

Synthesis, Characterisation and Structural Derivation of Ni(II) Complexes with Diammine Derivative of 1, 2, 4-Triazole Schiff's Base

Jamaluddin M.

Assistant Professor, Dept. of Chemistry, V.B.M.College, Siwan, 841226, (Bihar) India

Abstract: Synthesis of Ni(II) Complexes with ligand 4-(2,4-diaminobenzaldimino)-3,5-dimercapto-1,2,4-triazole(L) as $[NiLX_3].H_2O$, X= Pyridine, pyridine-oxide, Morpholine and picoline. Ligand [L] is synthesized by the condensation of 3,5-dimercapto-1,2,4-triazole and 2,4-diaminobenzaldehyde. The complexes are synthesized by refluxing the ligand and Ni(II) in presence of base. The complexes are characterized by the elemental analyses, magnetic moment measurement, IR, and spectral data analyses. The physical measurements and spectral data analyses and interpretation show that the ligand act as bidentate and coordinated through N and S of $>NH-NH_2$ and SH group ligand. The ligand is a schiff's base derivative. The complexes of ligand and Ni(II) analyses and the structures of the complexes suggested.

Keywords: 1,2,4-triazole, 4-(2,4-diaminobenzaldimino)-3,5-dimercapto-1,2,4-triazole, Schiff's base, IR and Spectral data

1. Introduction

The paper is related to the study on the co-ordination behaviour of the Nitrogen and Sulphur bidentate system. The ligand possess mercapto system. So a comprehensive survey of coordination behaviour of C=S, C=N and -SH is required. Nitrogen donor of many complexes studied.¹⁻¹⁰ Thiourea and its derivatives are the simplest ligands where as many schiff's bases with N and S donor system are also studied¹¹. There are number of works available on the coordination behaviour of schiff's bases of aldimines and ketoimines types¹²⁻¹³. The schiff's bases characterised by the presence of C=N double bond and are excellent chelating ligands and acyclic. The schiff's base metal complexes have a very special role in inorganic chemistry¹⁴⁻¹⁶. They are important because they are synthesised in different fields¹⁷. They are also found to have a number of pharmacological utility¹⁸. The coordination behaviour of chelates of schiff's bases containing nitrogen, sulphur and oxygen donor atoms works already reported. Ni(II) complexes with tridentate ONO donor schiff's base derivative derived by refluxing ethanolic solution.¹⁹ The low molar conductances indicate non-electrolytic nature of complexes. The μ_{eff} values of the complexes of Ni(II) indicate the octahedral around Ni(II) ions supported by electronic spectra. Metal complexes with schiff's base ligands derived from aromatic aldehyde with aromatic amines have been reported recently²⁰⁻²⁴. Solution ability constants of the complexes of schiff's bases with various metal ions have been intensively studied²⁵⁻³⁰. Polymetallic complexes of Fe(II), Co(II), Ni(II) and Cu(II) with ONO tridentate schiff's bases have been reported³¹. Physico-Chemical studies on Cr(III), Co(II), Ni(II), and Cu(II) complexes with bidentate schiff's bases have been reported³². The complexes have been synthesised and characterised on the basis of analytical, infrared and electronic spectral studies. Octahedral structures for Cr(III), Co(II), and Ni(II) and a square planar structure for Cu(II) complexes have been suggested. The Co(II), Ni(II) and Cu(II) complexes are non-electrolytic while Cr(III) complexes behave as

