar concentration of $10^{-3}M$ of their solutions at $(25 \pm 2^\circ)$ were measured. it is calculated from the results that Mn(II), V(IV) and Fe(III) are electrolytes in 1:1 and 1:2ratio respectively⁽¹⁴⁾.General suggested stereo chemistry structures of complexes:

According to the results obtained from the elemental and spectral analysis, the general structures of the above mentioned complexes can be illustrated as shown in Fig.(2) below:



Fig(2). The proposed structural prepared complexes

3.4. Theoretical Study

The ball and cylinders and some of selected structural parameters (bond length and angles) of the optimized geometries are shown in Table (3) ,Fig.(3). As shown in this figure, there is no obvious trend for the variation of these parameters. The values of the bond length and angles of the optimized geometries are quite similar to the experimental results of the corresponding compounds.

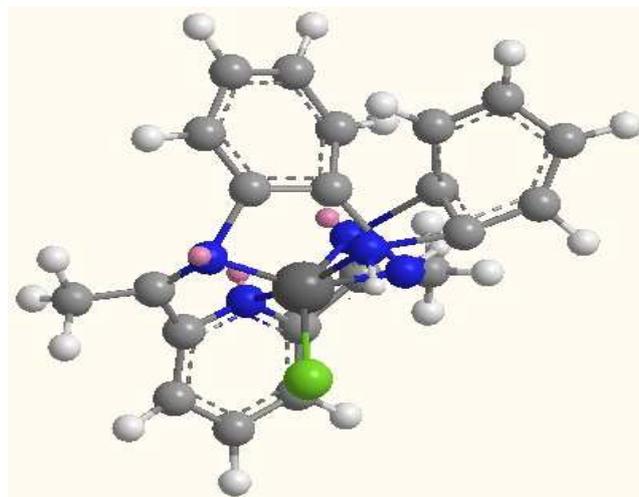


Fig (3). The optimized structural geometry of Fe(III) complex

Table (3). structural parameters, bond length (°A) and angles(°) of the [Fe(L)Cl]Cl₂ complex

Parameters		Parameters	
Bond lengths (°A)		Bond angles(°)	
H(44)-C(21)-C(22)	120.0001	H(44)-C(21)-C(22)	120.0001
H(44)-C(21)-C(20)	119.9995	H(44)-C(21)-C(20)	119.9995
C(22)-C(21)-C(20)	120.0004	C(22)-C(21)-C(20)	120.0004
H(43)-C(20)-C(25)	120.0026	H(43)-C(20)-C(25)	120.0026
H(43)-C(20)-C(21)	120.0022	H(43)-C(20)-C(21)	120.0022
C(25)-C(20)-C(21)	119.9952	C(25)-C(20)-C(21)	119.9952
H(46)-C(25)-C(24)	120.0002	H(46)-C(25)-C(24)	120.0002
H(46)-C(25)-C(20)	119.9999	H(46)-C(25)-C(20)	119.9999
C(24)-C(25)-C(20)	119.9999	C(24)-C(25)-C(20)	119.9999
H(45)-C(22)-C(23)	119.9999	H(45)-C(22)-C(23)	119.9999
H(45)-C(22)-C(21)	120.0002	H(45)-C(22)-C(21)	120.0002
C(23)-C(22)-C(21)	119.9999	C(23)-C(22)-C(21)	119.9999
N(26)-C(23)-C(24)	33.3326	N(26)-C(23)-C(24)	33.3326
N(26)-C(23)-C(22)	153.3310	N(26)-C(23)-C(22)	153.3310
C(24)-C(23)-C(22)	119.9996	C(24)-C(23)-C(22)	119.9996
H(40)-C(17)-C(18)	120.0007	H(40)-C(17)-C(18)	120.0007
H(40)-C(17)-C(16)	120.0006	H(40)-C(17)-C(16)	120.0006
C(18)-C(17)-C(16)	119.9987	C(18)-C(17)-C(16)	119.9987

