



Preparation, Characterization, and Theoretical Treatment Complexes Of Some Transition Metals with N5 Acyclic Derived From 2, 6-diacetyl pyridine

*Omar Hamad Shehab AL- Obaidi, Mahmmod Al-Jubori
*Chemistry department, Women Education College, Al-Anbar University
e-mail: dromaralobaidi@yahoo.com
Chemistry department, College of science , Al-Mustansrya University

Abstract:

A series of transition metal complexes with [2,6-diacetiminophenylenediamine –[2,2'diyl] pyridine]of the general formula $[MLCl]Cl$, $M= Co(II)$, $Ni(II)$ and $Cu(II)$, respectively have been synthesized and fully characterized on the bases of C.H.N.M elemental analysis, 1H NMR , UV- Visible and FTIR spectra , in addition the structure of complexes was characterized by magnetic moments and molar conductance in DMSO solution ,and molar ratio of metal were also determined. From the above of these studies and measurements suggest an octahedral geometry around $Co(II)$, $Ni(II)$ and $Cu(II)$.

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 Treatment, N_5 acyclic, transition metal.



Council for Innovative Research

Peer Review Research Publishing System

Journal: Journal of Advances in Chemistry

Vol 2, No. 2

editor@cirworld.com

www.cirworld.com, member.cirworld.com

1. Introduction:

Complexes of metal ions with synthetic macro cyclic ligand are of great importance, in part because of their research lance to many natural system e.g. , porphyrin and s, calamines publication of several reviews and books covering various aspects of synthetic macro cyclic ligands⁽¹⁻³⁾.

Acyclic model N_2O_2, N_2S_2 and N_4 system derived from 2,6 di acetyl pyridine are used in some chemical processes as catalysts^(4,5). They are also used in biological models to understand the structure of bio-molecules^(6,7). In the present paper the Co(II) , Ni(II) and Cu(II) complexes with N_4 -macrocyclic ligand derived from 2,6-dimethylpyridine and O-phenylene diamine have prepared, fully characterized by spectral and analytical techniques .

2. Experimental

2.1 INSTRUMENTATION:

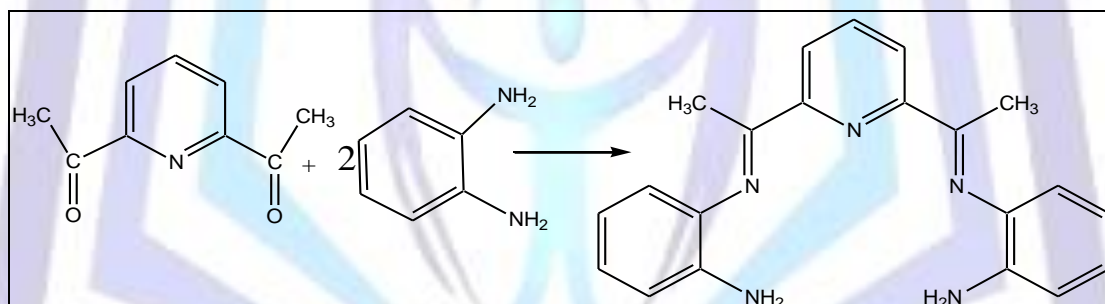
IR spectra were recorded using KBr pellets in the range of 4000-400 cm^{-1} on a shimadzu spectra photometer ,Micro analyses (C.H.N.) were obtained using a perkin-Elmer 2400 (C.H.N.) Micro analyzer .Electronic spectra absorptions were made on a shimadzo UV-visible spectrophotometer 160 C model for (10 $^{-3}$ -10 $^{-4}$ M) solution of N_4 ligand and metal complexes in DMSO and absolute ethanol solvents . The H1 nmr of the N_4 ligand chelate was tested on Bruker 300 MHZ 1H nmr spectrophotometer at Al-albiat university in Jordan using d_6 -DMSO solvent and TMS calibrate .

2.2 MATERIALS:

Reagents were supplied from Fluka , BDH chemicals.

A- Preparation of the ligand [L]:

A 20 ml methanolic solution of 2,6-diacetyl pyridine (0.01 mole) was refluxed with 100 ml methanolic solution of re crystallized O-phenyleneamine (0.02 mole) for about 4 hrs. A few drops of glacial acetic acid were added to the mixture and refluxed continued for (12-24) hrs. The mixture was concentrated to half of its volume and kept in desiccators for days .The ligand was filtered, washed with methanol , acetone and ether , dried in vacuum , over $CaCl_2$ pellets , in yield 80% , Scheme(1)The physical properties and analytical data, are shown in "Table 1".



