ELECTRONIC AND INFRARED SPECTRAL STUDIES OF COBALT(II) AND NICKEL(II) CYANIDE COMPLEXES WITH SOME NITROGEN DONOR LIGANDS

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ABSTRACT

Complexes of the composition $ML_2(CN)_2$ [where M = Co(II), or Ni(II), L = Pyridine (Py), Aniline, hydrazine, phenylhydrazine, ethylenediamine(en) or *o*-phenylenediamine (OPD)] have been prepared and characterized through elemental analysis and various physico-chemical studies. Molar conductances of the ethylenediamine and *o*-phenylenediamine complexes in DMSO show that they are non-ionic. Electronic spectral studies suggest mixed stereochemistry ($O_h + D_{4h}$) for $Ni(C_5H_5NH_2)_2(CN)_2$ and octahedral geometry for the rest of the complexes. Magnetic moments for $Ni(en)_2(CN)_2$ and $Ni(OPD)_2(CN)_2$ are consistant with spin-free octahedral geometry but subnormal magnetic moments have been observed for all other complexes. IR spectral studies indicate bidentate behaviour of ethylenediamine and *o*-phenylenediamine, unidentate and/or bidentate behaviour of cyanide ion.

INTRODUCTION

A SURVEY of the literature shows that some complexes of Co(II) and Ni(II) cyanides with nitrogen donor ligands have been prepared[1–4] and in some cases their structures also studied, but no work appears to have been done on these cyanide complexes with pyridine, aniline, hydrazine, phenylhydraine, ethylenediamine and *o*-phenylenediamine except for the synthesis of $Ni(Py)_2(CN)_2$[1] and the determination of formation constants of $Ni(N_2H_4)_2(CN)_2$[5]. A synthetic and structural study of the complexes of Co(II) and Ni(II) cyanides with these nitrogen donors has therefore been undertaken and the results of this study are discussed in the present paper.

EXPERIMENTAL

All the chemicals used were of BDH or equivalent grade. Ethanol, pyridine, aniline, hydrazine, phenylhydrazine and ethylenediamine were made anhydrous before use.

All the complexes were prepared by mixing and stirring the ethanolic solution of the ligand and ethanolic suspension of metal cyanide for 7–8 hrs keeping the ligand to metal ratio Ca 2 : 1. Co(II) complexes were prepared in nitrogen atmosphere to avoid oxidation. The complexes thus obtained were suction filtered, washed successively with ethanol and ether and dried *in vacuo*. Attempts to prepare the aniline complex of $Co(CN)_2$ were unsuccessful.

Cyanide was estimated as AgCN. All other details pertaining to analysis and physico-chemical studies of the complexes were the same as described in our previous paper[6]. Analytical data, μ_{eff} values and molar conductances are given in Table I. Electronic spectral bands, alongwith their assignments and ligand-field parameters are listed in Table II.

RESULTS AND DISCUSSION

All the complexes are insoluble in common organic solvents. Ethylenediamine and *o*-pherylenediamine complexes are soluble in coordinating solvents like THF, DMSO, DMF but all other complexes are insoluble in these solvents too. Complexes of ethylenediamine and *o*-phenylenediamine melt in the 162–207° C range but the remaining complexes do not melt upto 250° C. The insolubility and nonmelting nature of the pyridine, aniline, hydrazine and phenylhydrazine complexes indicate that they are polymeric. The molar conductances of the ethylenediamine and *o*-phenylenediamine complexes lying in the 3·60–5·31 mhos cm^2 $mole^{-1}$ range, suggest their non-electrolytic nature[7].

Electronic Spectra

The electronic spectra of Co(II) complexes yield two *d–d* transition bands in 9091–10740 and 16370–18870 cm^{-1} regions assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions respectively characteristic of octahedral geometry around the Co(II) ion[8].