Parameters		Parameters	
H(39)-C(16)-C(17)	120.0016	H(39)-C(16)-C(17)	120.0016
H(39)-C(16)-C(15)	120.0007	H(39)-C(16)-C(15)	120.0007
C(17)-C(16)-C(15)	119.9977	C(17)-C(16)-C(15)	119.9977
H(41)-C(18)-C(17)	120.0003	H(41)-C(18)-C(17)	120.0003
H(41)-C(18)-C(13)	119.9998	H(41)-C(18)-C(13)	119.9998
C(17)-C(18)-C(13)	119.9999	C(17)-C(18)-C(13)	119.9999
H(38)-C(15)-C(16)	119.9998	H(38)-C(15)-C(16)	119.9998
H(38)-C(15)-C(14)	119.9999	H(38)-C(15)-C(14)	119.9999
C(16)-C(15)-C(14)	120.0003	C(16)-C(15)-C(14)	120.0003
N(19)-C(14)-C(15)	105.0733	N(19)-C(14)-C(15)	105.0733
N(19)-C(14)-C(13)	120.7995	N(19)-C(14)-C(13)	120.7995
C(15)-C(14)-C(13)	119.9999	C(15)-C(14)-C(13)	119.9999
H(47)-N(26)-Fe(27)	124.6682	H(47)-N(26)-Fe(27)	124.6682
H(47)-N(26)-C(23)	124.6693	H(47)-N(26)-C(23)	124.6693
Fe(27)-N(26)-C(23)	110.6624	Fe(27)-N(26)-C(23)	110.6624
H(42)-N(19)-Fe(27)	130.2129	H(42)-N(19)-Fe(27)	130.2129
H(42)-N(19)-C(14)	130.2130	H(42)-N(19)-C(14)	130.2130
Fe(27)-N(19)-C(14)	99.5741	Fe(27)-N(19)-C(14)	99.5741
C(25)-C(24)-C(23)	119.9986	C(25)-C(24)-C(23)	119.9986
C(25)-C(24)-N(12)	128.9979	C(25)-C(24)-N(12)	128.9979
C(23)-C(24)-N(12)	111.0001	C(23)-C(24)-N(12)	111.0001
H(37)-C(11)-H(36)	109.5200	H(37)-C(11)-H(36)	109.5200
H(37)-C(11)-H(35)	109.4614	H(37)-C(11)-H(35)	109.4614
H(37)-C(11)-C(9)	109.4618	H(37)-C(11)-C(9)	109.4618
H(36)-C(11)-H(35)	109.4419	H(36)-C(11)-H(35)	109.4419
H(36)-C(11)-C(9)	109.4424	H(36)-C(11)-C(9)	109.4424
H(35)-C(11)-C(9)	109.4999	H(35)-C(11)-C(9)	109.4999
Fe(27)-N(12)-C(24)	103.9999	Fe(27)-N(12)-C(24)	103.9999
Fe(27)-N(12)-C(9)	82.9100	Fe(27)-N(12)-C(9)	82.9100
C(24)-N(12)-C(9)	115.0003	C(24)-N(12)-C(9)	115.0003
C(18)-C(13)-C(14)	119.9984	C(18)-C(13)-C(14)	119.9984
C(18)-C(13)-N(8)	128.9982	C(18)-C(13)-N(8)	128.9982
C(14)-C(13)-N(8)	110.9999	C(14)-C(13)-N(8)	110.9999
H(34)-C(10)-H(33)	109.5197	H(34)-C(10)-H(33)	109.5197
H(34)-C(10)-H(32)	109.4619	H(34)-C(10)-H(32)	109.4619
H(34)-C(10)-C(7)	109.4621	H(34)-C(10)-C(7)	109.4621
H(33)-C(10)-H(32)	109.4416	H(33)-C(10)-H(32)	109.4416
H(33)-C(10)-C(7)	109.4420	H(33)-C(10)-C(7)	109.4420
H(32)-C(10)-C(7)	109.5000	H(32)-C(10)-C(7)	109.5000
Fe(27)-N(8)-C(13)	104.0001	Fe(27)-N(8)-C(13)	104.0001
Fe(27)-N(8)-C(7)	84.3869	Fe(27)-N(8)-C(7)	84.3869
C(13)-N(8)-C(7)	145.3303	C(13)-N(8)-C(7)	145.3303
H(31)-C(6)-C(5)	122.1913	H(31)-C(6)-C(5)	122.1913
H(31)-C(6)-C(1)	122.1913	H(31)-C(6)-C(1)	122.1913
C(5)-C(6)-C(1)	115.6174	C(5)-C(6)-C(1)	115.6174
C(10)-C(7)-N(8)	129.3801	C(10)-C(7)-N(8)	129.3801
C(10)-C(7)-C(4)	129.3802	C(10)-C(7)-C(4)	129.3802
N(8)-C(7)-C(4)	101.2398	N(8)-C(7)-C(4)	101.2398
H(30)-C(5)-C(6)	115.3083	H(30)-C(5)-C(6)	115.3083
H(30)-C(5)-C(4)	115.3094	H(30)-C(5)-C(4)	115.3094
C(6)-C(5)-C(4)	129.3823	C(6)-C(5)-C(4)	129.3823
Cl(28)-Fe(27)-N(26)	154.7606	Cl(28)-Fe(27)-N(26)	154.7606
Cl(28)-Fe(27)-N(19)	154.7606	Cl(28)-Fe(27)-N(19)	154.7606
Cl(28)-Fe(27)-N(12)	154.7606	Cl(28)-Fe(27)-N(12)	154.7606
Cl(28)-Fe(27)-N(8)	107.5482	Cl(28)-Fe(27)-N(8)	107.5482
Cl(28)-Fe(27)-N(3)	107.5484	Cl(28)-Fe(27)-N(3)	107.5484
N(26)-Fe(27)-N(19)	0.0000	N(26)-Fe(27)-N(19)	0.0000
N(26)-Fe(27)-N(12)	0.0000	N(26)-Fe(27)-N(12)	0.0000
N(26)-Fe(27)-N(8)	90.0001	N(26)-Fe(27)-N(8)	90.0001
N(26)-Fe(27)-N(3)	90.0001	N(26)-Fe(27)-N(3)	90.0001
N(19)-Fe(27)-N(12)	0.0000	N(19)-Fe(27)-N(12)	0.0000
N(19)-Fe(27)-N(8)	90.0001	N(19)-Fe(27)-N(8)	90.0001
N(19)-Fe(27)-N(3)	90.0001	N(19)-Fe(27)-N(3)	90.0001
N(12)-Fe(27)-N(8)	90.0001	N(12)-Fe(27)-N(8)	90.0001
N(12)-Fe(27)-N(3)	90.0001	N(12)-Fe(27)-N(3)	90.0001
N(8)-Fe(27)-N(3)	89.9999	N(8)-Fe(27)-N(3)	89.9999