Scheme 1 : synthesis of acyclic ligand N_5 [L].

B-General procedure for preparation of complexes :

The preparation of complexes was carried according to the method published in literature (8), (0.344gm,1 mmole) of N_5 ligand in (10 ml) absolute ethanol was added drop wise with stirring to a solution of 1 mmole of $(CoCl_2 \cdot 6H_2O, 0.236gm)$ in absolute ethanol (10 ml). The reaction were carried out for 24-36 hrs and colored precipitate formed . These were filtered off washed with ethanol, petroleum ether and dried on air ; yield : 70% [$Co(L)Cl_2$]. A similar method was used to prepare, ($NiCl_2 \cdot 6H_2O, 0.237gm$), ($CuCl_2 \cdot 2H_2O, 0.170gm$) , yields: 80% ($Ni LCl_2$) and 81% ($Cu L Cl_2$). The physical properties of metal complexes are shown in "Table 1".

3. Result and Discussion

3.1 Stoichiometric Study:

The estimation of the complex structure was carried out by using mole-ratio method in spectrophotometric technique. The results were referred to the (M:L) ratios for all synthesized complexes were(1:1).

3.2 Conductivity measurement

The conductivity for 10 $^{-3}$ M solutions of metal complexes Table (3) in (DMSO) , show that Co(II), Ni(II) and Cu(II) to be their (1:1) electrolytic (9).



3.3 IR and ¹H-NMR Spectra:

The IR spectra of the N4 ligand and its metal complexes provide information about the metal-ligand bonding. The medium doublet band in the region 3389-3325cm⁻¹ are assigned to -NH₂ group(10). The strong absorption bands at 1637cm⁻¹ and 1589-1541cm⁻¹ are assigned to azomethine groups of C=N (terminal) and C=N of pyridine ring (8). These bands are shifted to lower wave number in the spectra of complexes (1620-1631cm⁻¹), which confirms the coordination of nitrogen atoms of C=N and nitrogen pyridine ring to metal ion via formation of six-membered ring, that is kinetically stable (3). The change in intensity and sharpness of a -NH₂ absorptions in the 3300-3400cm⁻¹ reveals participation of NH₂ group in coordination with metal ions. Therefore, the acyclic ligand behaves as a pentadentate N5-system. Weak absorption bands in the far red regions 400-600 cm⁻¹. The spectra of all metal complexes, provides good indication for M-N band(11).

The proton nmr spectroscopy is a helpful tool for identification of organic compounds in conjunction with other spectrometric information's.

"Figure 1" shows ¹H-NMR of free ligand in d₆-DMSO solvent. ¹H-NMR spectra of the ligand displayed signals corresponding to the various protons of aromatic of benzyl and pyridine ring, as well as the deshielded absorptions of NH₂ protons (4H) in (6.5-9.5) ppm region. The condensation of one mole of 2,6-diacetylpyridine with two moles of o-phenylenediamine to form acyclic ligand of N5 type(13).

The singlet absorption in the 2-2.5ppm regions investigates as six hydrogen atoms of methyl groups attached to positions 2 and 6 of pyridine ring(14).

A multiple absorptions of chemical shift in the 7-8 ppm regions could be assigned to aromatic Ar-H and three protons of pyridine ring respectively (15).

The absence of any coupling interactions by H-N free groups due to the lack of availability of H neighbouring atoms render singlet peaks for imino -C=N protons(15).

