

## Synthesis and Characterization of Nickel(II) Complexes of 2-(2'-Aminophenyl) Benzimidazole

GITA SETH\* and NARENDRA K. MOURYA

Department of Chemistry, University of Rajasthan, Jaipur-302 004, India

Nickel(II) halides reacts with 2-(2'-aminophenyl) benzimidazole to give complex of the formula  $NiX_2L_2$  where  $X = Cl^-, Br^-$ ,  $L = 2-(2'-aminophenyl) benzimidazole$ . (APBI). These complexes react with other ligands like glycine, oxalic acid, carboxylic acid and phenol to form ternary metal complexes. These complexes have been characterised on the basis of their elemental analysis, conductance measurement, IR, NMR and electronic Spectra. The fungicidal action of these metal complexes has been studied against *Alternaria alternata* and *Spergillus niger* by spore germination method compared with dithane M-45, a commercial fungicide.

**Key words:** Synthesis, nickel(II), ternary complexes, 2-(2'-aminophenyl) benzimidazole

### INTRODUCTION

Considerable attention is being paid in recent years to the study of transition metal complexes of substituted benzimidazole because of their biological significance and interesting spectral, magnetic and structural aspects<sup>1-3</sup>. The fact that the mixed ligand complexes could be expected to be more biologically active<sup>4</sup> than the binary complexes, prompted us to undertake the present work.

### EXPERIMENTAL

Nickel halides ( $NiCl_2 \cdot 6H_2O$  and  $NiBr_2 \cdot 6H_2O$ ) were obtained from BDH. The ligand, 2-(2'-aminophenyl) benzimidazole (APBI) was prepared according to the method described by Heins *et al.*<sup>5</sup> and modified by Vyas and coworker<sup>6</sup>. Melting points were determined in open capillaries and are uncorrected. IR spectra (KBr) were recorded on a Perkin-Elmer 577 grating IR spectrophotometer. The <sup>1</sup>H NMR spectrum (chemical shift in  $\delta$  ppm) obtained from FX90Q Jeol spectrometer at 90 MHz is DMSO-d<sub>6</sub> using TMS as an internal reference. The purity of all compounds was checked by running TLC on silica gel-G plates using chloroform-ethyl acetate (1 : 1) mixture and spots were visualized by iodine vapours. The metal contents of the complexes were determined by standard literature procedures. The analytical data and physical properties of ligand and complexes are given in Table-1.

Attempts have been made to isolate the following binary nickel complexes:

(a) nickel benzimidazole; (b) nickel glycinate; (c) nickel oxalate; (d) nickel formate; (e) nickel phenolate.

TABLE-1  
PHYSICAL AND ANALYTICAL DATA OF LIGANDS AND COMPLEXES

m.f. (Colour)	m.w.	Yield (%)	Decomposition temperature (°C)	Analysis (%), found (calcd.)				
				C	H	N	Ni	Cl/Br
C <sub>13</sub> H <sub>11</sub> N <sub>3</sub> (APBI) (White)	209	72	214	74.24 (74.69)	5.12 (5.29)	19.98 (20.08)	-	-
NiCl <sub>2</sub> (APBI) <sub>2</sub> (Greenish yellow)	338	73	298	45.95 (46.15)	3.02 (3.25)	12.38 (12.42)	17.08 (17.15)	20.98 (21.00)
NiBr <sub>2</sub> (APBI) (Greenish yellow)	427	72.5	282	36.43 (36.15)	2.50 (2.57)	9.80 (9.83)	13.48 (13.58)	37.42 (37.47)
NiCl(APBI)(Gly.) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (Green)	413	74	285	43.02 (43.58)	3.71 (3.87)	13.52 (13.55)	14.02 (14.04)	8.65 (8.71)
Ni(APBI)(Ox)(H <sub>2</sub> O) <sub>3</sub> (Green)	411	72	271	43.64 (43.79)	3.09 (3.16)	10.08 (10.02)	14.08 (14.11)	-
Ni(APBI)(OForm) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> (Green)	411	72	282	40.65 (40.87)	2.85 (2.91)	10.00 (10.02)	14.02 (14.11)	-
Ni(APBI)(OC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> (Green)	507	73	281	42.50 (42.60)	3.58 (3.65)	8.22 (8.28)	11.40 (11.43)	-

