Contribution from the Department of Chemistry, Meerut College, Meerut, India and Department of Chemistry, University of Roorkee, Roorkee, India

Stereochemical Features Vis-A-Vis Spectral Data on Some Nickel(II) Complexes of Amino Ligands Viz. 3,3'-Diamino-4,4'-Dihydroxy Diphenyl Sulphone and 8-Amino-7-Hydroxy-4-Methylcoumarin. I.

M.P. Teotia,[*] D.K. Rastogi,[*] and W.U. Malik[**]

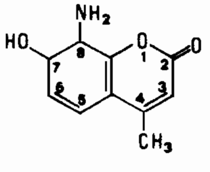
Received September 8, 1972

Nickel(II) complexes of 3,3'-diamino-4,4'-dihydroxy diphenyl sulphone (abbreviated as D(AHP)S) viz. $[Ni(C_{12}H_{10}N_2O_4S)(H_2O)_2]$, $[Ni(C_{12}H_{19}N_2O_4S)(NH_3)_2]$ *and 8-amino-7-hydroxy-4-methylcoumarin (AHMC)* viz. $H[Ni(C_{10}H_8NO_3)_2(Cl)(H_2O)]$, $K_2[Ni(C_{10}H_8NO_3)_2\text{-}(CN)_2]$ *have been isolated and characterised by analyses, .magnetic, conductivity, electronic and infrared spectral studies. The electronic spectral studies indicate the effect of distortion in case of AHMC complexes,, which is probably produced due to the unequal donor strengths of chloride and cyanide ligands. A possible correlation of which has been sought with the low values of magnetic moments observed in these complexes. Other ligand field parameters have also been calculated.*

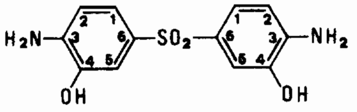
Introduction

According to ligand field theory, most of the stereochemical arrangementes found in the complexes of nickel (II) are based either on octahedron or tetrahedron[1] or else they may be derived by suitable distortion[2] e.g. square planar structure of complexes are considered the limit of tetragonal distortion of octahedral complexes. The theory of nickel (II) ion under the influence of ligand fields, intermediate between square planar and octahedral, have been discussed in detail.[3] The effect of distortion from a regular octahedral structure produced by ligands with unequal donor strengths, on the electronic spectra of the transition metal complexes has been a topic of recent interest.

3,3'-Diamino-4,4'-dihydroxy diphenyl sulphone, a potential dyware and pharmaceutical reagent and 8-amino-7-hydroxy-4-methylcoumarin, a known chelating reagent,[4-8] have been found to form octahedral and tetragonally distorted octahedral complexes with nickel (II) ion. The present paper describes the magnetic, conductivity, electronic and infrared spectral stdies of these complexes.



AHMC



D(AHP)S

Experimental Section

3,3'-Diamino-4,4'-dihydroxy diphenyl sulphone (M-YTD grade 1614) was procured from Midland-Yorkshire Tar Distillers Ltd., England and its solution in 50% ethanol was used throughout. 8-Amino-7-hydroxy-4-methylcoumarin was prepared from 8-nitro-7-hydroxy-4-methylcoumarin[9] by the method of Kumar.[10] All other chemicals used were of AnalaR grade.

ISOLATION OF COMPLEXES

Nickel (II) complexes of 3,3'-diamino-4,4'-dihydroxy diphenyl sulphone. $[Ni(C_{12}H_{10}N_2O_4S)(H_2O)_2]$ *and* $[Ni(C_{12}H_{10}N_2O_4S)(NH_3)_2]$. A dark-brown coloured solution was obtained at pH ~5.5 by mixing one mole of an aqueous solution of nickel(II) chloride to 1.5 mole solution of the ligand (prepared in 50% ethanol). Concentration of the reaction mixture yielded dark brown coloured crystals of $[Ni(C_{12}H_{10}N_2O_4S)(H_2O)_2]$ which were washed successively with water, ethanol and finally with ether and dried in vacuum at room temperature. Yeld 80 per cent. On raising the pH of the above brown coloured solution to ~9.2 by the dropwise addition of ammonium hydroxide solution, a distinct pinkish-brown coloured precipitate of

---

(*) Department of Chemistry, Meerut College, Meerut.