Parameters		Parameters	
C(7)-C(4)-C(5)	128.9979	C(7)-C(4)-C(5)	128.9979
C(7)-C(4)-N(3)	110.9996	C(7)-C(4)-N(3)	110.9996
C(5)-C(4)-N(3)	119.9999	C(5)-C(4)-N(3)	119.9999
N(12)-C(9)-C(11)	129.7038	N(12)-C(9)-C(11)	129.7038
N(12)-C(9)-C(2)	100.5917	N(12)-C(9)-C(2)	100.5917
C(11)-C(9)-C(2)	129.7045	C(11)-C(9)-C(2)	129.7045
Fe(27)-N(3)-C(4)	104.0001	Fe(27)-N(3)-C(4)	104.0001
Fe(27)-N(3)-C(2)	103.9997	Fe(27)-N(3)-C(2)	103.9997
C(4)-N(3)-C(2)	115.0006	C(4)-N(3)-C(2)	115.0006
C(9)-C(2)-N(3)	110.9996	C(9)-C(2)-N(3)	110.9996
C(9)-C(2)-C(1)	128.9986	C(9)-C(2)-C(1)	128.9986
N(3)-C(2)-C(1)	119.9992	N(3)-C(2)-C(1)	119.9992
H(29)-C(1)-C(6)	119.9997	H(29)-C(1)-C(6)	119.9997
H(29)-C(1)-C(2)	119.9997	H(29)-C(1)-C(2)	119.9997
C(6)-C(1)-C(2)	120.0006	C(6)-C(1)-C(2)	120.0006