electrolytic. Synthesis, spectral and magnetic studies of Ni(II) complexes of heterocyclic schiff's bases have been reported³³. The value of Racah parameter B and C were calculated by using different sitting procedures as described by König³⁴, to study the nephelauxetic effect which describes the fact that B values lower on complexation whereas free metal ion values are relatively higher. Jørgensen³⁵ attributed the nephelauxetic effect to central field covalency and symmetry restricted covalency. The magnetic moment data coupled with electronic spectral data have suggested octahedral geometry to all the complexes. The complexes of Co(II), Ni(II) and Cu(II) with schiff's bases ligands prepared by condensing pyridol-2-carboxaldehyde with m-nitroaniline and p-nitroaniline complexes³⁶. The complexes derived from p-nitroaniline are ionic, paramagnetic and octahedral and the complexes of m-nitroaniline are non-ionic, paramagnetic, tetrahedral Co(II), Cu(II) and square planar Ni(II). The fungicidal activity of ligands and complexes reported against the fungicidal activity of vegetative plants at different concentrations in the form of solution or suspensions. The metal complexes reported more fungitoxic than the free ligands which is observed for four coordinated complexes of Co, Ni and Cu with p-nitroaniline. It may be due to unsaturation of coordination number. The fungistatic activity of metal chelates were found in order of Cu, Ni and Co. The role in biological processes,³⁷⁻³⁸ of mixed ligand complexes of metal ions, Cyanopyridines with different aryl and alkyl groups found to possess various biological activities³⁹⁻⁴⁰. The metal complexes of schiff's bases are the subject of intensive research due to their novel structural features, spectral, magnetic properties, their industrial and biological importance are much accountable. The biological activities, catalytic properties and analytical applications can be correlated to the structure of schiff's bases⁴¹⁻⁴³. A brief survey of work already reported as the complexes of schiff's bases of substituted 5-triazoles. There is great pharmacological importance of d-metal complexes of schiff's bases obtained from substituted 1,2,4-triazole. The schiff's base obtained from benzaldehyde and 4-amino-3-ethyl-5-mercapto-5-triazole

has been reported to form complexes with some metal ions⁴⁴. S.N.Dubey and Beena kausik⁴⁵, synthesised 4-amino-5-mercapto-3-n-propyl-5-triazole and 5-mercapto-3-n-propyl-4-salicylaldimino-5-triazole and prepared complexes with Ni(II). The IR spectra of ligand and complexes have suggested the bidentate (N and S donor atoms). The octahedral geometry of Ni(II) complexes represented by the electronic spectral data coupled with magnetic values.

2. Experiment

All chemicals were used of AR grade. The compound 4-(2,4-diaminobenzaldimino)-3,5-dimercapto-1,2,4-triazole was prepared by literature⁴⁶⁻⁴⁹.

4-(2,4-diaminobenzaldimino)-3,5-dimercapto-1,2,4-triazole is prepared by the condensation of thiocarbohydrazine (10.5 gm, 0.1 M) and carbondisulphide (11.5 ml, 0.20 M). The mixture is taken in round bottom flask fitted with Leibig condenser containing 100 ml pyridine and refluxed on an oil bath for one hour, from the boiling solution a precipitate is formed and after cooling pale yellow prisms are obtained. The pyridinium salt (4.6 gm) obtained is dissolved in hot water (20 ml) and conc. HCl (3 ml) is added. The coloured rods of free ligand separated out. The melting point of crude product is found to be 216-217 °C. The preparation of ligand is achieved by refluxing the mixture containing equimolar quantities of 4-amino-3,5-dimercapto-1,2,4-triazole and 2,4-diaminobenzaldehyde in ethanol for one hour. The volume of mixture is allowed to stand overnight at room temperature. The yellow crystals are obtained. The compound is recrystallised from ethanol, (C₉H₁₀N₆S₂).

The complexes of Ni(II) are prepared by mixing the ethanolic solution of hydrated Ni(II) separately with (0.5 ml) salt and ethanolic solution of ligand (3.6 gm, 0.5 ml). Both solutions of 1:1 molar ratio are mixed together. The mixture is refluxed on a water bath for 2-3 hours. On refluxion, the complexes were separated. The mixture was cooled to room temperature, filtered and washed with water and dried. The complexes and the ligand gave the satisfactory M, N and S analysis.

The alcoholic solution of 0.0051 M metal chloride and the alcoholic solution of 0.01 M ligand were mixed together with about 2 ml of appropriate base and the contents were refluxed on a water bath at low temperature. On cooling, the precipitate separated out. The contents on dilution with water insured the complete precipitation. The precipitate was filtered, washed with water, followed by several portions of alcoholic water and aqueous base solution. The precipitate was dried in a desiccator over anhydrous CaCl₂. On elemental analysis all complexes gave satisfactory results of the elemental measurement. The magnetic measurement of the complexes were made on Gouy balance using appropriate calibrant. The IR recorded in KBr disc in 4000-3500 cm⁻¹. The electronic spectra of the complexes were recorded by UV-Vis spectrophotometer.