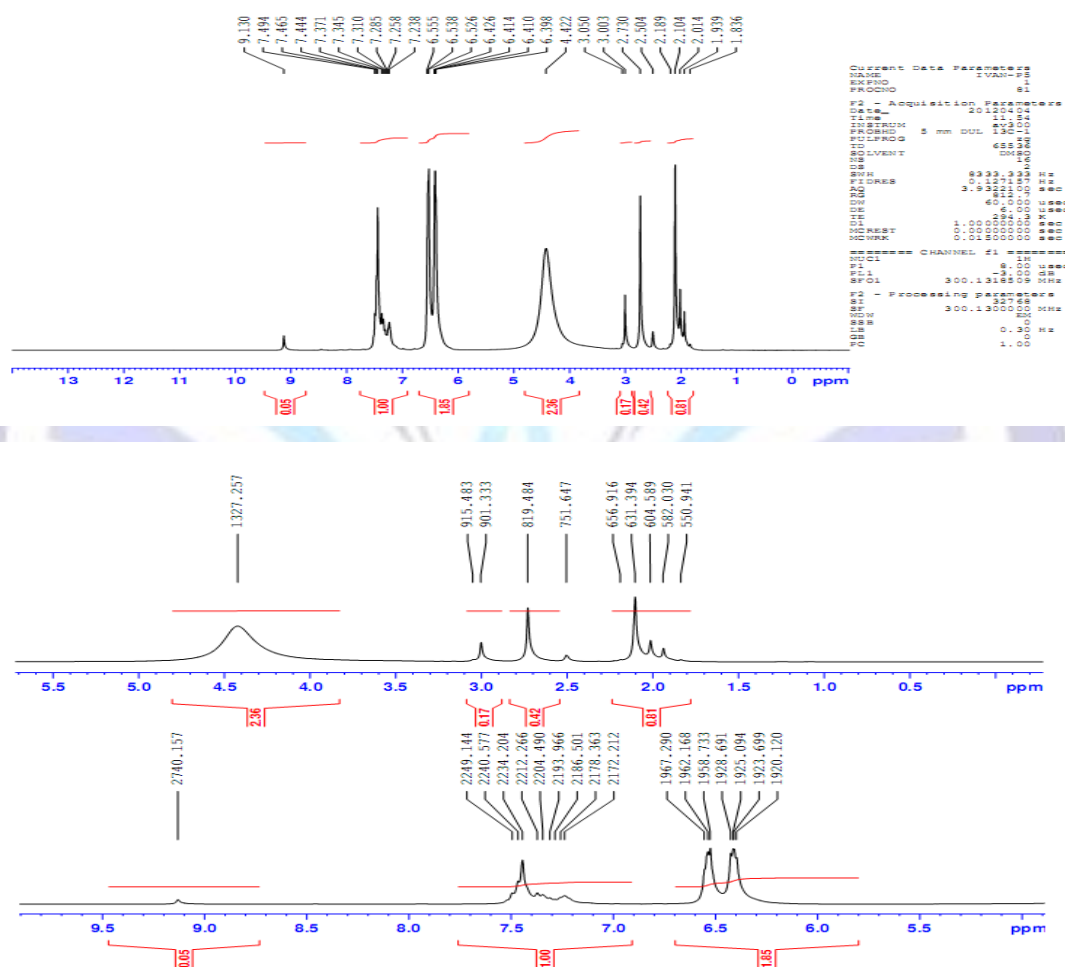


Fig 1: ¹H -NMR spectrum of ligand in d₆-DMSO.



3.4 UV-Visible spectra

The electronic spectra of the ligand and metal complexes were recorded in absorbent ethanol and DMSO solution respectively. The ligand exhibits bands at 234 and 266 nm, these are related to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition of C=N, C=C chromophores in the free ligand. The spectra of the complexes show bands in visible regions of spin-allowed transitions. As well as the Co(II), Ni(II) and Cu(II) complexes showed weak absorption peaks in the visible region, corresponding to the octahedral environments around ions which investigate its octahedral geometry from elemental analysis and mass spectra (16,17).

3.5 The magnetic moments

The magnetic moments of divalent Cobalt, nickel, and copper complexes lie in the 3.70, 2.25 and 1.30 BM ranges respectively at room temperature and are close to the predicted value for octahedral geometry around the metal atom (16).

3.6 The proposed structure

The data obtained from UV-Visible and FT-IR spectra, along with expected magnetic moment for all complexes supports the high spin geometry of Co(II), Ni(II) and Cu(II) complexes (17,18).

It is obvious, observed that free ligand of N5 system differs from N6-system, percent in literature (19-21), where the reaction conditions of metal salts sported coordination with N4 system proceeds rapidly, rather than template system, this fact has investigation the basis of data obtained from ¹H NMR, FT-IR, UV-Vis., and others measurements.

According to the elemental analysis, IR, UV-Visible spectra and magnetic moment of complexes, all the complexes could have the proposed structure in "Figure 2" where the ligand behavior pentadentate of N5 system.

