

THE SPECTRAL STUDIES OF NICKEL(II) COMPLEXES MULTIDENTATE LIGAND

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Abstract

The Nickel (II) complexes with formula $[Ni(C_{20}H_{22}N_4S)X_2]$ as $X = NO_3^- > CH_3COO^- > HCOO^- > SCN^- > Cl^- > NCS^-$ have been synthesized and characterized utilizing a multidentate ligand. The NMR data lies in the range of +70 – 185 ppm 1H NMR typical of high spin Ni (II) Complexes and No doubling of peaks observed in NMR spectra. The U.V so the $\pi \rightarrow \pi^*$ transitions with in a benzimidazolyl group.

Introduction

Nickel shows a wide range of oxidation states varying from (-1) to (+IV) but its chemistry is predominantly that of the (+II) state. Nickel (II) forms a large number of complexes with coordination numbers four to six. Octahedral complexes are characteristically blue or purple. Three spin allowed transitions $^3A_{2g} \rightarrow ^3T_{2g}$, $^3A_{2g} \rightarrow ^3T_{1g}(F)$, $^3A_{2g} \rightarrow ^3T_{1g}(P)$ are expected from the energy level diagram of a d^8 ion. Octahedral nickel (II) complexes having two unpaired electrons have magnetic moments ranging from 2.83 to 3.4 BM depending on the magnitude of orbital contribution.

A considerable number of trigonal bipyramidal (D_{3h}) and square pyramidal (C_{4v}) complexes are known² and both high and low spin examples of each geometry occur.³ If coordination number is known to be four, diamagnetism is indicative of planar (generally red or yellow complexes) as opposed

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to tetrahedral coordination. While in tetrahedral symmetry the d^8 configuration gives rise to a $^3T_1(F)$ ground state and transition to $^3T_1(P)$ state occurs in visible region. Therefore tetrahedral complexes are generally strongly coloured blue or green with magnetic moments⁴ of 3.5 to 4.0 BM.

Urease is a nickel-dependent metalloenzyme that catalyzes the hydrolysis of urea to ammonia and carbon dioxide (Hausinger, R.P., 1993) in conjunction with biological functions using urea as a nitrogen source. It was first isolated from jack beans in 1926 and later from various origins such as bacteria, fungi and plants. A recent X-ray crystallographic study on microbial urease from *Klebsiella aerogenes* has identified a dinickel active site (Jabri, E., 1995).

Experimental; Nickel salts (AR) grade were used as supplied. Other chemicals used were of reagent grade.

Preparation of Ligand; The multidentate ligand 1,5-bis(4-methyl, benzimidazol-2-yl)-3-thiapentane was synthesized by 3,3'-thiodipropionic acid and 3,4-diamino toluene was added to 4 M aqueous HCl. The solution was refluxed for 30-36 hours and was filtered while hot. On cooling, the filtrate blue crystals were formed which were washed with methanol and dried under vacuum over anhydrous calcium chloride.

Synthesis of Complexes; $[\text{Ni}(\text{C}_{20}\text{H}_{22}\text{N}_4\text{S})(\text{NO}_3)_2]$: To a stirred solution of 2 mmol of ligand BMBES in 30 ml of MeOH, green solution of $\text{Ni}(\text{NO}_3)_2$ in 10 ml MeOH was added. Stirring was continued for 7-8 hours. Resulting blue solution was refluxed and concentrated to approximately 5 ml on a rotatory evaporator. On cooling it produces blue coloured crystalline mass.

$[\text{Ni}(\text{C}_{20}\text{H}_{22}\text{N}_4\text{S})\text{X}_2]$; ($\text{X}=\text{CH}_3\text{COO}^-$, HCOO^-): To an aqueous solution of NiCl_2 , an aqueous solution of NaOH was added and precipitated nickel hydroxide was washed and suspended in methanol. A dilute solution of acetic acid or formic acid in methanol (1 : 1) was added dropwise till the precipitate dissolved to give a clear solution. This was then added to a solution of ligand. The resulting green solution was stirred for 5-6 hours. Dry diethyl ether was layered above the solution and the mixture on cooling bluish green coloured mass.