(**) Professor and Head of the Chemistry Department, University of Roorkee, Roorkee.

(1) F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry', 2nd edn. (Wiley, New York) p. 883 (1966).

(2) F.A. Cotton, 'Progress in Inorganic Chemistry' (Interscience. N.Y.) Vol. VI p. 87 (1964).

(3) Idem, Ibid p. 206.

(4) D.K. Rastogi, A.K. Scrivastava, P.C. Jain, and B.R. Agarwal, *J. Inorg. Nucl. Chem.*, 32, 3849 (1970).

(5) D.K. Rastogi, *Ibid*, *34*, 619 (1972).

(6) D.K. Rastogi, A.K. Srivastava, P.C. Jain, and B.R. Agarwal, *J. Less-Common Metals*, *24*, 383 (1971).

(7) Idem, *Inorg. Chim. Acta.*, 6, 145 (1972).

(8) D.K. Rastogi, *Aust. J. Chem.*, 25, 929 (1972).

(9) N.M. Shah and D.M. Metha, *J. Indian Chem. Soc.*, *31*, 784 (1954).

(10) S.Kumar, *Ph. D. Thesis, Agra University*, Agra, India (1966).

$[Ni(C_{12}H_{10}N_2O_4S)(NH_3)_2]$ was obtained. It was digested, cooled and filtered off and washed with ethanol, ether and dried. Yield 70 per cent.

The complexes do not melt upto 350°C but changes their colour to steel-gray beyond 300°C. They are insoluble in water and other organic solvents.

Nickel (II) complexes of 8-amino-7-hydroxy-4-methylcoumarin. $H[Ni(C_{10}H_8NO_3)_2(Cl)(H_2O)]$. A yellow-ochre coloured solution was obtained by adding 75 ml of 0.02M aqueous solution of nickel (II) chloride to 300 ml of an equimolar ethanolic solution of AHMC and the pH of the solution was lowered down to ~2.0. The reaction mixture was concentrated and the yellowish-green concentrate was kept in a refrigerator for few days, when yellowish-green crystals of $[Ni(C_{10}H_8NO_3)_2(Cl)(H_2O)]$ separated out. These were washed thoroughly with ethano-ether mixture and dried in vacuum at room temperature. The complex does not melt upto 350°C but changes its colour to black through yellow beyond 150°C. The acidic nature of the complex was established by the determination of its neutralization equivalent and the fact that one gm equivalent of alkali was used for the complete neutralization, indicates the presence of only one proton in the complex.

$K_2[Ni(C_{10}H_8NO_3)_2(CN)_2]$. A yellow coloured solution, obtained at pH ~ 4.5 by mixing metal and ligand (1:2), was found to change to a brownish coloured solution when added in an aqueous solution of potassium cyanide (2 moles) at pH ~ 8.7. The reaction mixture, after refluxing for about two hours and keeping over night, throws brown coloured crystals of $K_2[Ni(C_{10}H_6NO_3)_2(CN)_2]$. These were filtered off, washed several times with ethanol-ether mixture and dried. Yield 40 per cent. The complex does not melt upto 350°C.

The anionic nature of the complexes was revealed by the migration of coloured ions during electrolysis.

ANALYSES AND APPARATUS

The micro-analyses for carbon, hydrogen and nitrogen were done at Indian Institute of Technology Kanpur-16, India. Table I records the analytical data of the complexes. The conductance measurements were carried out on a Toshniwal Conductivity bridge (CL-Ol/Ol) using a dip type cell. Magnetic studies of the complexes in powder form were made on a Gouy balance using mercury (II) tetrathiocyanato cobaltate (II) as a calibrant. The results are given in table I. The electronic spectra of the complexes were recorded in nujol mull on a Cary-14 recording spectrophotometer. The bands and relevent ligand field parameters are cited in table II. The infrared spectra of the complexes were recorded on a Perkin-Elmer Infracord spectrophotometer, model 521, in KBr pellets and the tentative assignements of the bands are given in table III and IV.

Results and Discussion

Analytical results show a 1:1 and 1:2 metal to ligand stoichiometry for D(AHP)S and AHMC complexes of nickel (II), respectively.

