MAGNETIC AND SPECTRAL STUDIES OF COMPLEXES OF ISONITROSO-ACETOPHENONE (HINAP) WITH Ni(II), Pd(II) AND Pt(II)

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(Received 15 August 1979; received for publication 12 September 1979)

Abstract—The preparation and properties of the complexes of isonitrosoacetophenone (HINAP) with Ni(II), Pd(II) and Pt(II) and the imino derivatives of Ni(II) and Pd(II) complexes have been described. Their structures have been discussed on the basis of magnetic and spectral studies. The two colored varieties of (isonitrosoacetophenonato) Ni(II) are paramagnetic and have octahedral configuration, whereas Pd(INAP)₂, Pt(INAP)₂, Ni(C₈H₇N₂O)₂ and Pd(C₈H₇N₂O)₂ are diamagnetic and spuare planar. The reaction products of complexes of Ni(II) and Pd(II) with pyridine have also been isolated and examined.

INTRODUCTION

A tris- complex of Co(III) with isonitrosoacetophenone (HINAP) has been studied by Pathak and Haldar[1] and its structure has been established. Attempts of Taylor and Ewbank[2] to prepare a complex of Ni(II) by the reaction of HINAP with nickel acetate resulted in the formation of a compound of indefinite composition. Complexes of HINAP with Pd(II) and Pt(II) have not been studied.

In the present paper, the preparation and properties of complexes of Ni(II), Pd(II) and Pt(II) with HINAP and imino derivatives of Ni(II) and Pd(II) complexes are reported. The reaction products of complexes of Ni(II) and Pd(II) with pyridine have also been studied. The structure of these complexes have been discussed on the basis of the results of conductance, magnetic and spectral studies.

EXPERIMENTAL

Apparatus and instruments employed are described elsewhere [3, 4]. Chemicals used were of A.R. grade. HINAP was prepared by following the procedure recommended by Welcher [5].

(Isonitrosoacetophenonato) nickel(II), $[Ni(INAP)_2]_x$ (lightgreen) was prepared by treating a solution of HINAP in 0.1 M NaOH with an aqueous solution of nickel sulphate and allowing the solid to settle. It was filtered, washed with hot water and dried at 105°C.

(Isonitrosoacetophenonato) nickel(II), $[Ni(INAP)_2]_y$ (brown) was obtained by the crystallization of the light green form from chloroform.

The orange-red $Pd(INAP)_2$ was formed by the addition of an alcoholic solution of HINAP to a solution of palladium chloride in dilute HCl and raising the pH of the mixture to 4.6-5.2 with NaOH solution. It was filtered, washed with water and alcohol.

The dark brown $Pt(INAP)_2$ was prepared by adding an alcoholic solution of HINAP to an aqueous solution of chloroplatinic acid and digesting the mixtures on a hot water bath for about 1 hr. The solid was washed with hot water and 40% alcohol.

The pyridine adducts of the two forms of Ni(II) complex and of $Pd(INAP)_2$ were obtained by dissolving the respective complex in minimum quantity of hot pyridine and concentrating the solution. The adducts were air-dried.

 $Ni(C_8H_7N_2O)_2$ or $Pd(C_8H_7N_2O)_2$ was prepared by treating a

solution of HINAP in 1:1 ammonia with a solution of nickel sulphate in liquor ammonia or with a solution of palladium chloride in dilute HCl and digesting on a hot water bath. The separated compound was washed with dilute ammonia and water. Ni(C H N Q) = $P_{4}(C H N Q)$

 $Ni(C_8H_7N_2O)_2$, $Pd(C_8H_7N_2O)_2$, $Pd(INAP)_2$ and $Pt(INAP)_2$ were dried at 105°C and recrystallized from chloroform.