$[\text{Ni}(\text{C}_{20}\text{H}_{22}\text{N}_4\text{S})\text{Cl}_2]$: To a solution of ligand 1,5-bis(4-methyl, benzimidazol-2-yl)-3-thiapentane in 30 ml MeOH was added. The resulting bluish green solution was stirred for 8 hours. Addition of ether to this solution was continued till a turbidity was obtained on subsequent cooling overnight in refrigerator produced a light green microcrystalline product. $[\text{Ni}(\text{C}_{20}\text{H}_{22}\text{N}_4\text{S})(\text{NCS})_2]$: To a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ slight excess of a methanolic solution of KSCN was added. Precipitated potassium chloride was filtered off to give a clear green solution containing $\text{Ni}(\text{CNS})_2$. This was then added to a solution of ligand. The resulting clear bluish green solution was stirred for 4-5 hours. Light bluish green microcrystalline product separated out.

The electronic and magnetic moment of the complexes are given in Table 1.

TABLE 1 Magnetic and electronic spectral data of the complexes.

Compound	λ_{max} (nm)	Log ϵ
$[\text{Ni}(\text{C}_{20}\text{H}_{22}\text{N}_4\text{S})(\text{NO}_3)_2]$	240	4.14
	269	4.10
	276	4.15
	378	1.60
	608	1.24
	802	-
	1020	-
$[\text{Ni}(\text{C}_{20}\text{H}_{22}\text{N}_4\text{S})(\text{CH}_3\text{COO})_2]$	240	4.18
	270	4.28

	276	4.18
	380	1.40
	620	1.14
	800	-
	954	-
	1046	-
[Ni(C ₂₀ H ₂₂ N ₄ S)Cl ₂]	240	4.18
	270	4.25
	277	4.23
	390	1.26
	653	0.97
	778	-
	1088	-
[Ni(C ₂₀ H ₂₂ N ₄ S)(HCOO ₂)	240	4.18
	270	4.23
	278	4.22
	382	1.54
	626	1.14
	800	-
	1068	-
[Ni(C ₂₀ H ₂₂ N ₄ S)(NCS) ₂]	240	4.24
	270	4.28
	278	4.26
	388	1.44
	638	1.08
	778	-
	993	-
	1068	-

Result and Discussion

U.V. Spectroscopy; The UV spectra of nickel (II) complexes show characteristic absorption bands in the region of 270-280 nm and are assigned to the $\pi \rightarrow \pi^*$ transitions within the benzimidazolyl group (Barandika, M.G.2000). Their absorption maxima and respective extinction coefficients are reported in Table 1. The UV bands are slightly blue shifted and enhance in intensity (Rubak-Akimova, E.V., 1998) in their respective complexes showing evidence of imine nitrogen coordination to the nickel (II) center.

The crystal field spectra of six coordinated octahedral nickel(II) complexes are known to exhibit a simple spectrum involving three spin allowed transitions from $^3A_{2g}$ to $^3T_{2g}(F)$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$ levels. These occur in the range of 7000-13000 cm^{-1} , 11000-20,000 cm^{-1} and 19,000-29,000 cm^{-1} regions respectively, with molar intensities less than 30 $\text{M}^{-1}\text{cm}^{-1}$, in regular octahedral systems.

It is well known that five coordinate complexes of nickel(II) can be high- or low-spin in both trigonal bipyramidal and square pyramidal geometries. The energy of the ground term is raised and the energy of the excited term lowered to a significant extent on the introduction of square pyramidal or trigonal bipyramidal ligand field around nickel(II) even with small amount of covalent character in the nickel(II) ligand bond. This places the highest energy band in such complexes to a maximum of 25,000 cm^{-1} (400 nm).

A study of absorption spectra could be used to distinguish between the octahedral complexes that often have two bands at 10,000 cm^{-1} and 16000-16800 cm^{-1} and the five coordinate species which shows

a greater multiplicity of bands in the visible spectrum with molar intensity of $30\text{-}50\text{ M}^{-1}\text{cm}^{-1}$. The orbital energy diagram arising for the triplet states of d^8 configuration with a axial ligand distortion is shown in Fig. 4.1 and the origin of multiplicity of bands in such tetragonal complexes is interpreted to be due to the lifting of the degeneracy of orbital triplet arising from the 3F and 3P free ion terms.