Magnetic Studies. Nickel (II) has electronic configuration $3d^8$ and should exhibit a magnetic moment higher than expected for two unpaired electrons in

Table I. Analytical and Magnetic Data of Complexes.

Compound		C %	H %	N %	Cl %	Metal %	Λm in $10^{-3}M$ aqueous solution	$\chi_M \times 10^6$ (c.g.s.) corrected	μ_{eff} at 300°K (B.M.)
$[Ni(C_{12}H_{10}N_2O_4S)(H_2O)_2]$	Calcd:	38.63	3.78	7.50	—	15.73	—	4251	3.21
	Found:	38.52	3.81	7.44	—	15.50			
$[Ni(C_{12}H_{10}N_2O_4S)(NH_3)_2]$	Calcd:	38.84	4.34	15.09	—	15.82	—	4224	3.20
	Found:	38.91	4.48	14.95	—	15.70			
$H[Ni(C_{10}H_8NO_3)_2(Cl)(H_2O)]$	Calcd:	48.68	3.88	5.67	7.18	11.90	115 (uni-univalent)	2832	2.62
	Found:	48.56	3.97	5.56	7.01	11.82			
$K_2[Ni(C_{10}H_8NO_3)_2(CN)_2]$	Calcd:	46.23	2.83	10.19	—	10.31	280 (uni-bivalent)	2767	2.59
	Found:	46.09	2.91	10.10	—	10.27			

Table II. Electronic Spectra Data of Complexes (nujol-mull, cm^{-1}).

Compound	Observed bands and their assignment. $^3A_{2g}(F) \longrightarrow$ $^3T_{2g}(F)$ (ν_1)	$^3T_{1g}(F)$ (ν_2)	$^3T_{1g}(P)$ (ν_3)	Calculated band positions (ν_2)	(ν_3)	$[(\nu_3-\nu_2)_{calc}-(\nu_3-\nu_{2obs})]$	ν_2/ν_1	Electron repulsion parameter B	Nephelauxetic ratio β^a	Splitting energy 10 Dq	L.F.S.E. Kcal/mole
$[Ni(C_{12}H_{10}N_2O_4S)(H_2O)_2]$	9800 12000(wsh)	16000	27910	16135	28765	720	1.63	966	0.894	9800	33.6
$[Ni(C_{12}H_{10}N_2O_4S)(NH_3)_2]$	1040 12100(wsh)	16900	19130	16020	28780	530	1.62	989	0.916	10400	35.6
$H[Ni(C_{10}H_8NO_3)_2(Cl)(H_2O)]$	8540 12500	15330	27060	14335	27835	1770	1.80	1111	—	—	—
$K_2[Ni(C_{10}H_8NO_3)_2(CN)_2]$	11000 12740	19900	30060	18180	31780	3440	1.81	1131	—	—	—
$[Ni(C_{10}H_8NO_3)_2(H_2O)]^c$	9302^b	16940	28000	16920	28280	300	—	960	0.88	—	32.2

$^a\beta$ = B/1080 (Reference 16). ^{b}Band not observed experimentally. ^{c}Reference 7.

Table III. Tentative Assignment of the Bands in the I.R.Spectra of D(AHP)S and its Nickel(II) Complexes (cm^{-1}).