**NiX<sub>2</sub>(APBI)<sub>2</sub>:** To a solution of nickel halo hexahydrate (0.005 mole) in ethanol was added 2-(2'-amonophenyl benzimidazole) (0.01 mole) in ethanol. On refluxing for about 5 h a greenish yellow coloured compound separated, which was washed with ethanol and dried under *vacuo*.

**Ni(gly)<sub>2</sub>·2H<sub>2</sub>O:** To a solution of nickel halo hexahydrate (0.005 mole) in ethanol added (0.01 mole) of glycine taken in 30 mL of methanol. The contents were refluxed for about 4 h. Then pH was raised to 5.5 to 6.0 by adding 1 : 4 aq NH<sub>3</sub>. On continuation of the refluxion, a green coloured precipitate separated out. The hot contents were filtered, washed with methanol and dried *in vacuo*.

**[Ni(Ox)<sub>2</sub>](H<sub>2</sub>O)<sub>3</sub>:** To a solution of nickel chloride hexahydrate (0.005 mole) in ethanol was added 0.01 mole of sodium oxalate solution in ethanol. The contents were refluxed for about 3 h when a green coloured compound separated which was washed with ethanol and dried *in vacuo*.

**[Ni(Form)<sub>2</sub>](H<sub>2</sub>O)<sub>3</sub>:** To a solution of nickel halide hexahydrate (0.005 mole) in ethanol was added (0.01 mole) of sodium formate solution in ethanol. The contents were refluxed for about 3 h when a green coloured compound separated out which was washed with ethanol and dried under *vacuo*.

**[Ni(OC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]:** It was prepared by refluxing nickel halide hexahydrate with excess of phenol at 180°C on an oil bath till the evolution of hydrogen chloride gas ceased. The solution was treated with carbon tetrachloride when a light green coloured compound was obtained. It was filtered and washed with carbon tetrachloride and dried under *vacuo*.

Ternary metal complexes of nickel(II) involving APBI as one of the ligands and glycine, oxalic acid, formic acid and phenol as secondary ligand have been isolated by using the following method.

**1. Simultaneous addition procedure:** The procedure involves the simultaneous addition of three components. Thus the ternary complex is obtained by mixing all its three components *i.e.*, metal salt, substituted benzimidazole and other ligand (L).



**2. Stepwise addition procedure:** This procedure involves the isolation of a binary complex MA or ML and subsequent addition of other ligand L or A to the binary complex as



where M = Ni(II), A = 2-(2'-aminophenyl) benzimidazole, L = secondary ligand (glycine, oxalate, formate and phenolate).

However, analytical studies like colour, physical state, solubilities, decomposition temperature, conductance and IR studies have indicated that the products obtained by both the procedures are almost identical. Thus,

1. No depression in decomposition temperatures has been noted when the products obtained by different methods have been mixed together.

2. IR spectra of the products obtained by either method were same.

(a) *Simultaneous addition procedure for the preparation of ternary complex:* 0.005 mole of NiCl<sub>2</sub>·6H<sub>2</sub>O dissolved in ethanol was added to a solution containing 0.01 mole of APBI and 0.005 mole of secondary ligand dissolved in ethanol and the contents were refluxed for about 3 h. The complex separated out was filtered and washed with ethanol and dried under *vacuo*.