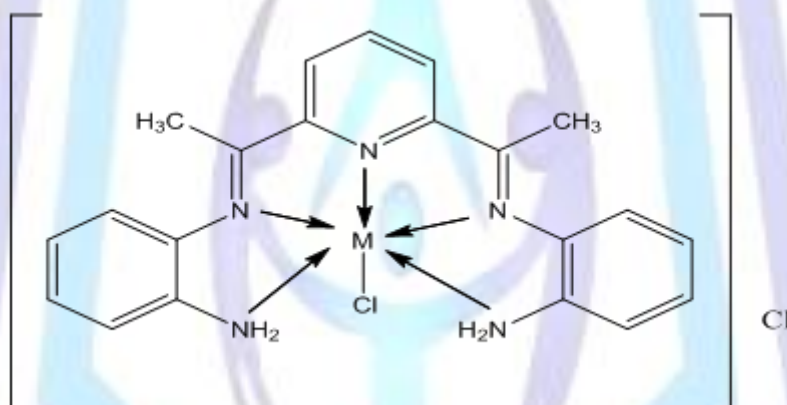


Fig 2 : The proposed structure of Metal complexes

3.7 Theoretical Study:

The ball and cylinders and some of selected structural parameters (bond length and angles) of the optimized geometries are shown in "Table 4", "Figure 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.

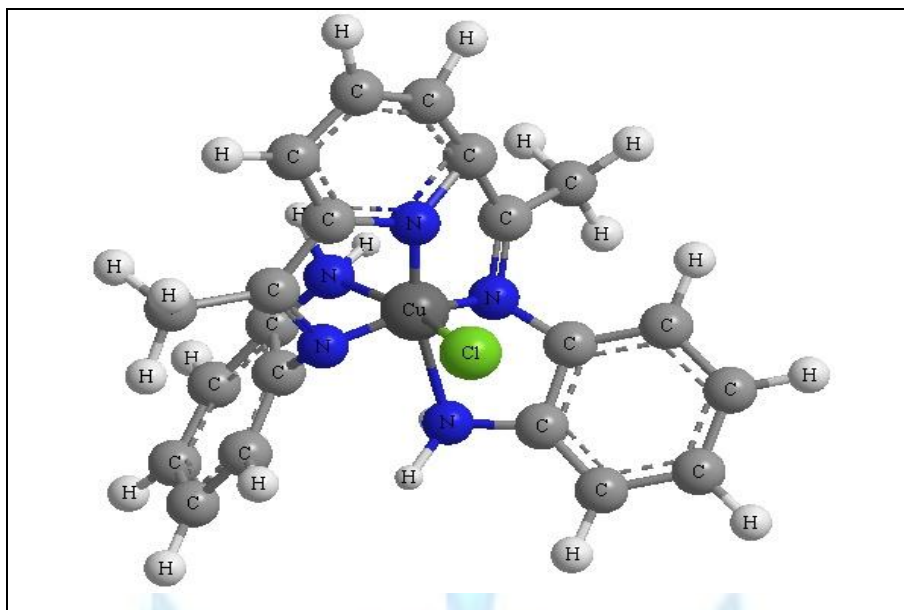


Fig 3 : The optimized structural geometry of Cu(II) complex

Table 1: Micro Elemental analysis (C.H.N.M) data of ligand

compound	Molecular formula	M.p. °C	color	%C Calc. (Found)	%H Calc. (Found)	%N Calc. (Found)	%Metal Calc. (Found)
L	343	225-227	brown	746.4 (44.31)	6.12 (5.81)	20.40 (19.71)	-
[CoLCI]Cl	473	280	Pale violet	53.29 (51.21)	4.43 (3.93)	14.66 (14.96)	13.30 (12.11)
[NiLCI]Cl	472	273	Pale green	41.70 (42.33)	3.475 (3.61)	4.861 (15.09)	11.03
[CuLCI]Cl	477	295	blue	52.78 (50.88)	4.43 (3.87)	14.66 (14.98)	13.30

 Table 2: Infrared spectral bands (cm^{-1}) and their assignments in the ligand and metal complexes

compound	$\nu(\text{C=N})$	$\nu(\text{NH}_2)$	$\nu(\text{C-N})$ $\nu(\text{C=N(py)})$	$\nu(\text{M-N})$	$\nu(\text{M-Cl})$
L	1637(s)	3389-365(m)	1589-1600	-	-
[CoLCI]Cl	1631-1591(s)	3549-3525(m)	1558-1521(s)	460-530(m)	295(w)
[NiLCI]Cl	1620(s)	3564-3408(br)	1575-1562(s)	434-484(w)	360(w)
[CuLCI]Cl	1654(s)	3379(br)	1559(s)	534-462	310(w)