D(AHP)S	$[Ni(C_{12}H_{10}N_2O_4S)(H_2O)_2]$	$[Ni(C_{12}H_{10}N_2O_4S)(NH_3)_2]$	Tentative Assignments
3460 (s)	—	—	ν(OH) of phenol
—	3420 (s)	—	ν(OH) of H_2O
—	—	3390 (s)	ν(NH_3)
3380 (s)	3320 (s)	3325 (s)	νassym.(NH_2)
3360 (s)			
3300 (s)	3280 (s)	3290 (s)	νsym.(NH_2)
	3250 (s)	3208 (s)	
3150-	3140 (wsh)	3140 (w)	ν(C—H)
3140 (sb)	3030 (wsh)		
3080 (s)			
1600-1590 (sb)	1590 (s) [a]	1595 (s)	δ(NH_2)+δ(H_2O)
1575 (s)	1545 (msh)	1570 (s)	
1510 (s)	1510 (msh)	1500 (s) [a]	ν(C=C)
1500 (s)	1480 (s)	1435 (m)	
1445 (s)	1410 (s)		
1375 (s)	—	—	δ(OH) of phenol
1300-1280 (sb)	1305 (s)	1305 (w)	νassym. (SO_2)
1255 (m)	1290-1280 (sb)	1300-1295 (sb)	
	1250 (m)	1295 (s) [b]	
1140 (s)	1140 (w)	1135 (m)	νsym. (SO_2)
1100 (m)	1120 (m)	1115 (w)	
—	1030 (m)	1030 (w)	δw(NH_2)
940 (s)	920 (m) [d]	930 (m)	
895 (m)			
860 (m)	825 (m)	850 (msh)	δ(C—H) out of plane
830 (w)	790 (w)	805 (m) [c]	
825 (m)			
775 (m)			
—	740 (w) [c]	742 (w)	δr(NH_2)
695 (s)	705 (s)	700 (s)	
660 (w)	670 (w)	650 (w)	
600 (m)	590 (m)	590 (s)	
535 (m)	540 (w)	535 (m)	
—	500 (w)	500 (w)	ν(M—N)
—	435-425 (wb)	430-420 (wb)	ν(M—O)
335 (w)	370 (w)	400 (w)	
300 (w)	345 (m)	340-330 (wb)	

[a] δassym.(NH_3); [b] δsym.(NH_3); [c] δr(NH_3); [d] coupled with δr (H_2O); [e] coupled with δw coordinated H_2O.

octahedral (2.8 - 3.8 B.M.) and tetrahedral complexes (3.4 - 4.2 B.M.) whereas its square planar complexes would be diamagnetic. This increase in the magnetic moment value from that of the spin-only value has been discussed by Nyholm,[11] who considered it to be due to some « mixing in » of upper states via spin-orbit coupling. The paramagnetism observed for the present complexes; $[Ni(C_{12}H_{10}N_2O_4S)(H_2O)_2]$ (complex I, 3.21 B.M.) and $[Ni(C_{12}H_{10}N_2O_4S)(NH_3)_2]$ (complex II, 3.20 B.M.) is consistent with the assignment of the octahedral symmetry. Further, it has also been observed in case of Ni^{II} that if the symmetry is allowed to be lower than cubic (as observed in the present AHMC complexes of Ni^{II} vide their electronic spectral discussion) and if the low symmetry component is large, then a spin-paired term may be found in the neighbourhood.[2] A recent X-ray investigation[12] of the paramagnetic (2.58 B.M.) bis(mesostilbenediamine) nickel (II) dichloro acetate, has shown that crysstal of this complex consists of a mixture of paramagnetic octahedral molecules and diamagnetic planar molecules. Therefore, the low values of magnetic moment observed for the present complexes $H[Ni(C_{10}H_8NO_3)_2(Cl)(H_2O)]$ (complex III, 2.62 B.M.) and $K_2[Ni(C_{10}H_8NO_3)_2(CN)_2]$ (complex IV, 2.59 B.M.) may be explained by assuming them a mixture of paramagnetic octahedral molecules and diamagnetic planar molecules. The distortion of O_h symmetry in these complexes has been confirmed by their electronic spectral studies.

Electronic Spectral Studies. The spectra of the complexes consist of three main bands, now well established for the majority of octahedral nickel (II) complexes[13] which occur in the region 8000 - 11000 cm^{-1} (ν_1), 15000 - 19000 cm^{-1} (ν_2) and 26000 - 29000 cm^{-1} (ν_3). In addition to these bands, weak shoulders around 12000 cm^{-1} have been observed in the spectra of D(AHP)S complexes in contrast to AHMC complexes in which an additional absorption band at 12500 cm^{-1} and 12470 cm^{-1} has been observed.

In a cubic field, the ^3F ground state of the Ni^{II} ion is split into three levels, the orbital singlet $^3A_2$ and the orbital triplets $^3T_1$ and $^3T_2$. The first excited term of the free nickel(II) ion, ^3P transforms as $^3T_{1g}$ under cubic symmetry. These are therefore, three spin-allowed transition; $\nu_1[^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)]$; $\nu_2[^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)]$ and $\nu_3[^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)]$ observed in octahedral complexes. The energies of these transitions are readily expressed as functions of 10 Dq and B.[14] For

---

[11] R.S. Nyholm, *Proc. Roy. Soc. London*, August (1961).

