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Tetragonal Distortion Parameter of Some Nickel(II) Complexes

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A macrocyclic ligand *viz.*, 3,8-dimethyl-3,7-diene-5,6-(2',3'-pyridino)-4,7-diaza-2,9-decadihydroxomine (MPAH) was used for complexation with Ni(II) salts. The general formula of the complexes was found $NiLX_2$ where L = MPAH and X = Cl^-, Br^-, CNS^- and ClO_4^-. The complexes were characterized by their micro analysis, infrared spectra, magnetic moment measurement and electronic spectra. All the complexes except one are found paramagnetic with μ_{eff} values 3.15-3.20 BM, higher than μ_{eff} value (2.828 BM). Ni(II) is a d^8 system with ground term ^3F which splits under octahedral crystal field perturbation with ground state crystal field term $^3A_{2g}$. As it is singly degenerate, orbital contribution to the magnetic moment of the complexes is not possible. So, certainly there is spin-orbit mixing of the ground term with the next excited term. The appearance of four absorption bands in their electronic spectra reveals the tetragonal distortion in the symmetry of complexes. The zero field splitting parameter (D) is found 1.37 to 2.90 cm^{-1} while the tetragonal distortion parameter is found 126-183 cm^{-1}. The ligand field splitting parameter for axial ligands, *i.e.*, Dq^Z is found 640-870 cm^{-1}.

Key Words: Tetragonal distortion, Dq^Z, Zero field splitting parameter.

INTRODUCTION

The variation in the coordinating abilities of ligands along a four fold axis, by means of which square planar complexes may ultimately be derived from octahedral ones are of particular interest of inorganic chemists and theoretical chemists. The description of this class of distortion is substantially in advance of the experimental facts[1-8]. A number of tetradentate macrocyclic ligands have been reported[9] which fix the spacial arrangement and ligand field strength of four coplanar donor sites simplifies the study of tetragonally distorted six coordinated Ni(II) complexes. Recently the electronic spectra of Ni(II) octahedral complexes have been reported[10-12] which largely concern with the role of spin orbit coupling in influencing the band shape of the lowest energy spin allowed transition. Similar study has also been made with Co(III) by Bruce *et al.*[13] in which closed tetradentate ligand encircles the metal ion. Thompson and Busch[14] have reported Ni(II) complexes like $NiLX_2$ ($X = CNS^-, Br^-, ClO_4^-$) and suggested that the cross over between singlet and triplet ground states occurs for an axial ligand field strength. In the present paper, we

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report the effect of variation in extra planar ligands on the electronic properties of NiL^{2+} ($L = N_4$ ligand) to produce a range of axial ligand field strength which embraces both singlet and triplet ground sates.

EXPERIMENTAL

For the preparation of the ligand, 0.05 mol (6.9 g) of 2,3-diamino pyridine and 0.1 mol (10.1 g) of diacetyl monoxime were mixed together and were heated together for 15 min. The solution was transferred into a beaker and it was stirred vigorously for 2 h when the solution turned viscous. It was cooled in ice cooled water when viscous substance converted into solid. It was recrystallized from ethanol when yellow crystal with m.p. 184 ºC were obtained. The complexes were prepared by the usual method of refluxing the Ni(II) salt and ligand in 1:1 molar ratio. The magnetic moments were measured by Gouy method using $Hg[Co(NCS)_4]$ as the calibrating substance at room temperature. The infrared spectra were obtained using a Perkin-Elmer model 337 recording spectrophotometer using KBr disk technique. The reflectance spectra were obtained using a Carry model-14 recording spectrophotometer. The elemental analysis were carried out by usual methods.

RESULTS AND DISCUSSION

The data of microanalysis of the various complexes of Ni(II) have been given in Table-1, on the basis of which the complexes were formulated as $NiLX_2$ where L = 3,8-diamethyl-3,7-diene-5,6-(2'3'-pyridino)-4,7-diaza-2,9-decadihydroxomine (MPAH) and X = Cl^-, Br^- CNS^- and ClO_4^-.