References

- [1] S.Tuba ,T.Serap and Cigdem I., J. Chem and Eng.(2011),54(4),pp.978-983.
- [2] S.D.Poonam, Amit R.Yaud, J.Bohjan, and S.A.Aswar, World J. of Chem.,(2010),5(1),pp.57-61.
- [3] A.S. Munde, V.A. Shelke, S.M.Jadhav, A.S. Kirdant and T.K. Chondhekar , Appl .Sci. J.(2012),3(1),pp.157-182.
- [4] K.Popov,P.Igor,W.Hams,and,V.Andrey,Internationalprof.Tes t.J.,(2007),9(2),pp.13-17.
- [5] Smith, R.M, Martel,A.E."The selection of critical stability constants in chemical equilibrium and reaction models" American J. Chem. ,(1995),soc.42.
- [6] Tubas, chin. Chem. Letters,(2003),14,No.11,pp.1207-1210.
- [7] B.M.Kalshetty, S.S.Surarkandin, P.S.Hiremath and M.B. Kalashetti" International J. of Appl. Techn",(2011),2,Issu2.
- [8]
- [9] Majia.R.,A.Kassim, S.Ahmed Zaher,Nor.Azah Y.and HossR in A.,Int J.Electrochem.,(2011),sci.6.pp.4378-4387.
- [10] R.Marie, V.Peter and V.K. Krizovna, "Inorg. Chem. J",(2009),3,pp.26-32.
- [11] "Fundamentals of Analytical chemistry",Interscience, Skoog, and,D.A.,NewYork, (1998),p.536.
- [12] "Textbook of Quantitative an Inorganic Analysis", A.I. Vogel, Longmous Green London,(1961).
- [13] W.H.Brock, K.A.Jensem, C.K.Jorgensem and, G.B.Kaufmam, Polyhedron, (1983),2,pp.1-7.
- [14] "Principle of Inorganic Chem.5thed.",Cotton and Wikons,(1981).
- [15] Conductivity of coordination compounds in oraganic solvent, W.Geary,(1970).
- [16] Heterocyclic chemistry ,Yamanaka H.Obba S. and Sokamoto,(1975), 31,pp. 1115- 1127.
- [17] Ain seough A.W.,and Plowmam R.A.Aust.J.Chem,(1970),699,p.23.
- [18] A.K.Rama and ShahJ.R.,Indian J.Chem.,(1981),soc.58.
- [19] "Infrared and Ramam spectra of Inorganic coordination compounds", K.Nakamoto,John Wiely and Sous,(1986).
- [20] "Determination of chemical structure",Pasto DJ and UK., Prentcehall, (1969) .
- [21] H.C.Zahid,M.A.AKhter and T.Scloud in bioinorg. chem. And application ,article, (2006), ID83131, pp.1-13.
- [22] Pandeya,K.B,ompraksh and Singh R.P. , Indian J.Chem.,(1983),soc.531.
- [23] "Elements of magneto chemistery,2nded",Data R.L and Symal A., west east press New Delhi,(1993),p.101.
- [24] Satish,M. Annigeri, M.P.Suthish and V.K. Revankar, "Spectroscopic studies of bridge binuclear complexes of Co(II),Ni(II),Cu(II) and Zn(II) transition metal Chem." , springer,(2007),32,pp.81-87.
- [25] An introduction to ligand field,Figgis B.N,NewDelhi,(1976).