W=weak, br=broad, s=strong, and m=medium



Table 3: Electronic spectra, magnetic moments and molar conductance of the prepared complexes

Compound	λ_{\max} (nm)	assignment	μ_{eff} BM	$^*\Delta M$ (Ω^{-1} $\text{cm}^2\text{mol}^{-1}$)
L	266 225	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$	-	-
[CoLCI]Cl ₂	288, 404, 470	$^4T_{1g}(F) \rightarrow ^4T_{2g}$ $^4T_{1g} \rightarrow A_{2g}^4$ $^4T_{1g}(F) \rightarrow ^4T_{1g}(p)$	3.79	73
[NiLCI]Cl	359, 377, 470	$A_{2g}^3 \rightarrow T_{2g}^3$ $A_{2g}^3 \rightarrow T_{1g}^3$ $A_{2g}^3 \rightarrow T_{1g}^3(P)$	2.25	65
[CuLCI]Cl ₂	345, 550, 590	$^2B_{1g}(F) \rightarrow ^2B_{1g}(F)$ $^2B_{2g}^2(F) \rightarrow ^2A_{2g}(p)$ C.T	1.30	82

*=molar conductance in 0.001M solutions in DMSO,C.T=charge transfer of L to M type.

Table 4 : structural parameters, bond length (Å) and angles(°) of the [Cu(L)Cl]Cl complex.

Parameters		Parameters		Parameters	
Bond lengths (Å)		Bond angles(°)		Bond angles(°)	
Cu(27)-Cl(28)	2.1600	Cu(27)-Cl(28)	2.1600	C(18)-C(17)-C(16)	119.9986
N(26)-H(47)	1.0500	N(26)-H(47)	1.0500	H(39)-C(16)-C(17)	120.0014
N(26)-Cu(27)	1.8460	N(26)-Cu(27)	1.8460	H(39)-C(16)-C(15)	120.0007
C(25)-H(46)	1.1000	C(25)-H(46)	1.1000	C(17)-C(16)-C(15)	119.9979
C(24)-C(25)	1.3370	C(24)-C(25)	1.3370	H(41)-C(18)-C(17)	120.0000
C(23)-N(26)	1.6241	C(23)-N(26)	1.6241	H(41)-C(18)-C(13)	119.9999
C(23)-C(24)	1.3370	C(23)-C(24)	1.3370	C(17)-C(18)-C(13)	120.0001
C(22)-H(45)	1.1000	C(22)-H(45)	1.1000	H(38)-C(15)-C(16)	119.9999
C(22)-C(23)	1.3370	C(22)-C(23)	1.3370	H(38)-C(15)-C(14)	120.0003
C(21)-H(44)	1.1000	C(21)-H(44)	1.1000	C(16)-C(15)-C(14)	119.9998
C(21)-C(22)	1.3370	C(21)-C(22)	1.3370	N(19)-C(14)-C(15)	107.0733
C(20)-H(43)	1.1000	C(20)-H(43)	1.1000	N(19)-C(14)-C(13)	118.4057
C(25)-C(20)	1.3370	C(25)-C(20)	1.3370	C(15)-C(14)-C(13)	120.0001
C(20)-C(21)	1.3377	C(20)-C(21)	1.3377	H(47)-N(26)-Cu(27)	110.8667
N(19)-H(42)	1.0500	N(19)-H(42)	1.0500	H(47)-N(26)-C(23)	110.8675
N(19)-Cu(27)	1.8460	N(19)-Cu(27)	1.8460	Cu(27)-N(26)-C(23)	138.2659
C(18)-H(41)	1.1000	C(18)-H(41)	1.1000	H(42)-N(19)-Cu(27)	135.7281
C(17)-H(40)	1.1000	C(17)-H(40)	1.1000	H(42)-N(19)-C(14)	135.7282
C(17)-C(18)	1.3370	C(17)-C(18)	1.3370	Cu(27)-N(19)-C(14)	88.5436
C(16)-H(39)	1.1000	C(16)-H(39)	1.1000	C(25)-C(24)-C(23)	119.9979
C(16)-C(17)	1.3371	C(16)-C(17)	1.3371	C(25)-C(24)-N(12)	128.9982
C(15)-H(38)	1.1000	C(15)-H(38)	1.1000	C(23)-C(24)-N(12)	111.0004
C(15)-C(16)	1.3370	C(15)-C(16)	1.3370	H(37)-C(11)-H(36)	109.5200
C(14)-N(19)	1.1762	C(14)-N(19)	1.1762	H(37)-C(11)-H(35)	109.4618