TABLE-1

	Elemental analysis (%): Found (Calcd.)						
	Ni	C	H	N	S	Cl	Br
1. Ligand (MPAH)	–	57.50	6.00	25	–	–	–
		(56.72)	(6.18)	(25.45)			
2. $NiLCl_2$	15.00	39.25	4.00	7.30	17.00	–	–
	(14.50)	(38.55)	(4.20)	17.30)	(17.52)		
3. $NiLBr_2$	12.25	33.25	3.10	14.00	–	–	32.00
	(11.89)	(31.61)	(3.44)	14.18)	–		(32.38)
4. $NiL(CNS)_2$	12.60	34.00	3.25	1.50	13.50	–	–
	(12.49)	(33.21)	(3.61)	20.86)	(13.62)		
5. $NiL(ClO_4)$	11.95	30.35	3.50	13.65	–	14.0	–
	(11.01)	(29.28)	(3.19)	13.14)	–	(13.32)	

The free ligand absorbs at 3360 cm^{-1} due to O-H stretching vibration of the N-OH group. The band is broad due to intra molecular H-bonding. This band remains almost intact in all the complexes which shows the non deprotonation of -OH groups and non participation in coordination. The spectrum of the pure ligand as well as that of the metal complexes in the frequency region 1650-900 cm^{-1} are most valuable for the elucidation of structural study of the complexes. In the spectra of all the metal complexes, there appear two sharp bands at the 1600 and 1500 cm^{-1}, respectively. Considering their sharpness and intensity, they have been assigned to ν(CN) stretching vibrations. As the ligand contains two kinds of CN groups relating to azomethine and oxime groups, the locations of these bands near 1600 and 1500 cm^{-1} clearly manifest that the vibrational energies of these groups are significantly different from each other. On the basis of the available data on structurally related molecules such as dimethyl glyoxime and Schiff-bases, the high frequency and the low frequency bands are assigned to the azomethine and oxime, C=N groups, respectively. The ν(C=N) stretching band due to C=N-OH group of H_2dmg appears at 1450 cm^{-1} which shifts to a higher frequency regions in its complexes and appears in the region of 1590-1550 cm^{-1}. It provides further support to the above assignment.

Besides these two bands which are more perturbed on complexation, four bands have been observed at 1580, 1480 and 1440 cm^{-1}. These are the characteristic bands of phenyl ring vibrations. However, these bands remain unperturbed in all the metal complexes. The band around 1370 cm^{-1} present in free ligand is assigned to $\delta(CH_3)$ deformation vibration which remains intact in all the metal complexes. The medium intensity bands appearing at *ca.* 1300 and *ca.* 1200 cm^{-1} may be assigned to $\nu(C\text{-}CH_3)$ stretching or CH_3 rocking vibrations. The bands at 1250 and 770 cm^{-1} are assigned to ν(C-H) in plane vibration of the phenyl ring and C-H out of plane vibration, respectively. In the spectrum of the pure ligand three distinct bands appear in the region of 1100-900 cm^{-1}, with strongest one being at 1010 cm^{-1}. This band is assigned to ν(N-O) stretching vibration which in all the complexes shifts to a higher frequency region appearing at 1120-1090 cm^{-1}. In complexes some additional bands appear which are assigned as below.

In all the complexes, the band at 495-470 cm^{-1} is assigned to ν(Ni-N) stretching vibration which further confirms the Coordination of the ligand through nitrogen. In complex no. **IV** a strong band appears at 1100 cm^{-1} which is indicative of the ionic nature of the perchlorate in this complex. Vibrational band at 900 cm^{-1} indicates that coordinated perchlorate is not present in the complex which supports our presumption that perchlorates are present out side the coordination sphere as free ions[15-17]. The appearance of new bands nearly 300 cm^{-1}, assigned to ν(Ni-Cl) (*ca.* 300 cm^{-1}), ν(Ni-Br) (*ca.* 290 cm^{-1}) shows the presence of chloride, bromide and thiocyanate ions respectively within the coordination sphere.