(b) *Stepwise addition procedure for the preparation of ternary complex:* 0.01 mole of APBI was added to 0.005 mole of ML<sub>2</sub> or 0.005 mole of NiCl<sub>2</sub>(APBI)<sub>2</sub> was added to 0.005 mole of ligand in ethanol and refluxed for about 3 h. The complex separated was filtered and washed with ethanol and dried under *vacuo*.

## RESULTS AND DISCUSSION

The analytical data of the complexes are given in Table-1. The complexes are solids and are soluble in DMSO and DMF. The low value of molar conductance (10–20 ohm<sup>-1</sup> cm<sup>2</sup> mole<sup>-1</sup>) in DMF at room temperature show them to be non-electrolytes in nature.

The infrared spectrum of 2-(2'-aminophenyl) benzimidazole shows two bands, one at 3410 cm<sup>-1</sup> and another split band at 3140 and 3040 cm<sup>-1</sup>. The former has been assigned to N—H of —NH<sub>2</sub> of the phenyl ring and the latter to the ν(NH)

of the benzimidazole ring. A shoulder at  $1620\text{ cm}^{-1}$  has been assigned to  $\text{C}=\text{N}$  of benzimidazole ring. The band at  $1665\text{ cm}^{-1}$  may be assigned to  $-\text{NH}_2$  in-plane bending mode. The O-substituted phenyl group shows ring vibrations at  $1485$  and  $745\text{ cm}^{-1}$ . A band at  $1040\text{ cm}^{-1}$  may be assigned to  $\text{C}-\text{N}$  of aminophenyl ring<sup>7</sup> and another at  $855\text{ cm}^{-1}$  to the  $-\text{NH}_2$  out-of-plane bending vibrations. The other bands in the spectrum due to benzimidazole moiety appear more or less at the same positions as reported in literature<sup>7</sup>.

The infrared spectra of the metal benzimidazole complex are similar to the benzimidazole ligand spectrum except for slight shifts in their positions and changes in their intensities due to coordination. In case of the IR spectra of binary complex of glycinate, a correlation with free ligand reveals that the coordination of the ligand to the metal ion leads to the following changes: Bands due to  $\delta_d(\text{NH}_3^+)$ ,  $\delta(\text{NH}_3^+)$ ,  $\rho_s(\text{NH}_3^+)$ ,  $\rho_t(\text{NH}_3^+)$  disappear. New bands corresponding to  $\delta\text{NH}_2$ ,  $\rho_t(\text{NH}_2)$ ,  $\rho_w(\text{NH}_2)$ ,  $\rho_r(\text{NH}_2)$ ,  $\nu(\text{Ni}-\text{O})$  and  $\nu(\text{Ni}-\text{N})$  appear.  $\nu_{\text{asym}}(\text{COO})$  increases.  $\nu_{\text{sym}}(\text{COO})$  decreases.

All the above changes suggest that the amino acid (gly) coordinates to the metal ion as bidentate chelating agent through the nitrogen and oxygen atoms.

The IR spectra of other ligands and their binary metal complexes are observed at the same region as reported in literature<sup>9,10</sup>.

IR spectra of ternary complexes are non-superimposable with those of binary complexes and thus it is assumed that the new compound formed is a ternary metal complex. Further confirmation of a ternary complex formation is by the fact that its IR spectrum reveals the presence of the bands corresponding to the characteristic vibrations of both the ligand moieties, *i.e.*, 2,2'-aminophenyl benzimidazole and secondary ligand. It is not unusual to expect the bands characteristic of the component ligands in the IR spectrum of the corresponding ternary metal complex. Thus, the general features of IR spectrum of ternary metal complex will be an overlap of the spectra of two ligands. Because of strong coupling between each other, assignment of the observed bands to a specific  $\nu(\text{Ni}-\text{O})$ ,  $\nu(\text{Ni}-\text{N})$  and  $\nu(\text{Ni}-\text{Cl})$  vibration mode is not possible. In the present studies IR active  $\nu(\text{Ni}-\text{N})$  and  $\nu(\text{Ni}-\text{O})$  bands in the far IR spectra are observed at  $445$ ,  $410$ ,  $293\text{ cm}^{-1}$  which are similar to those reported in literature<sup>11,12</sup> (Table-2).