C(14)-C(15)	1.3370	C(14)-C(15)	1.3370	H(37)-C(11)-C(9)	109.4619
C(18)-C(13)	1.3370	C(18)-C(13)	1.3370	H(36)-C(11)-H(35)	109.4416
C(13)-C(14)	1.3370	C(13)-C(14)	1.3370	H(36)-C(11)-C(9)	109.4422
N(12)-Cu(27)	1.3030	N(12)-Cu(27)	1.3030	H(35)-C(11)-C(9)	109.4999
C(24)-N(12)	1.2600	C(24)-N(12)	1.2600	Cu(27)-N(12)-C(24)	104.0000
C(11)-H(37)	1.1130	C(11)-H(37)	1.1130	Cu(27)-N(12)-C(9)	93.4067
C(11)-H(36)	1.1130	C(11)-H(36)	1.1130	C(24)-N(12)-C(9)	114.9999
C(11)-H(35)	1.1130	C(11)-H(35)	1.1130	C(18)-C(13)-C(14)	119.9984
C(10)-H(34)	1.1130	C(10)-H(34)	1.1130	C(18)-C(13)-N(8)	128.9982
C(10)-H(33)	1.1130	C(10)-H(33)	1.1130	C(14)-C(13)-N(8)	110.9999
C(10)-H(32)	1.1130	C(10)-H(32)	1.1130	H(34)-C(10)-H(33)	109.5204
C(9)-N(12)	2.0384	C(9)-N(12)	2.0384	H(34)-C(10)-H(32)	109.4616
C(9)-C(11)	1.4970	C(9)-C(11)	1.4970	H(34)-C(10)-C(7)	109.4620
N(8)-Cu(27)	1.3030	N(8)-Cu(27)	1.3030	H(33)-C(10)-H(32)	109.4417
C(13)-N(8)	1.2600	C(13)-N(8)	1.2600	H(33)-C(10)-C(7)	109.4418
C(7)-C(10)	1.4970	C(7)-C(10)	1.4970	H(32)-C(10)-C(7)	109.4999
C(7)-N(8)	1.9464	C(7)-N(8)	1.9464	Cu(27)-N(8)-C(13)	104.0002
C(6)-H(31)	1.1000	C(6)-H(31)	1.1000	Cu(27)-N(8)-C(7)	97.7309
C(5)-H(30)	1.1000	C(5)-H(30)	1.1000	C(13)-N(8)-C(7)	148.5777
C(5)-C(6)	1.0286	C(5)-C(6)	1.0286	H(31)-C(6)-C(5)	122.1912
C(4)-C(7)	1.3370	C(4)-C(7)	1.3370	H(31)-C(6)-C(1)	122.1914
C(4)-C(5)	1.3370	C(4)-C(5)	1.3370	C(5)-C(6)-C(1)	115.6173
N(3)-Cu(27)	1.3030	N(3)-Cu(27)	1.3030	C(10)-C(7)-N(8)	137.2290
N(3)-C(4)	1.2600	N(3)-C(4)	1.2600	C(10)-C(7)-C(4)	137.2291
C(2)-C(9)	1.3370	C(2)-C(9)	1.3370	N(8)-C(7)-C(4)	85.5420
C(2)-N(3)	1.2600	C(2)-N(3)	1.2600	H(30)-C(5)-C(6)	115.3087
C(1)-H(29)	1.1000	C(1)-H(29)	1.1000	H(30)-C(5)-C(4)	115.3086
C(6)-C(1)	1.3370	C(6)-C(1)	1.3370	C(6)-C(5)-C(4)	129.3826
C(1)-C(2)	1.3370	C(1)-C(2)	1.3370	Cl(28)-Cu(27)-N(26)	53.2011
		H(44)-C(21)-C(22)	120.0177	Cl(28)-Cu(27)-N(19)	47.3262
		H(44)-C(21)-C(20)	120.0172	Cl(28)-Cu(27)-N(12)	50.5084
		C(22)-C(21)-C(20)	119.9652	Cl(28)-Cu(27)-N(8)	63.0505
		H(43)-C(20)-C(25)	120.0131	Cl(28)-Cu(27)-N(3)	96.4633
		H(43)-C(20)-C(21)	120.0132	N(26)-Cu(27)-N(19)	5.9331
		C(25)-C(20)-C(21)	119.9737	N(26)-Cu(27)-N(12)	5.9330
		H(46)-C(25)-C(24)	119.9996	N(26)-Cu(27)-N(8)	109.5001
		H(46)-C(25)-C(20)	120.0002	N(26)-Cu(27)-N(3)	109.5000
		C(24)-C(25)-C(20)	120.0003	N(19)-Cu(27)-N(12)	6.6846
		H(45)-C(22)-C(23)	120.0002	N(19)-Cu(27)-N(8)	104.0000
		H(45)-C(22)-C(21)	120.0000	N(19)-Cu(27)-N(3)	109.5000
		C(23)-C(22)-C(21)	119.9997	N(12)-Cu(27)-N(8)	109.4998
		N(26)-C(23)-C(24)	40.4207	N(12)-Cu(27)-N(3)	104.0000
		N(26)-C(23)-C(22)	160.4180	N(8)-Cu(27)-N(3)	104.0001
		C(24)-C(23)-C(22)	119.9999	C(7)-C(4)-C(5)	128.9987