Analytical Table:

S.N O.	Compound	% M Calc Found	% C Calc Found	% H Calc Found	% N Calc Found	% S Calc Found	% O Calc Found
1.	C ₉ H ₁₀ N ₆ S ₂ (LH)	---	40.6 0 40.7 5	3.75 3.60	31.5 8 31.6 8	24.0 6 24.0 0	---
2.	[NiL.3H ₂ O]. H ₂ O.	14.8 3 14.5 0	27.2 9 27.2 0	4.30 4.10	21.2 3 21.0 0	16.1 7 16.0 0	16.1 7 16.0 0
3.	[NiL.Py ₃]	10.4 7 10.3 0	51.3 7 51.4 0	4.28 4.20	22.4 7 22.3 0	11.4 1 11.2 0	---
4.	[NiL(py-O) ₃]	9.64 9.50	47.3 1 47.2 0	3.94 3.70	20.7 0 20.5 0	10.5 1 10.5 0	7.89 7.70
5.	[NiL(Mor) ₃]	10.0 4 10.0 0	43.1 0 43.0 0	6.16 6.00	21.5 5 21.4 0	10.9 5 10.5 0	8.21 8.20
6.	[NiL(α-Pic-O) ₃]	9.02 9.00	49.7 9 50.0 0	4.61 4.50	19.3 6 20.0 0	9.84 10.0 0	7.38 7.20

3. Result and Discussion

The formation of complexes represented by the physical measurements as magnetic moment measurement values, electronic spectra and IR values, change from free state of metal ions ligand. The magnetic moment values are tabulated as;

S.No.	Complexes	$\mu_{eff}(BM)$
1.	[NiL.3H ₂ O]. H ₂ O	2.85
2.	[NiL.Py ₃]	2.79
3.	[NiL.(Py-O) ₃]	2.84
4.	[NiL.(Mor) ₃]	2.85
5.	[NiL(α-Pic-O) ₃]	2.78

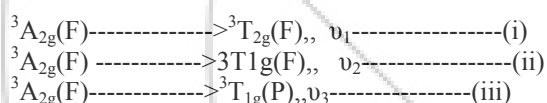
Ni(II) complexes generally form four coordinated tetrahedral or planar and six coordinated octahedral complexes depending upon the electronegativity and geometry of the ligand. If the complex is diamagnetic, it can have either square planar or trigonal bipyramidal configuration. If the complex is paramagnetic, then the configuration is octahedral geometry. In an octahedral field the triplet t_{2g} lies lower in energy than the doublet e_g . The electronic configuration in ground state is $(t_{2g})^6(e_g)^2$ in which only one arrangement of the electrons and therefore non-degenerate and not liable to Jahn-Teller distortion⁵⁰. The six ligands are identical one may expect the complexes to be quite regular. The two e_g electrons are spin parallel and since there is no resultant orbital angular momentum once the degeneracy of the d-orbitals is lifted, magnetic moment should be close to the spin only value of 2.8 BM. The first excited triplet level ($^3T_{2g}$) has essentially

the configurations $(t_{2g})^5(e_g)^3$, therefore, three possible ways of arranging the five t_{2g} electrons and d_{yz} orbitals retain their rotational properties with respect to the Z-axis. This level, therefore has orbital angular momentum⁵¹ and the spin orbital coupling of Ni(II) is large enough to allow the mixing of this level with the lowest level to produce the true ground state. The effective result is that the orbital angular momentum is not completely "quenched" by the ligand field and moment found for octahedral Ni(II) complexes are within the range of 2.9-3.4BM, the values being independent of temperature.

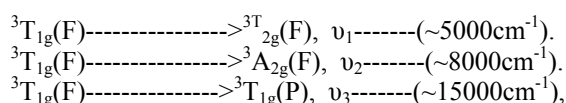
In my work, the magnetic moment of different Ni(II) complexes have been measured at room temperature. Magnetic values of complexes as observed are in the range of 2.78-2.85BM. The μ_{eff} of chelated complexes are straight forward and are in the range expected for octahedral Ni(II) complexes. The magnetic moment values of mixed ligand complexes are lower than high spin O_h and T_d Ni(II) complexes may be attributed to the presence of some square surround by O_h or T_d Ni(II) species.