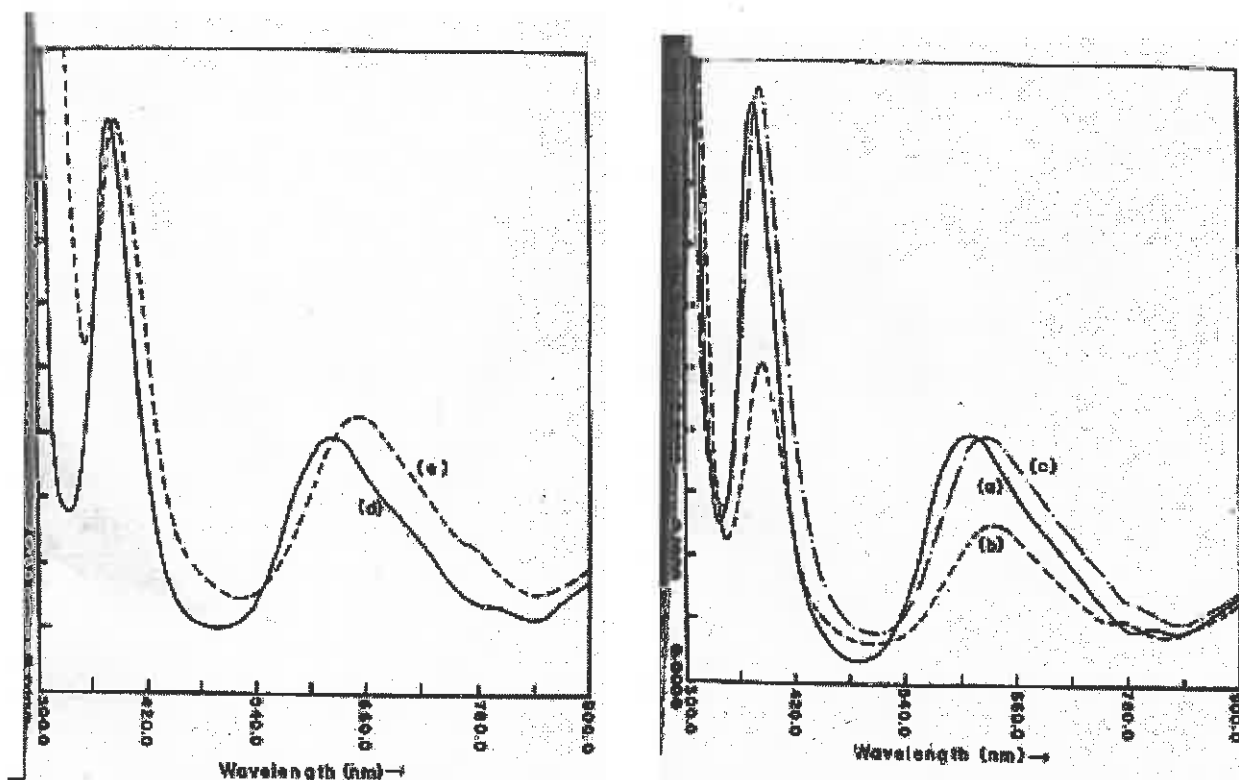


Fig 4.1 Spectra of U.V.

The visible spectrum of all the Ni(II) complexes taken in MeOH. The λ_{max} of these bands along with their extinction coefficients. The stoichiometry of our complexes is suggestive of five coordinate geometry in the solid state. However since the solution spectra indicate a high energy band in the region $\geq 25000\text{ cm}^{-1}$. We suggest that in solution the five coordinate Ni^{II} complexes acquire a sixth weakly bound solvent molecule. Also the spectra show a large number of bands with extinction coefficients higher than $30\text{ M}^{-1}\text{cm}^{-1}$ indicative of lowering of symmetry of a regular octahedral to tetragonal. Thus the solution spectra of the Ni^{II} complexes are interpreted in terms of six coordinated tetragonal complex, rather than a distorted trigonal bipyramidal or square pyramidal complex.