The electronic spectra of the Ni(II) complexes are also consistent with octahedral stereochemistry[9] in as much as they show three *d–d* transition bands in the 10000–11490, 17040–18870 and 25550–28170 cm^{-1} regions attributable to $^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3) transitions respectively. The proposed octahedral geometry for the Ni(II) complexes draws further support from ν_2/ν_1 ratio lying in the 1·65–1·72 range[10]. In addition to the three bands characteristic of octahedral geometry,

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TABLE I

Analytical data and general behaviour of the complexes

Complex	Colour	Co/Ni %	CN %	N %	μ_{eff} (B.M.)	Molar conductance (mhos cm² mole⁻¹)
$Co(Py)_2(CN)_2$	Brown	21·5 (21·9)	19·0 (19·3)	20·4 (20·8)	3·72	..
$Ni(Py)_2(CN)_2$	Pink	21·5 (21·8)	19·1 (19·4)	20·5 (20·8)	2·22	..
$Ni(C_5H_5NH_2)_2(CN)_2$	Blue	20·0 (19·8)	17·3 (17·5)	18·6 (18·9)	2·21	..
$Co(N_2H_4)_2(CN)_2$	Brown	33·4 (33·7)	29·8 (29·7)	47·8 (48·0)	3·89	..
$Ni(N_2H_4)_2(CN)_2$	Pink	33·5 (33·6)	30·0 (29·8)	48·2 (48·1)	2·19	..
$Co(C_5H_5NHNH_2)_2(CN)_2$	Brown	17·8 (18·0)	15·6 (15·9)	25·4 (25·7)	3·69	..
$Ni(C_5H_5NHNH_2)_2(CN)_2$	Blue	17·7 (18·0)	15·7 (15·9)	25·5 (25·7)	2·28	..
$Co(en)_2(CN)_2$	Brown	25·2 (25·5)	22·3 (22·5)	36·1 (36·4)	3·33	5·31
$Ni(en)_2(CN)_2$	Pink	25·3 (25·4)	22·2 (22·5)	36·2 (36·4)	2·78	4·50
$Co(OPD)_2(CN)_2$	Brown	17·8 (18·0)	15·6 (15·9)	25·5 (25·7)	3·87	3·87
$Ni(OPD)_2(CN)_2$	Pink	17·6 (17·9)	15·7 (15·9)	25·3 (25·7)	2·82	3·60

* Calculated values are given in parentheses.

TABLE II

Electronic spectral data and various ligand-field parameters of the Co(II) and Ni(II) complexes

Complex	ν_1 (cm⁻¹)	ν_2 (cm⁻¹)	ν_3 (cm⁻¹)	Dq (cm⁻¹)	B′ (cm⁻¹)	β	β° (%)	LFSE (KJ/mole)
$Co(Py)_2(CN)_2$	10740	..	18870	1180	614·4	0·64	36·46	120·8
$Co(N_2H_4)_2(CN)_2$	9091	..	16370	1006	548·0	0·57	43·33	103·1
$Co(C_5H_5NH_2)_2(CN)_2$	10420	..	18390	1150	602·9	0·62	37·65	118·0
$Co(en)_2(CN)_2$	9524	..	17150	1054	574·1	0·59	40·63	108·1
$Co(OPD)_2(CN)_2$	10540	..	18180	1145	571·9	0·59	40·86	117·4
$Ni(Py)_2(CN)_2$	10580	17540	26850	1058	843·3	0·80	20·14	151·2
$Ni(C_5H_5NH_2)_2(CN)_2$	10000	17040	25550	1000	839·3	0·80	20·52	142·9
$Ni(N_2H_4)_2(CN)_2$	11490	18520	..	1149	966·8	0·92	8·45	168·1
$Ni(C_5H_5NHNH_2)_2(CN)_2$	10810	17790	26180	1081	769·3	0·73	27·16	154·5
$Ni(en)_2(CN)_2$	10870	18700	27580	1087	908·6	0·86	13·96	159·0
$Ni(OPD)_2(CN)_2$	11240	18870	28170	1124	888·0	0·84	15·84	164·4

the electronic spectrum of $Ni(C_5H_5NH_2)_2(CN)_2$ shows a band at 22470 cm⁻¹ assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$ transition in the square planar environment around Ni(II) ion[11]. The positions and assignments of electronic spectral bands thus indicate mixed stereochemistry $(O_h + D_{4h})$ for the above complex.