4. Electronic Spectra of Complexes

The complex compounds of divalent Ni(II) have been obtained in different stereochemistry but the complexes with coordination number four and six are most common. The Ni(II) ion has 3F ground state and the next higher state having the same multiplicity is 3P . The transition in octahedral geometry in weak field are as⁵²-



The value of $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$ is directly taken to be ligand field strength and expected to fall in the range of 8000-11,500 cm^{-1} . The expected range of second and third transitions are 15,000-19,000 cm^{-1} and 25,000-29,000 cm^{-1} . These are Leport forbidden transition and so their extinction constant lie between 1 and 30. Ballhausen⁵³ has calculated the energy and measured the spectra of fairly large number of octahedral complexes. The ratio of $\nu_2:\nu_1$ is found to be 1.8, which according to Ballhausen is one of the reliable criterion of octahedral Ni(II) complexes. Jorgensen, however found experimentally that the ratio of $\nu_2:\nu_1$ comes to be 1.6-1.8. In the case of distorted octahedral complexes O_h symmetry changes to D_{4h} symmetry. Brubakar et al⁵⁴ have made an exhaustive studies on the spectral behaviour of complexes with D_{4h} symmetry and calculated their energies. The $^3T_{1g}(F)$ state term become ground state in tetrahedral symmetry. The splitting of the energy level in tetrahedral symmetry, the absorption bands are:



It is somewhat different to analyse the spectra of tetrahedral complexes because of the effect of spin orbital coupling. The reliable identifying characteristic of T_d complexes have been suggested⁵⁴. The first criterion for

distinguishing between two cases in the value of extinction coefficient of the band at maximum. Practically, all tetrahedral complexes have rather intense blue or green colour due to presence of an absorption band in the red part of the visible region.

The electronic spectra of Ni(II) complexes under investigation have been studied, the bands are obvious in the region 200-450 nm, however, the bands are absent in the region beyond 450 or 470 nm, clearly show the absence of tetrahedral geometry of complexes. Had, the complexes possess tetrahedral geometry, they would have exhibited the strong absorption band in the region 650-800 nm. Hence, octahedral geometry for the complexes is predicted. The band positions are not clearly observed due to obscuring by ligand absorption and charge transfer bands. The band in the region 220-260 nm are assigned to $n \rightarrow \pi^*$ whereas the bands in the region 320-480 nm are assigned to combination of $\pi \rightarrow \pi^*$ and $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$. The bands ~ 460 nm are assigned as combination of bands of charge transfer and $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$.

S.No.	Complexes	Medium	Charge transfer (nm)	d-d-transition with assignment (nm)
1.	[NiL.3H ₂ O].H ₂ O	Ethanol	405	575
2.	[NiL.Py ₃]	Ethanol	395	675
3.	[NiL.(Py-O) ₃]	Ethanol	385	575
4.	[NiL.(Mor) ₃]	Ethanol	380	385
5.	[NiL.(α -Pic-O) ₃]	Ethanol	380	675

IR Spectral Study of Complexes

S.No.	Complexes	NH (cm^{-1})	OH (cm^{-1})	SH (cm^{-1})	M-N (cm^{-1})	M-S (cm^{-1})	M-O (cm^{-1})
1.	C ₉ H ₁₀ N ₆ S ₂ (LH)	3265	-	2565	-	-	-
2.	[NiL.3H ₂ O].H ₂ O	---	2860	2555	310	275	450
3.	[NiL.Py ₃]	---	2860	2550	300	270	-
4.	[NiL.(Py-O) ₃]	---	2865	2555	310	275	-
5.	[NiL.(Mor) ₃]	---	2855	2545	315	270	-
6.	[NiL.(α -Pic-O) ₃]	---	2860	2545	315	270	-

Important absorption band in IR spectrum of the ligand and their assignment:

S.No.	Frequencies (cm^{-1}) $LH(C_9H_{10}N_6S_2)$.	Assignment
1.	3270	$\nu(>N-H)$ stretching
2.	3025	$\nu(>C-H)$ stretching
3.	2565	$\nu(-S-H)$ stretching
4.	1525 1445	Skeletal vibration of benzene ring
5.	760	$\delta(C-H)$
6.	700	$\nu(>C-S)$

IR spectra of ligand and complexes have been studied and their band positions of important groups and those of M – N and M – S have been tabulated. The band positions have been assigned on the basis of works reported earlier⁵⁵⁻⁶⁰. The sharp and strong bands near 3270 cm^{-1} , 3025 cm^{-1} , 700 cm^{-1} have been assigned to stretching (ν_{vib}) vibrations. The lower values of -NH bands are assignable due to H – bonding — intramolecular / intermolecular⁶¹⁻⁶⁶. In complexes, the -NH frequency is lowered very minutely which may be due to the coordination of one of the three -NH₂ in complex formation and others remain free. The aromatic ring vibrations are observed as expected in the spectra of the complexes. The bands in the lower range near 315 , 275 cm^{-1} are assigned to M-N and M-S respectively.