TABLE-2  
KEY IR SPECTRAL DATA ( $\text{cm}^{-1}$ ) OF LIGANDS AND COMPLEXES

	$\nu_{\text{asym}}(\text{NH})$	$\nu(\text{NH})$	$\nu_{\text{asym}}(\text{NH}_2)$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$
APBI	3140 3040	1420	3410	-	1620	1595
$\text{NiCl}_2(\text{APBI})_2$	3128	1418	3385	-	1600	1500
$\text{NiCl}(\text{APBI})(\text{Gly})(\text{H}_2\text{O})_2$	3102	1410	3380	-	1610	1510
$\text{Ni}(\text{APBI})(\text{Ox})(\text{H}_2\text{O})_3$	3108	1406	3378	-	1600	1511
$\text{Ni}(\text{APBI})(\text{O Form})_2(\text{H}_2\text{O})_3$	3110	1408	3382	-	1609	1510
$\text{Ni}(\text{APBI})(\text{OC}_6\text{H}_5)_2(\text{H}_2\text{O})_3$	3120	1405	3380	-	1610	1508

$^1\text{H}$  NMR spectra of all the ligands and complexes recorded in  $d_6$ -DMSO solvent: The chemical shifts ( $\delta$ ) are given in ppm downfield from TMS. In  $^1\text{H}$  NMR spectra of 2-(2'-aminophenyl) benzimidazole the  $-\text{NH}_2$  protons of the phenyl ring appeared at  $\delta 5.2$  ppm. The slight downfield shift in the position of the amino proton of the ligand molecule is further indicative of inter- and intra-molecular hydrogen bonding. In binary and ternary complexes proton signals are due to  $-\text{NH}_2$  protons of the ligand shifted slightly downfield indicating the deshielding and coordination of  $-\text{NH}_2$  group to the metal. Similarly a downfield shift is also seen in the resonating signals of aromatic protons in the region  $\delta 6.9$ – $7.8$  ppm. The shift of  $\delta 0.1$ – $0.3$  ppm in the  $^1\text{H}$  NMR spectra of complex is due to coordination. On the basis of analytical data, IR, NMR, the geometry observed for the binary complex and ternary complex is octahedral.

**Antifungal Studies:** The antifungal activities of the ligands and their corresponding binary and ternary metal complexes have been evaluated by testing these against *Alternaria alternata* and *Aspergillus niger* at different concentrations. The results of fungicidal screening are recorded in Table-3. The ligand APBI is moderately active against *Alternaria alternata*, the fungicidal activity increases as the concentrate increases. The metal salt has negligible activity but on complexation it is found to be active. The enhanced biocidal activity of complexes is in accordance with the literature<sup>13</sup>.

TABLE-3  
FUNGICIDAL SCREENING DATA

Compound	Average % inhibition of spore germination after 72 h.					
	<i>Alternaria alternata</i> (Conc. in ppm)			<i>Aspergillus niger</i> (Conc. in ppm)		
	100	500	1000	100	500	1000
ABPI	28	39	58	22	35	52
$\text{NiCl}_2(\text{APBI})_2$	33	45	62	31	40	60
$\text{NiCl}(\text{APBI})(\text{Gly})(\text{H}_2\text{O})_2$	39	51	72	38	47	67
$\text{Ni}(\text{APBI})(\text{Ox})(\text{H}_2\text{O})_2$	38	50	71	36	45	64
$\text{Ni}(\text{APBI})(\text{OForm})_2(\text{H}_2\text{O})_3$	37	49	70	35	44	63
$\text{Ni}(\text{APBI})(\text{OC}_6\text{H}_5)_2(\text{H}_2\text{O})_3$	40	52	63	39	48	67

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