RESULTS AND DISCUSSION

Chemical analysis data (Table 1) indicate that the complexes of Ni(II), Pd(II) and Pt(II) with HINAP may be represented by the general formula M(INAP)₂, where M = Ni(II), Pd(II) or Pt(II). (Isonitrosoacetophenonato) Ni(II) has been obtained in two forms, light-green and brown. The brown form is obtained by the crystallization of the light-green variety from chloroform. Both these varieties dissolve in organic solvents to produce a brown colored solution. The two colored varieties of Ni(II) complex and Pd(INAP)₂ form pyridine adducts of the composition $M(INAP)_2 \cdot 2Py$, where M = Ni(II) or Pd(II). The red-brown Ni(II) and the yellow Pd(II) complexes prepared in the presence of ammonia have the composition $M(C_8H_7N_2O)_2$, where M = Ni(II) or Pd(II). Attempts to prepare the corresponding compound of Pt(II) were not successful.

The complexes mentioned above are insoluble in water but soluble in organic solvents like chloroform, nitrobenzene, pyridine etc. However, they are sparingly soluble in benzene or carbon tetrachloride. Their molar conductance in nitrobenzene solution suggest that they are non-ionic in nature. Cryoscopy measurements indicate that the brown variety of the complex of Ni(II) with HINAP is dimeric in nitrobenzene solution. Since the light-green variety produces brown color in organic solvents, it probably changes into the brown form in solution. The light-green and brown forms may therefore, be formulated as [Ni(INAP)₂]_x and [Ni(INAP)₂]y respectively.

Electronic spectra

The bands observed in electronic spectra and their assignments are given in Table 2. The electronic spectra of the two colored forms of (isonitrosoacetophenonato) Ni(II) in chloroform solution are characterised by the two absorption bands bands at 10.20 kK ($\epsilon_{g} = 15$ for light-green; $\epsilon_{b} = 19$ for brown) and 16.55 kK ($\epsilon_{g} = 90$ and $\epsilon_{b} = 96$) (Table 2). Apparently the conversion of the

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Table 1. Analytical data of the metal complexes

Compound	Colour	Found (%)			Calculated(%)				
		M	2	н	N	M	С	н	N
[Ni(INAP)2]×	Light-green	16.55	54•2	4 • 1	7•60	16.55	54.1	3.4	7.89
[N1(INAP)2]y	Brown	17.10	54.0	3.8	7.57	16.55	54.1	3•4	7.89
Pd(INAP) ₂	Orange-red	36.36	47.0	3.6	6•94	36•44	47•7	3.0	6.96
Pt(INAP) ₂	Dark-brown	38 • 48	38.0	3.1	5.72	39•70	39•1	2•4	5.70
Ni(INAP) ₂ ·2Py from light- green form	Light-brown	11.30	60.0	4•6	10.90	11.50	60.9	4.3	10.90
Ni(INAP) ₂ .2Py from brown form	Light-brown	11.20	60.3	4.7	10.90	11.50	60.9	4.3	10.90
Pd(INAP) ₂ -2Py	Yellow-orange	18.90	55.0	4 • 3	9.95	19.00	55.7	3.9	9.99
Ni(C8 ^H 7 ^N 2 ^D)2	Red-brown	16.30	53.6	4-1	15.70	16.00	54.5	4.07	15.9
Pd(C ₈ H ₇ N ₂ 0) ₂	Yellow	26-40	47.7	4.0	13.6	26•60	48•0	3.5	14.0
	_ <u> </u>								