[12] S.L. Hoet, Jr. and R.L. Carlin, *J. Am. Chem. Soc.*, *86*, 3017 (1964).

[13] C.K. Jorgenson, *Acta. Chem. Scand. 10*, 887 (1956).

[14] R.L. Carlin, 'Transition Metal Chemistry' (Marcel Dekker, Inc., N.Y.) Vol. IV, p. 211 (1968).

Table IV. Tentative Assignment of the Bands in the I.R.Spe ctra of AHMC and its Nickel(II) Complexes. (values in cm^{-1})

AHMC	$H[Ni(C_{10}H_8NO_3)_2(Cl)(H_2O)]$	$K_2[Ni(C_{10}H_8NO_3)_2(CN)_2]$	Tentative Assignments
3442 (s)	—	—	ν(OH) of phenol
—	3400 (s)	—	ν(OH) of H_2O
3368 (s)	3310 (s)	3308 (s)	νassym.(NH_2)
3302 (s)	3208 (s)	3230 (s)	νsym.(NH_2)
3287 (s)		3225 (s)	
3238 (s)			
3154 (s)	3140 (s)	3145 (s)	ν(C–H)
3140 (s)			
—	—	2120 (s)	ν(C≡N) of cyanide
		2100 (m)	
1677 (s)	1710 (s)	1775 (w)	ν(C=O) of ketone
		1710 (s)	
1614 (s)	1595 (s)	1610 (s)	δ(NH_2)+conjugated-O-hydroxyphenyl+δ(H_2O)
1569 (s)	1572 (s)	1575 (s)	ν(C=C)
1511 (s)	1484 (m)	1536 (w)	
1464 (s)		1490 (s)	
1433 (w)	1436 (m)	1442 (m)	δassym.(C–CH_3)
1380 (s)	1385 (s)	1388 (s)	δsym.(C–CH_3)
	1370 (ssh)	1370 (s)	
1334 (s)	—	—	δ(OH) of phenol
1294 (s)	1325 (s)	1295 (s)	
1240 (m)	1292 (s)	1230 (m)	
1199 (m)	1225 (w)	1135 (w)	
—	1075 (m)	1095 (s)	δw(NH_2)
1040 (s)	—	1040 (m)	
1029 (msh)		1005 (m)	
—	935 (w)	—	δr(H_2O) of coordinated water
858 (w)	845 (m)	830 (m)	δ(C–H) out of plane
843 (s)	805 (m)	818 (m)	
800 (s)			
794 (s)			
—	650 (w)[a]	722 (w)	δr(NH_2)
594 (m)	—	614 (m)	
560 (m)		596 (m)	
—	—	546 (m)	ν(M–C) of cyanide
		535 (m)	
—	498 (w)	505 (m)	ν(M–N)
—	478 (m)	—	ν(M–O)
	417 (w)		
—	—	436 (m)[b]	bending (M–C≡N) of cyanide
		425 (w)	
—	375 (w)	—	ν(M–Cl)
456 (w)			
430 (w)			
407 (w)			

[a] coupled with ν(M–O) of coordinated water; [b] coupled with stretching metal - oxygen bond.

terms of maximum multiplicity, the energy difference is dependent upon B and in case of nickel (II), $E(^3F - {}^3P) = 15\ B$.

The electronic spectra of the present complexes I and II consists of three main bands appearing at 9800 cm^{-1}, 10400 cm^{-1} (ν_1); 16000 cm^{-1}, 16900 cm^{-1} (ν_2) and 27910 cm^{-1}, 29130 cm^{-1} (ν_3) and a weak shoulder at 12000 cm^{-1}, 12100 cm^{-1}, respectively. The three principal bands are the d-d transitions and the weak shoulders may be considered to have arisen due to spin-forbidden transitions. The value of B for these complexes, calculated from ν_1, ν_2 and ν_3 band energies and using the diagonal sum rule,[15] $15B = \nu_2 + \nu_3 - 3\nu_1$, comes out to be 966 cm^{-1} and 989 cm^{-1}, respectively (as against the free gaseous ion value of 1080 cm^{-1}).[16] Using the value of first spin-allowed band (ν_1) as 10 Dq, the energies of bands were calculated from the equations.[17]