The reflectance spectra and the μ_{eff} value of the complexes are given in Table-2.

TABLE-2

Complex	(m^{-1})				μ_{eff} (BM)
	ν_1	ν_2	ν_3	ν_4	
(I) $NiLCl_2$	9300	10850	18600	24200	3.16
(II) $NiLBr_2$	8000	9600	8500	24000	3.20
(III) $NiL(CNS)_2$	9800	10900	8300	24500	3.15
(IV) $NiL(ClO_4)_2$	16000	20000	25000	–	Diamagnetic

The appearance of three absorption bands in the spectra of $NiL(ClO_4)_2$ is indicative of its square planar symmetry around Ni(ii). In the true C_{2v} symmetry, these may be assigned[6,7] as below:

$$v_1\ ({}^1B_{1g}\leftarrow{}^1A_{1g}) = 16000\ cm^{-1}$$

$$v_2\ ({}^1A_{2g}\leftarrow{}^1A_{1mg}) = 2000\ cm^{-1}$$

$$v_3\ ({}^1A_{2g}\leftarrow{}^1A_{1g}) = 25000\ cm^{-1}$$

The diamagnetic character of the complex is also indicative of its square planar geometry.

The reflectance spectra of complexes **I**, **II** and **III** show four absorption bands which are indicative of axially distorted Oh symmetry around Ni(II) in these complexes. These bands may be assigned as below[18]:

$$v_1 = {}^3E_{ga} \leftarrow {}^3B_{1g} \qquad 10\ Dq\text{-}35/4Dt$$

$$v_2 = {}^3B_{2g} \leftarrow {}^3B_{1g} \qquad 10\ Dq$$

$$v_3 = {}^3A_{2g} \leftarrow {}^3B_{1g} \qquad 10\ Dq\text{-}4Ds\text{-}\ 5Dt$$

$$v_3 = {}^3E_{gb} \leftarrow {}^3B_{1g} \qquad 10\ Dq\text{-}2Ds\text{-}\ 25/4Dt$$

The transition ${}^3B_{1g}\rightarrow{}^3E_{ga}$, is the measure of the tetragonal character. The transition ${}^3B_{1g}\rightarrow{}^3B_{2g}$, however, is free from the influence of Ds and Dt and virtually it is the measure of infield splitting parameter Dq^{xy}.

The axial distortion Dt is calculated by Wentworth & Piper formula[8], *i.e.* $Dt = 4/7(Dq^{xy} – Dq^{Z})$ or by $35/4\ Dt = v_2 – v_1$. Dq^Z has been derived from the expression $2v_1 – v_2/10$.

The zero field splitting parameter (D) has also been calculated using the expression $D = 9k_1/\alpha^2\ \{(\mu_{eff}/\mu_0)^2 – (\mu_{eff}/\mu_0) + 1S\}$ while k_1, which is the splitting of the first excited state is given as $k_1 = 35/4Dt$.

The values of the different parameters have been given in the Table-3.

TABLE-3

	$10Dq^{xy}$ (cm^{-1})	Dq^Z (cm^{-1})	Dq (cm^{-1})	K_1 (cm^{-1})	D (cm^{-1})
$NiLCl_2$	10850	775	177.14	1550	1.94
$NiLBr_2$	9600	640	183.00	1600	2.90
$NiL(CNS)_2$	10900	8700	12600	100	1.37

On the basis of these results the observed spectrochemical series within the formation may be given as: Br^- - < Cl^- - < NCS^-

The order of distorting capability is as: $NCS^- < Cl^- < Br^-$

And the order of zero field splitting as as: $NCS^- < Cl^- < Br^-$

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