Table 2. Electronic spectral data of metal complexes of HINAP

Compound	v max kK	[£] max	Tentative Assignment
Pd(INAP) ₂	32 • 26	27,000	π - π [#]
	30•30sh	21,000	Charge transfer
	23.91	16,400	Charge tr ansfe r
	20•00sh	500	Charge transfer
	(21.39)		¹ A _{1g} > ¹ B _{1u}
	(21•74sh		¹ A _{1g} > ¹ E _u
	(18.87)		¹ A ₁₉ > ¹ A _{2u}
Pt(IN AP)₂	28.99	14,000	Charge transfer
	26.67	9,5000	Charge transfer
	23,26	10,250	Charge transfer
	20•41sh		Charge transfer
	16•13 hump	78	d-d transition
[NI(INAP)2]x	28.99	16,700	Charge transfer
Light-graen	16.65 hump	90	$^{3}A_{2g} \longrightarrow ^{3}T_{1g}(F)$
	10.20	15	³ A ₂₉ > ³ T ₂₉
	(15+62) hump		$3_{A_{2g}} \rightarrow 3_{T_{1g}(F)}$
	(9.52-10.00)		³ A ₂₉ ³ T ₂₉

contd.

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Compound	V max kK	i max	Tentative Assignment
[Ni(INAP) ₂] _y Brown	(15.62) hump		³ A _{2g} 3 _{71g(F)}
	(10.20)		$^{3}A_{2q} \longrightarrow ^{3}T_{2q}$
	29 • 41	16,400	Charge transfer
	16.66 hump	95	$^{3}A_{2q} \longrightarrow ^{3}T_{1q}(F)$
	10.20	19	$^{3}A_{2g} \longrightarrow ^{3}T_{2g}$
Pyridine addu	ct(27•03)		Charge tr ansfer
Light-green	(20•41)hump		$^{3}A_{2g} \longrightarrow ^{3}T_{1g}(F)$
(NI(INAP)2)x	(11.90)		³ A _{2g} > ³ T _{2g}
Pyridine addu	ct(27•03)		Charge transfer
promu promu	(20•41)hump		³ A _{2g} > ³ T _{1g(F)}
[N1[IN A7 2Jy	(12.20)		${}^{3}A_{2g} \longrightarrow {}^{3}T_{2g}$
Pd(C _A H ₇ N ₂ O) ₂	29 • 41	23,000	Charge transfer
	22.99	2150	Charge transfer
	(22.73)		Charge transfer
	(20.41)		Charge transfer
	(17.24)		d-d
	(15.87)		d-d
	(14.49)		d∼d
Ni(C ₈ H ₇ N ₂ D) ₂	31.25	12,570	ππ*
	28.57	14,140	Charge transfer
	21.74	48 57	Charge transfer
	17.54		d- d
	16.13		d-d
	(27.78)		Charge transfer
	(21.28)		Charge transfer
	(17.85)		d-d
	(16.39)		d – d
	(15.15)		d-d
Ni(C8H7N2D)2	27•38	9,424	Charge transfer
(in pyridine)	22.22	2,848	Charge transfer
	15.87 hump	49	d - d

sh : shoulder

Solvent : Chloroform, unless mentioned otherwise.

Values in parentheses indicate reflectance spectral data.

light-green form into the brown form is not complete in chloroform solution. The bands at 10.20 kK and 16.55 kK are assigned to the first and second spin-allowed transitions ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$ and ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ (F) respectively in octahedral Ni(II). The ratio of 1.62 for ν_2/ν_1 is consistent with the assignment. The value of the Racah interelectronic repulsion parameter B', calculated with the

help of the eqns(6), $(6Dqp - 16Dq^2) + (-6Dq - p) E + E^2 = 0$ and p = 15 B', is found to be 905.4 cm⁻¹ and the ratio $\beta = B'/B$ corresponds to 0.86. Different terms have their usual significance. The third ligand field band, which is expected to occur at 27.62 kK, is not observed probably because of it being masked by the tail-end of the strong charge transfer band around 28.99 kK. The

diffuse reflectance spectrum of the light-green form shows the first spin-allowed d-d transition near 9.52-10.00 kK, while the brown form exhibits it at 10.20 kK. Both the varieties reveal the second spin-allowed transition as a hump near 15.62 kK. The reflectance spectra of the pyridine adducts obtained from the light-green and the brown forms show the first ligand field band at 11.90 and 12.20 kK respectively. The second ligand field band in the adducts appears at 20.41 kK. It may be inferred that the attachment of pyridine molecules at the two of the six octahedral sites around Ni(II) leads to the increase in the value of 10 Dq.