$$E[^3A_{2g}(F)-{}^3T_{1g}(F)] = 15/B + 3/(10Dq) - \tfrac{1}{2}[(9B-10Dq)^2 + 144B^2]^{\frac{1}{2}}$$

$$E[^3A_{2g}(F)-{}^3T_{1g}(P)] = 15/B + 3/2(10Dq) + \tfrac{1}{2}[(9B-10Dq)^2 + 144B^2]^{\frac{1}{2}}$$

The calculated values of ν_2 and ν_3 were checked against the observed values, since this is the justification of having the cubic symmetry. The calculated values of ν_2 and ν_3 for the complexes I and II are 16135 cm^{-1}, 16020 cm^{1-} (ν_2) and 28765 cm^{-1}, 28780 cm^{-1} (ν_3) respectively, revealing a close agreement with their experimental values (Table II).

Inconstrast to the electronic spectra of D(AHP)S complexes, the spectra of AHMC complexes; $H[Ni\text{-}C_{10}H_3NO_3)_2(Cl)(H_2O)]$ and $K_2[Ni(C_{10}H_8NO_3)_2(CN)_2]$ consist an additional absorption band at 12500 cm^{-1} and 12740 cm^{-1}, respectively which lies in between

---

(15) O. Bostoup and C.K. Jørgenson, *Acta Chem. Scand.*, *11*, 1223 (1957).

(16) B.N. Figgis, 'Introduction to Ligand Fields' (Interscience, N.Y.) p. 52 (1966).

(17) K. Nakamoto and P.J. McCarthy, S.J., 'Spectroscopy and Structure of Metal Chelate Compounds' (John Wiley and Sons. Inc., N.Y.) p. 83 (1968).

ν_1 and ν_2. Such a band may either be caused by the spin-forbidden transition of by the low symmetry of the ligand field. This band is too intense for a spin-forbidden transition, particularly when there is no possibility of borrowing intensity in this region.

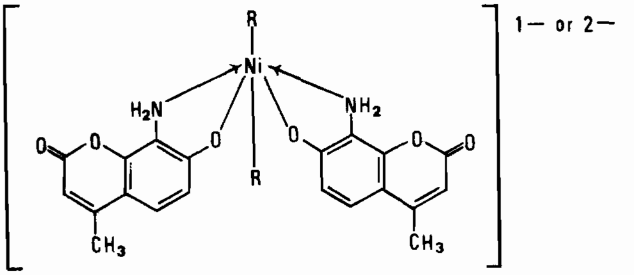


Figure 1. A possible formulation of nickel(II) complexes of AHMC(R=Cl, H_2O or CN).

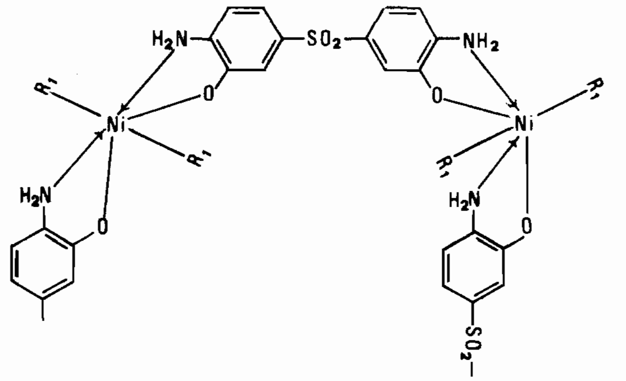


Figure 2. A possible formulation of nickel(II) complexes of D(AMP)S(R_1=H_2O or NH_3).