Magnetic measurements :

Co(II) is known to form spin-paired complexes with strong field ligands and spin-free complexes with weak field ligands[12]. Equilibrium between these two states has also been reported with ligands of border line strengths[13,14]. $Co(CN)_2$ forms low spin complexes

with strong field ligands like 2,2'-bipyridyl and *o*-phenanthroline[1]. With the cyanide ion occurring at the extreme right and the nitrogen donor ligands in the middle of the spectrochemical series, the co-existence of spin-free and spin-paired states may be expected in our Co(II) complexes and the subnormal magnetic moments (3·33–3·89 BM) observed for these complexes are in line with the above reasoning. The coexistence of low spin and high spin states in these oomplexes is further supported by their Dq B ratio (1·84–2·0) which approaches the limiting point where change over occurs from $^4T_{1g}$ to ^3E_g ground state[15].

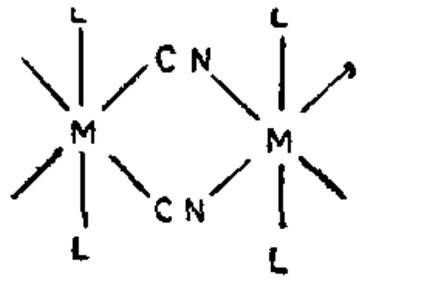
The magnetic moments of the ethylenediamine and *o*-phenylenediamine complexes of $Ni(CN)_2$ are normal and indicate octahedral geometry for Ni(II) in these complexes[16]. The remaining Ni(II) complexes have subnormal magnetic moments of the order 2·19–2·28 BM. The subnormal magnetic moment of $Ni(C_6H_5NH_2)_2(CN)_2$ can be explained on the basis of mixed stereochemistry. Due to the simultaneous existence of square planar and spin free octahedral Ni(II) ions in the above complex, the observed magnetic moment per Ni(II) ion is 2·21 BM. Although the pyridine, hydrazine and phenylhydrazine complexes of $Ni(CN)_2$ also have subnormal magnetic moments, this type of mixed stereochemistry for them is ruled out because of the absence of bands characteristic of square planar Ni(II) in their electronic spectra. The subnormal magnetic moments of these complexes may, however, be explained on the basis of polymetallic structures arising from cyanide bridging just as in the hydrated Ni(II) cyanide[17].

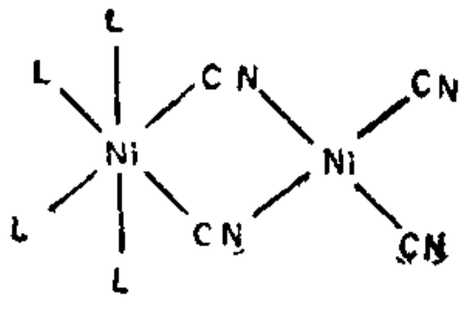
IR Spectra :

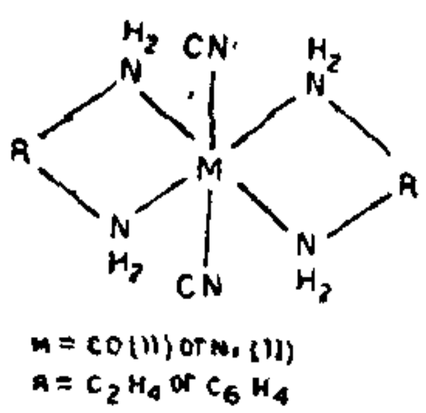
The IR spectrum of the free cyanide ion yields a ν(CN) band at 2080 cm^{-1} [18]. This band is reported to shift to higher frequencies on coordination and is obtained near 2100 cm^{-1} when cyanide is unidentate and Ca 2200 cm^{-1} when it is bridging through both carbon and nitrogen[18]. Lowering in ν(CN) is observed when cyanide ion bridges through carbon atom only. The ν(CN) band is observed in the 2118–2146 cm^{-1} region in our ethylenediamine and *o*-phenylenediamine complexes and Ca 2175 cm^{-1} in the spectra of pyridine, hydrazine and phenylhydrazine complexes indicating that cyanide ion is monodentate in the former complexes and bidentate bridging through carbon and nitrogen in the latter complexes. IR spectrum of $Ni(C_6H_5NH_2)_2(CN)_2$ gives two ν(CN) bands at 2176 and 2128 cm^{-1} suggesting the presence of both bridging and terminal cyanide ions in the above complex.