The shoulders near 17.54 and 16.13 kK in Ni(C₈H₇N₂O)₂ and at 16.13 kK ($\epsilon = 78$) in Pt(INAP)₂ may arise due to d-d transition in square planar Ni(II) and Pt(II) complexes. The electronic spectra of Ni(C₈H₇N₂O)₂ seem to indicate that it maintains the same configuration in chloroform and pyridine solutions. Its reflectance spectrum shows ligand field bands in the region 17.86–15.15 kK, while that of Pt(INAP)₂ reveals a broad ligand field band near 13.51 kK. The three weak intensity bands at 14.49, 15.87 and 17.24 kK in the reflectance spectrum of Pd(C₈H₇N₂O)₂ are possibly due to ligand field transitions. Pd(INAP)₂ does not exhibit distinguishable ligand field bands.

All the complexes investigated reveal charge transfer and $\pi - \pi^*$ transition bands.

PMR and IR spectra

PMR spectra of diamagnetic Pd(INAP)₂, Pt(INAP)₂ and Ni(C₈H₇N₂O)₂ in CDCl₃ solution (Table 3) show signals due to phenyl and methine protons and suggest the replacement of proton of the=NOH group in the ligand by the metal. The reason for the broadness of the methine proton signal at 2, 02 τ in Pt(INAP)₂ is not obvious. Ni(C₈H₇N₂O)₂ reveals a broad proton signal at 0.55τ , which is tentatively assigned to the imine proton because it is reported [7] that the proton reasonance signal due to the =NOH group of HINAP in CDCl₃ occurs as a medium sharp signal at 0.94 τ . The absence of a free =NOH group in the complex is also indicated by its insolubility in dilute alkali solution.

IR spectra of HINAP and partially deuterated HINAP are in agreement with those reported by Pathak and Haldar[1]. Some of the important vibrational bands of the metal complexes investigated and their assignments are given in the Table 4. The absence of OH group in Ni(II) complex (light-green and brown forms), $Ni(INAP)_2 \cdot 2Py$, $Pd(INAP)_2$, $Pd(INAP)_2 \cdot 2Py$, and Pt(INAP)₂ is supported by their IR spectra in the region 3600-3200 cm⁻¹. The bonded C=O and C=N stretching frequencies occur in these complexes at 1600-1590 and 1500 cm⁻¹ respectively. The mono-substituted phenyl band near 1600 cm^{-1} probably overlaps with the perturbed C=O stretching mode in the range $1600-1580 \text{ cm}^{-1}$. Other mono-substituted phenyl bands appear around 1450, 775 and 690 cm⁻¹. The N-O stretching, which appears in HINAP at 980 cm⁻¹, is observed in the range 1175-1200 cm⁻¹. This implies that the double bond character of the N-O linkage increases on complexation. Magnetic and spectral data support a five membered planar ring structure (a) for Pd(INAP)₂ and Pt(INAP)₂ and structure (b) for $Ni(C_8H_7N_2O)_2$ and $Pd(C_8H_7N_2O)_2$.

The magnetic moments of the light-green and brown forms of the complex of Ni(II), calculated on the basis of formula weight, are 2.76 B.M. and 2.73 B.M. respectively at 293°K, which are very close to the spin-only value for two unpaired electrons in octahedral Ni(II). They vary from 2.76 B.M. at 293°K to 1.98 B. M. at 80°K for the light-green form and from 2.73 B.M. at 293°K to 1.97 B.M. at 80°K for the brown form, indicating antiferromagnetic interaction. Measurements at room temperature suggest that they do not differ significantly from

Compeund	Sølvent	Observed shift in T	Assignment
HINAP *	Dioxane	-1.3	= NC H
		1.6	-CH
		2.2	-C ₆ H ₅
	CDC13	0.94	=NOH
Pd(INAP) ₂	coc1 ₃	2.10	-СН
		2 • 4 0	~C ₆ H ₅
Pt(INAP) ₂	CDC13	2.02	-сн
		2 • 49	-c ₆ H5
		2.62	-C ₆ H ₅
Ni(C ₈ H ₇ N ₂ 0) ₂	CDC13	0.55	-NH
		2.31	-CH
		2 • 43	
		2.63	~ ⁶ 6 ⁸ 5

Table 3. PMR spectral data of HINAP and its metal complexes

*Reported.