5. Conclusion

From the elemental analyses, magnetic moment measurements, electronic and IR spectral studies, Author concluded that Ni(II) forms the octahedral complexes with the ligand 4-(2,4-diaminobenzaldehydimino)-3,5-dimercapto-1,2,4-triazole(L) and in presence of suitable base. The Author on the basis of physical measurements proposed the structure of the complexes.

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References

- [1] D.Rabinovich and G.Parkin., J. Am. Soc. 115, 9822(1993).
- [2] M.G.Kanatzidis and Huang., Coord. Chem. Rev. 130, 509(1994).
- [3] J.A.Ibers et al., Inorg. Chem. 32, 3201(1993).
- [4] R.H.Grubbs et al., J. Am. Chem. Soc. 118, 100(1996).
- [5] W.A.Herrmann et al., Chem. Eur. J. 2, 773(1996).
- [6] F.A.Cotton and B.Hung., Prog. Inorg. Chem. 40, 179(1992).
- [7] F.A.Cotton et al., Inorg. Chem. Acta. 252, 251(1996).
- [8] R. L. Luck et al., Inorg. Chem. 26, 2422(1987).
- [9] K.C.Moloy and J.L.Petersou., J. Am. Chem. Soc. 7695(1995).
- [10] M.G.Kanatzidis et al., Inorg. Chem. 32, 2453 (1993).
- [11] A. Yamaguchi, R.B.Penland, S.Mizushima, T.J.Lane, C. Curran and J.V.Quagliana.,
- [12] J. Chem. Amer. Soc. 80, 527(1963).
- [13] R.H.Holm, G.W.Everett Jr, and A.Chakravorty., Prof. Inorg. Chem. 7, 83(1996).
- [14] S.Yamada, Y.Kuge and K.Yamanouchi., Bull. Chem. Soc. Japan, 40, 1964(1967).
- [15] Y.Sreenivasulu and K.HussainReddy., J. Ind. Chem. Soc. 70, 1(1993).
- [16] R.Menif, A.E.Martell, P.J.Squatrito and A.Clearified., Inorg. Chem. 29, 4723(1990).
- [17] A.Z.Sami and C.R.Jejukar., Ind. J. Chem. 34A, 241(1993).
- [18] B.K.Patel and S.C.Choudhary., Ind. J. Chem. 25, 661(1988).
- [19] A.Mahindra, J.M.Fischer and M.Rabinnoritz., Nature (London), 303, 64(1983).
- [20] S.Sama, M.R.Sudarsan kumar, C.G.R.Nair, and C.P.Prabhakaran., Ind. J. Chem. 32A, 67(1993).
- [21] P.Singh, V.Singh and V.Rani., J. Ind. Chem. Soc. 57, 934(19980).
- [22] M.A.Pujari and T.D.Bhazamagoudar., J. Ind. Chem. Soc. 57, 462 (1980).
- [23] N.S.Biradar and S.D.Angadi., Manatsh. Chem. 108, 525 (1977).
- [24] N.S.Biradar and S.D.Angadi., J. Inorg. Nucl. Chem. 38, 1405 (1976).
- [25] P.S.Phabhu and S.S.Dodwad., J. Ind. Chem. Soc. 60, 546 (1983).
- [26] S.S.Dowad, M.G.Datar and J.R.Patik., J. Ind. Chem. Soc. A. 22, 83 (1983).
- [27] M.Nagar and R.K.Baslas., J. Inorg. Nucl. Chem. 57, 848 (1980).
- [28] D.V.Jahagirdar and D.D.Khanalkar., J. Inorg. Nucl. Chem. 35, 921(1973).
- [29] M.R.Mahmoud, A.Wad, A.M.Hammam and H.Shaber., Ind. J. Chem. Sect. A. 19, 1131 (1980).
- [30] R.S.Saxena and M.K.Sharma., J. Ind. Chem. Soc. 60, 543 (1983).
- [31] M.S.Mayadeo and S.Bhattacharjee., J. Ind. Chem. Soc. 60, 606 (1983).
- [32] Bipin B.Prabhu and Dilip K.Das., J. Ind. Chem. Soc. 67, 504, (1990).
- [33] Sr.Rosamma Thomas and Geetha Paramshwaran., J. Ind. Chem. Soc. 69, 117(1992).
- [34] P.G.More and pawar., J. Ind. Chem. Soc. 70, 154(1993).
- [35] E.Konig., Struct. bonding, 9, 175 (1971).
- [36] C.K.Jorgensen., Struct. bonding 1, 3(1966).
- [37] Mithilesh kumar and A.K.Singh., Asian J. Chem. 10(2), 233 (1998).
- [38] L.Hellerman and C.C.Stock., Chem. 125, 771 (1938)(J. Biol.).
- [39] G.Nalmstron., Arch. Biol. Chem. Bio. Phys. 58, 398 (1953).
- [40] H.H.Mausa, L.M.Chaboka and P.Laki., Egpt. J. Chem. 26, 469 (1983).
- [41] C.M.Carson, R.J.Bhr and R.B.Rogers., Chem. Abstr. 92, 6537 (1980).