A negative shift in the ν(N–H) (14–124 cm^{-1}), $\delta(NH)_2$ (5–22 cm^{-1}), and ν(C–N) (28–63 cm^{-1}) in the aniline, ethylenediamine and *o*-phenylenediamine complexes as compared to similar bands in the spectra of free ligands and a positive shift in ν(N–N) (27–89 cm^{-1}) in the spectra of hydrazine and phenylhydrazine complexes indicate coordination of these ligands through nitrogen(s)[19–21]. Coordination of pyridine is suggested by positive shifts (38–47 cm^{-1}) in its in-plane and out-of-plane ring deformation modes in the spectra of its complexes[18]. Occurrence of a single ν(C–N) band in 1032–1052 and 1232–1248 cm^{-1} regions in the spectra of ethylenediamine and *o*-phenylenediamine complexes respectively shows that both the nitrogens of these diamines are involved in coordination. The non ligand bands Ca 450 cm^{-1} and in the 396–261 cm^{-1} region are tentatively assigned to ν(M–CN) and ν(M–N) modes respectively[18].

The following structures may be proposed for the complexes based upon their chemical composition, general behaviour and physico-chemical studies:







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5-HT AND 5-HYDROXYINDOLEACETIC ACID LEVELS IN SUCCESSIVE SAMPLES OF CISTERNAL CSF OF RHESUS MONKEYS*

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ABSTRACT

The 5–HT and 5–hydroxyindoleacetic acid levels were assayed fluorometrically in successive samples—with no time interval between sampling—of cisternal CSF of anaesthetised rhesus monkeys. The basal levels were 39·78 ± 4·66 ng/ml and 68·29 ± 15·16 ng/ml respectively. The significance of the occurrence of 5–HT in CSF with regard to its possible role in regulating pituitary gonadotropin secretion is mentioned. The first 3 ml of CSF is found to be homogeneous with regard to 5–HT and 5–Hydroxyindoleacetic acid; successive samples collected subsequently contained higher levels of 5–HT and 5–hydroxyindoleacetic acid. Hence, a standardised sampling procedure is advocated to have comparable data.

INTRODUCTION

A CONSIDERABLE volume of evidence has accumulated to suggest that CSF may constitute a humoral link between different areas of the brain by transporting neural products affecting cellular function. Administered intraventricularly, 5–HT has been shown to inhibit pituitary leutinizing hormone secretion[1]. On the basis of this and other similar findings, it has been postulated that 5–HT of extrahypothalamic origin may reach the neural mechanism regulating pituitary gonadotropin secretion *via* CSF. However, on scanning the literature, very few references are found reporting the occurrence of 5–HT in CSF[2]; 5–HT as such has never been convincingly demonstrated in the CSF of rhesus monkeys. On the other hand, 5-Hydroxyindoleacetic acid (5–HIAA) has been repeatedly investigated in various psychopathological and neurological conditions[3–5].

Hence, in this work, we have assayed both 5–HT and 5–HIAA in successive samples collected on a single cisternal tap—without allowing any interval between successive sampling—mainly to look for the occurrence of 5–HT in CSF and also to look for any differences in 5–HT and 5–HIAA concentrations between successive samples.

MATERIALS AND METHODS

In this study, rhesus monkeys of both sexes were anaesthetised with 30 mg/kg *i.v.* nembutal sodium. Throughout the study, cisternal taps were done between 11 A.M. and 12 NOON to rule out diurnal variations. Successive 3 ml and 1·5 ml CSF samples were collected for 5–HT and 5–HIAA assay in the first and the second group of experiments respectively. Blood stained samples were discarded. Moreover, the samples were centrifuged in order to detect the presence of red blood cells; because it was difficult to see a coloration when a small amount of blood was present. The CSF samples were deproteinised and the solution was made 0·1 N with respect to hydrochloric acid[4]

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