Reference : TMS (Internal Standard)

Table 4. IR spectral data of HINAP and its metal comple

Compound	vC=0 cm ⁻¹	VC=N cm ⁻¹	VN-0 cm ⁻¹	°N-н см ^{−1}
HINAP	1685s	160 0s	980 s	-
Pd(INAP) ₂	15958	1495s	11803	-
Pd(INAP) ₂ • 2P y	1595m	1500sh	1195 s	-
Pt(INAP) ₂	1600s	15106	1185s	-
<pre>[Ni(INAP)2]x (light-green)</pre>	1600s	1555#	1170s	-
[Ni(INAP) ₂] _y (brown)	160 0s	15558	1175s	-
Pd(C8H7N20)2	-	1545s	1180m	3150 sb
Ni(C ₈ H ₇ N ₂ 0) ₂	-	1545s	1195s	3220 sb
Pyridine adduct obtained from light-green [Ni(INAP) ₂] _x	1600 s	1530s	1180 s	-
Pyridine adduct obtained from brown [Ni(INAP)2]y	1600s	1530s	1180 s	-

s = sharp, m = medium, w = weak, sh = shoulder, b = broad.









Fig. 2. Magnetic behaviour of brown Ni(II) complex.



Fig. 3. The structure of Ni₂(INAP)₄.

values obtained with chloroform solutions of the two colored varieties. A variation of the magnetic field in the range 4000-7500 guass does not have appreciable effect on the magnetic moment values. Considering that the brown form is dimeric in nitrobenzene solution and its spectral properties in chloroform solution and in solid form are very similar, it may also be dimeric in the solid state.

The temperature independent paramagnetism, N α , of the two forms was calculated with the help of the equation N $\alpha = (8N\beta^2/10Dq)$ (where terms have their usual significance), using 10Dq values obtained from their reflactance spectra. The plot of $1/\chi_{M_{corr}} - N\alpha$ vs T (Figs. 1 and 2) was a straight line graph with Weiss constant θ being -120°K and -130°K for the light-green and the brown forms respectively. The reciprocal of the slope gave the value of C, the Curie constant, which was usedto estimate g by employing the expression, C = $N\beta^2g^2[S(S+1)/3k]$ where S = 1. The observed susceptibilities of the two colored forms can be estimated within 150×10^{-6} c.g.s. by using the susceptibility equation for a Ni(II) dimer assuming the exchange constant J = -37 and -39 for the light-green and brown varieties respectively.

$$X' = \frac{3K}{T} \left[\frac{1 + 5e^{4J/kT}}{3 + 5e^{4J/kT} + e^{-2J/kT}} \right] + N\alpha$$

Different values of g and/or J are required to obtain the desired agreement between the observed and calculated susceptibility values below 159°K. A similar behaviour was observed by Lintvedt *et al.*[9] with bis -(1,5 - diphenyl - 1,3,5 - pentanetrionato) - tetraaquodinickel (II), Ni₂(DBA)₂(H₂O)₄.

On the basis of the present investigation the dimeric form $Ni_2(INAP)_4$ may be represented by the structure (Fig. 3).

Acknowledgements-The authors are thankful to The Tata Institute of Fundamental Research, Bombay (India) for the low temperature magnetic susceptibility measurements, and CIBA Research Centre, Bombay (India) for the PMR spectra.

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