REFERENCES

- [1] Tyagi M. and Chandra. 2012. ORen Journal of Inorg.Chem.2, pp 41-48
- [2] Mishra, D. Nastar s., Drew, M.G.B. and Gattopadhyay S.K. 2006. Inorg. chimica Actr.359, 585-592
- [3] Raja N. and Ramesh R. (2010), spectrochimica Acta A, 75, pp.713-718
- [4] Chandra S., Tyagi M. and Agrawal , S. 2010. journal of Saudi chem. Soc.15,pp.49- 54.
- [5] Sharma K., Singh, Fahnui, N. and Singh ,R.V. 2010. Spectrachimica Acta A. 75,pp. 422-427
- [6] FerraZ ,K.O, Waradell, S.M.SV and Beraldo H. .2009. *spectrachimica Acta. A*,737, Pp.140-145.
- [7] D.P. singh , S. Nupar, B.p. Yadar and V. B.rara . 1997. *polyhedron*.16 (13),pp.2229-2232.
- [8] Ali S.A . , soliman, M.M. Aboaly, R.M. Ramadam, *J.Coord.chem*.55. 2002.1161
- [9] Solooman , L..D, Kessling , G. Mobilition of cation –macrocylic Ligand complexes , *pure Appl. Chem*.1993. 65(7),1533.
- [10] Sliverstin R.M. ,G.c.Bassler, T.C. Morill, spectroscopic Identification of organic compounds 4thed.,Wiley, New York. 1981.
- [11] Nakmato K., Infrared and Raman spectra of Inorganic and coordination compounds, 4th ed., Wiley, New York. 1986.
- [12] Ferraro, J.R "Low frequency Vibration of Inorganic and coordination compound Plenum press, New York.1977.
- [13] Ayed , S.al. Shilri. 2004. Synthesis, characterization and thermal analysis of some new metal complexes of poly dentate Schiff base, *spectra chimica Acta, part A*, 60, 1189-1192.
- [14] Williams D.H. ,I.Fleming, *Spectroscopic Methods in Organic Compounds*,4th. Ed. Mc.Graw-Hill.1989. London.
- [15] Sreekanth,M.R.P.Kurup, *Spectrochim.Acta*,59A. 2003.1349.
- [16] Lever A.B.P. " *Electronic spectra of Inorganic and coordination compounds* "Elsevier. 1968.
- [17] wived D. , r., Sing V.Falimi N, Singh R.V. 2003. *Int. Chem. J. Sci*, (2)p.233.
- [18] Josey R.S. phus.C.J. Dhanara j and M.S Nair *Transition Met Chem*. 2006. 31, 699.
- [19] Canpolat E.A. Y. and M.Kayes, *transition .Met. Chem*. 2006. 31, 653.
- [20] Clark, R.J.H. and Williams., C.S. Inorganic chem. 1965. 4,350.
- [21] Singh D. P. and et al . *polyhedron*. 1977. 16(13) pp.2229-2232.