- [42] A.Syamal., *Coord. Chem. Rev.* 16, 309 (1979).
- [43] M.L.Gupta and K.K.Pande., *J.Ind.Chem.Soc.* 62, 34(1985).
- [44] M.S.Mayadev,P.S.Mane and T.K.Chondhekar., *Ind. J. Chem. A*,22,542 (1983).
- [45] C .V.Gadag and M.R.Gajendragad.,*Curr.Sci.* 48, 839(1979).
- [46] S.N.Dubey and Beena kausik.,*Ind. J. Chem.* 28A.425(1989).
- [47] G.R.Burna . , *Inorg . Chem .* 7, 277 (1998).
- [48] G.Brauar . , Edited, "Handbook of preparative inorganic chemistry."Academic press New York, 1570 (1965).
- [49] G. R . , *Inorg . Chem .* (1968).
- [50] I. Nellone., "Organic Reagent in Inorganic Analysis,"The Elakislon Co.Philadelphia(1941).
- [51] H.A.Jahn and E.Teller.,*Proc.Roy.Soc.A*, 161, 220(1937).
- [52] B.N.Figgis and J.Lewis., "Modern coordination chemistry,"(H.Lewis andR.G.Wilkins eds), Interscience,New York,400(1960).
- [53] C.K.Jorgensen., *Acta.Chem. Scand.* 9 . 1362. 16, 877(1955).
- [54] C.J.Ballhausen .,Dan . Mut .Fys . Medal . 29 Nov.(1954).
- [55] D.N.L.Goodgame,M.Googame and F.A.Cotton ., *J.Amer.Chem. Soc.* 83, 4161 (1961).
- [56] J.K.Cooley et al ., *J.Org. Chem.* 25, 1734(1960).
- [57] J.P.Freeman ., *J.Am. Chem. Soc.* 80 ,5954(1959).,
- [58] D.Hadzi and D.Prevrsek., *Chem. Abs.* 52 , 97661(1959).
- [59] E.E.Baumgarten, et al.,*J. Org. Chem.* 30. 1203 (1965).
- [60] K.K.Ramaswamy, et. al., *J. Ind. Chem. Soc.* 5, 156 (1967).
- [61] P. C. Miss Trivedi., *J. Ind. Chem. Soc.* 50, 81 (1973).
- [62] L. J. Bellamy., "The Infrared spectra of complex Molecules",Mathuen London 95-98(1954).
- [63] A. D. Cross., "An Introduction to practical IR spectroscopy." Butterworth(1964).
- [64] C. N. Rao., "Chemical Application of IR spetroscopy," Academic press (1963).
- [65] N. R. Jones and Sandorfy ., "Technique of Org. Chem.,"Vol. IX. Ed. W.West Chemical Applications of spectroscopy,(P-487),Interscience New York(1956).
- [66] B.Singh ,Lakshmi and U.Agrawala., *Inorg. Chem.* 8, 2341(1969).
- [67] C.Tanaka, K. Kurotani and S. Mizushima., *Spectro. Chem. Acta.* 9, 265(1957)