Examination of three principal absorption bands provides the following explanation which indicates that it is not a spin-forbidden transition but a low symmetry component of the ν_1 and/or ν_2 band. Firstly, assuming O_h symmetry, the value of B calculated for these complexes from the diagonal sum rule[15] comes out to be 1111 cm^{-1} and 1131 cm^{-1}, respectively, which are greater than the free ion value of 1080 cm^{-1}. Such values of B which are greater than their free ion value, suggest the distortion from O_h symmetry.[15] Secondly, for O_h symmetry, the calculated and experimental values of ν_2 and ν_3 should be in close agreement.[15] However, these values for the present complexes III and IV are not in agreement (Table II) suggesting thereby a tetragonal distortion of O_h symmetry. Thirdly, for the tetragonal Ni (II) complexes, a value of $(\nu_3 - \nu_2)_{calc}$ (calculated on the assumption of O_h symmetry) significantly greater than the observed value $(\nu_3 - \nu_2)_{obs.}$, has been taken as a measure of the tetragonal distortion.[15]. The $[(\nu_3 - \nu_2)_{calc} - (\nu_3 - \nu_2)_{obs}]$ values for the present complexes III and IV comes out to be 1770 cm^{-1} and 3440 cm^{-1}, respectively, which are considerably greater than the corresponding values of 720 cm^{-1} and 530 cm^{-1}, observed for the present octahedral nickel (II) complexes. Lastly, it has been shown that for nickel(II) complexes with O_h symmetry, as 10 Dq increases, configuration interaction[18] between the high spin T_{1g}(F) excited states generally lower the ratio ν_2/ν_1 from the theoretical value of 1.8 to Ca. 1.5-1.7.[14] The value of ν_2/ν_1 for the present complexes I and II comes out to be 1.63 and 1.62, respectively, confirming their O_h symmetry. However, the tetragonal distortion produces E-components of the T_{1g}(F) and T_{2g} levels and the subsequent interaction and repulsion between these levels would cause an increase in the ν_2/ν_1 ratio. The ratio ν_2/ν_1 for the complexes III and IV are 1.80 and 1.81, respectively, which are greater than the usual range for octahedral complexes, characterising thereby the AHMC complexes to be tetragonal from the octahedral complexes of D(AHP)S. Thus, it may be concluded that the bands appearing at 12500 cm^{-1} and 12740 cm^{-1} in complexes III and IV, respectively are low symmetry components. Hence all the four bands of AHMC complexes may be assigned to $B_1 \rightarrow E^a$ (8540 cm^{-1}, 11000 cm^{-1}) $B_1 \rightarrow B_2, A_2$ (12500 cm^{-1}, 12740 cm^{-1}); $B_1 \rightarrow E_b$ (15350 cm^{-1}, 19900 cm^{-1}) and $B_1 \rightarrow A_1$ (27060 cm^{-1}, 30060 cm^{-1}) transitions.

I.R. Studies. A comparison of the i.r. spectra of D(AHP)S, AHMC and their nickel(II) complexes reveals the disappearance of bands observed in the free ligands at 3442 cm^{-1}, 1334 cm^{-1} (AHMC) and 3460 cm^{-1}, 1375 cm^{-1} D(AHP)S usually associated with stretching and deformation OH of the phenolic group, indicating the loss of phenolic proton on complexation and forming the (M-O) link. The (M-O) stretching vibrations in D(AHP)S complexes appear as weak absorption bands in the region 435-420 cm^{-1}, whereas in the AHMC complex III, the weak absorption bands at 478 cm^{-1} and 417 cm^{-1} may be due to this vibration. The ν(M-O) vibration of complex IV has probably been masked by the bending (M-C≡N) modes of cyanide, which occur at 436 cm^{-1} and 425 cm^{-1}.

The presence of NH_3 vibration in complex II is indicated by the appearance of a strong absorption band at 3390 cm^{-1} and the lowering in its frequency from that of free ammonia may be due to the effect of coordination.

The C≡N stretching frequencies of complex IV have observed at 2120 cm^{-1} and 2100 cm^{-1} and the shifting in its frequency from that of the free ion (KCN, 2080 cm^{-1}) due to coordination in noteworthy.[20] In addition to the C≡N stretching bands, the mixed cyano complex also exhibit stretching (M-C) and bending (M-C≡N) vibrations at 546 cm^{-1}, 535 cm^{-1} and 436 cm^{-1}, 425 cm^{-1}, respectively. However, in other cyano complexes of nickel (II) the stretching (M-C) and bending (M-C≡N) vibrations have been observed at 543 cm^{-1} and 433 cm^{-1}, 421 cm^{-1}, respectively.[21]

The antisymmetric and symmetric SO_2 vibrations absorb in the region 1300-1255 cm^{-1} and 1140-1100 cm^{-1}, respectively in the free ligand D(AHP)S.[22-24]

---

(18) A.B.P. Lever, *Coordn. Chem. Rev.*, *3*, 119 (1968).