N.M.R. Spectroscopy; ^1H NMR signals of the paramagnetic Ni (II) complexes with ^1H NMR of the ligand ($\text{C}_{20}\text{H}_{22}\text{N}_4\text{S}$), it has been found that due to the paramagnetic effect, the resonance lines become extremely broad and actual integrated intensities are difficult to measure.

Moreover, some resonances with long nuclear τ_1 will saturate and will appear with diminished intensities at R_f power needed to detect resonances with short τ (broad peaks). Hence integrated peak intensities have not been considered in the present assignments (Comba,P.,2000). The ^1H NMR spectra of the above complexes lie in the range of -19.0 to $+55.0$ ppm with respect to the reference tetramethylsilane (TMS). The signal arising between $+50$ to $+55$ ppm (downfield with respect to TMS) is absent when the ^1H NMR is run in the presence of D_2O . This is expected if there is a rapid exchange between the

N-H proton in the benzimidazole nucleus and the D_2O present in the solvent. This thus ensures the assignment of N-H proton (Boeyens, J.C.A., 2009) in the present series of Ni(II) complexes.

IR Spectroscopy; On the basis of analytical and spectroscopic studies, the proposed structure for the Ni(II) complexes is as follows :

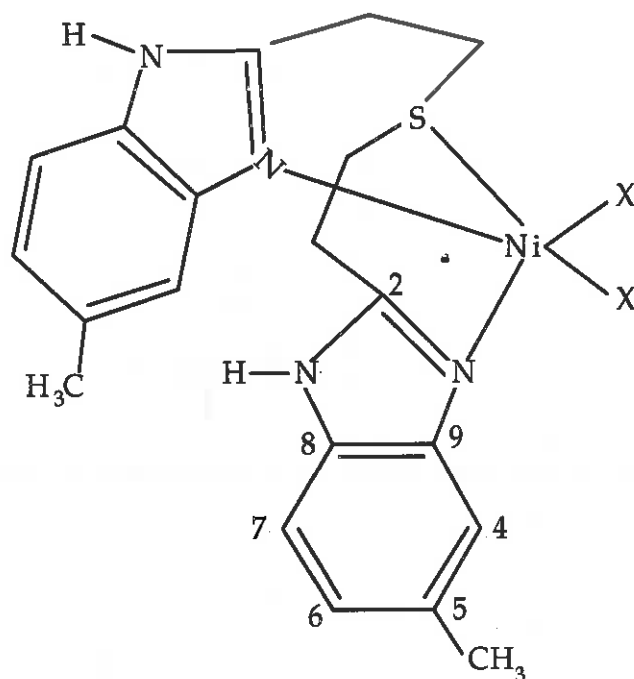


Figure 2. Proposed structure of nickel (II) complexes

REFERENCES

- BARANDIKA M. G, HERNANDEZ-PINO M. L., URTIAGAMK, CORTES R., LEZAMA L., ARRIORTUA M. I. & ROJO T. (2000). *J. Chem. Soc. Dalton Trans.*, 1469.
- BOEYENS J. C. A. & COMBA, P. (2009). *Coord. Chem. Rev.*, 212, 3.
- COMBA P. & HAMBLEY T. W. (2000). *Molecular Modelling of Inorganic and Coordination Compounds*, Second Edn. (VCH, Weinheim).
- DAGDIGIAN J. V. & REED C. A. (1979). *Inorg. Chem.*, 2623, 18.
- HAUSINGER R. P. (1993). *Biochemistry of Nickel*. Plenum Press, New York, Chapter 12, pp. 23-50.
- JABRI E., CARR M. B., HAUSINGER R. P. & KARPLUS P. A. (1995). *Science*, 998, 268.
- RUBAK-AKIMOVA E. V., ALCOCK N. W. & BUSCH D. H. (1998). *Inorg. Chem.*, 1563, 37.