(19) J. Fujita, K. Nakamoto, and M. Kobayashi, *J. Am. Chem. Soc.*, *78*, 3295 and 3963 (1956).

(20) K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds' (John Wiley and Sons. N.Y.)., p. 167 (1963).

(21) R.L. McCottough, L.H. Jones, and G.A. Crosby, *Spectrochim. Acta.*, *16*, 979 (1960).

(22) D. Barnard, K.M. Fabian, and H.P. Koch, *J. Chem. Soc.*, 2442 (1949).

The unaltered position of these bands on complexation suggests that sulphur is not taking part in coordination.

The antisymmetric NH_2 stretching vibration appears as strong absorption bands at 3368 cm^{-1} (AHMC) and 3380 cm^{-1}, 3360 cm^{-1} D(AHP)S whereas the symmetric NH_2 stretching vibration occur in the region 3300-3200 cm^{-1} in both the ligands. On complexation, both the ν-assym. and ν-sym. NH_2 modes have been considerably lowered and the changes in δNH_2, $\delta\omega NH_2$ and $\delta\nu NH_2$ vibrations, have also been observed (Table III and IV). Such a shift to lower frequancy on complex formation has earlier been interpreted by Rastogi[5] and others.[25-27] This is because of the fact that the electron density of the nitrogen atom being directed to the metal ion, leaving the amino proons less tightly bound to the nitrogen. This indicates that the nitrogen of the NH_2 group serves as a coordination centre in both the ligands. In the present studies the ν(M-N) vibrations have been observed as weak absorption bands around 500 cm^{-1}. A weak absorption band has also been observed at 375 cm^{-1} in complex III which may be due to ν(M-Cl) vibrations.[28]

Conclusions

The results of this investigation show that nickel (II) complexes of D(AHP)S are octahedral whereas its AHMC complexes are tetragonally distorted from their regular cubic symmetry. The effect of this distortion is produced due to the unequal donor strengths of chloride and cyanide ligands, which is concluded from the following observations:

(i) Values of magnetic moment observed for these complexes are lower than that required for octahedral complexes, suggesting them to be a mixture of paramagnetic octahedral molecules and diamagentic planar molecules.

(ii) Value of Racah's interelectronic repulsion parameter B for these complexes are greater than their free ion value.

(iii) Theoretical and experimental values of the spin-allowed ν_2 and ν_3 transitions are not in agreement.

(iv) The ratio ν_2/ν_1 for these complexes are greater (1.8) than the usual range (1.5 - 1.7) for octahedral complexes.

Hopefully, X-ray structure and electronic spectra at liquid nitrogen temperature, of these complexes can be obtained in future to clarify the bonding modes and substantiate the proposed structures.

Acknowledgements. The authors appreciate cooperation with Dr. V.N. Sarin, Physics Department, I.I.T. Kanpur in measurements of infrared spectra. Financial suport by the University Grants Commission, New Delhi is gratefully acknowledged.

---

(23) P.M.G. Bavin, G.W. Gray, and A. Stephenson, *Spectrochim. Acta.*, *16*, 1312 (1960).

(24) E.A. Robinson, *Can. J. Chem.*, 39, 247 (1961).

(25) J. Chatt, L.A. Doncanson, L.M. Venanzi, *J. Chem. Soc.*, 4461 (1955).

(26) Idem, *J. Chem. Soc.*, 2711 (1956).

(27) G.F. Swtos, C. Curran, and J.V. Quagliano, *J. Am. Chem. Soc.*, *77*, 6159 (1955).

(28) N.B. Colthup, L.H. Daly, and S.E. Wiberly, 'Introduction to Infrared and Raman Spectroscopy' (Academic Press N.Y.), p. 347 (1964).