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Cobalt(II) and Coper(II) Complexes of 1-NitrobenzyI-2-Nitrophenylbenzimidazole: Synthesis, Characterization and Antibacterial Activity Studies

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COBALT(II) AND COPPER(II) COMPLEXES OF 1-NITROBENZYL-2-NITROPHENYLBENZIMIDAZOLE: SYNTHESIS, CHARACTERIZATION

AND ANTIBACTERIAL ACTIVITY STUDIES

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ABSTRACT

Complexes of $Co(\Pi)$ and Cu(II) with the ligand 1-nitrobenzyl-2-nitrophenylbenzimidazole (NBPBI) have been synthesized. These complexes were characterized using various physico-chemical techniques like elemental analyses. conductance, magnetic susceptibility measurements, UV-visible, near-IR, IR, cyclic voltammetry, EPR, and thermal studies. The analytical data show that the cobalt complexes have the general formula, $[CoL_2X_2]$, (where, L = NBPBI and X = Cl, Br, or I) and

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the copper complexes $[CuL_2X_2]$ (where, L = NBPBI and X = Cl or Br). These studies suggest a tetrahedral structure for the the $cobalt(\Pi)$ complexes and a square planar geometry for copper(II) complexes. Cyclic voltammetric studies of the [CuL₂Cl₂] complex indicate that the redox reaction is irreversible and the reaction involves one electron transfer. The 'g ' values obtained from the EPR spectra of the copper(II) complexes suggest square planar geometry for these complexes. TG traces of the complexes show three stages of decomposition for the [CoL₂Cl₂] complex and two stages for the copper(II) complexes. The end products in all the cases were found to be metal oxides. The antibacterial activity of these complexes negative bacteria, Escherichia coli, against gram Vibrio costicola and Psuedomonas fluorescence, and gram positive Bacillus polymyxa, and Streptoverticillium sp., has also been studied.

INTRODUCTION

Complexes of benzimidazoles have attracted considerable attention in recent years. Benzimidazole derivatives were reported to hold antibacterial, antifungal, antiviral, anticancer, antiinflammatory, analgesic, antipyretic, antihelmentic, germicidal and immuno-chemical activities. Complex compounds of transition metal ions with imidazole,

benzimidazole and substituted compounds of these ligands have been studied extensively 1^{-5} . Recently, many low-molecular weight complexes of Cu(II) containing imidazole ligands have been proteins 6-8. proposed models of active site of Cu as Incorporation of a nitro group in the azole compounds contribute to their antiamoebic activity⁹. Some of the Co(II) and Cu(II)complexes, reported earlier, were shown to have better catalytic activity. particularly towards oxidation reactions of substituted phenols. Furthermore, copper(II) complexes are found to have herbicidal and growth regulating activity¹⁰. This, in fact, has created an interest in synthesising new complexes of Co(II) and Cu(II) with a derivative of benzimidazole. This derivative, 1-nitrobenzyl-2-nitrophenylbenzimidazole (NBPBI) is interesting from the structural point of view because of its bulky nature and steric effects.

As part a of our studies on metal complexes of benzimidazoles¹¹⁻¹⁵, we synthesized have cobalt(II)and copper(II) complexes of NBPBI. In this paper, we report the synthesis, characterization, and antibacterial activity studies of NBPBI complexes of cobalt(II) and copper(II).

RESULTS AND DISCUSSION

The complex formation reaction of the ligand, NBPBI, with cobalt(II) or copper(II) halides can be represented by the following equations.

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 CoX_2 + 2NBPBI \longrightarrow [Co(NBPBI)₂X₂] (1) (where, X = Cl, Br, or I)

 $CuX_2 + 2NBPBI \longrightarrow [Cu(NBPBI)_2X_2]$ (2) (where, X = Cl or Br)

All the complexes are crystalline, non-hygroscopic and stable to aerial oxidation. They are soluble in acetone, DMF and dioxane, and slightly soluble in dichloromethane and acetic acid, and insoluble in ether and ethanol. The analytical and molar conductance data of the complexes are presented in Table I. The analytical data show that the cobalt complexes have the general formula $[CoL_2X_2]$ (where, L = NBPBI and X = Cl, Br, or I) and for the copper complexes, the formula is $[CuL_2X_2]$, (where, X = Cl or Br). Molar conductance values of the complexes suggest that all complexes are non-electrolytes in acetone.

Infrared Spectra

IR spectrum of the free ligand, NBPBI, shows an intense band at 1475 cm⁻¹ which may be attributed to the ν (C=N) stretching vibration. This frequency is lowered in all the complexes, which indicates the participation of N-3 atom of NBPBI to the metal atom. Strong characteristic bands due to the nitro group in aromatic compounds are observed at 1522 cm⁻¹ and 1350 cm⁻¹ in the spectrum of the ligand. In the complexes, these bands appear at the same frequency which suggests the Downloaded by [Purdue University] at 09:43 18 January 2015

TABLE I Physical and Analytical Data

Substance	Formula	Color	Yield	M.P.		[(%)	Found (Calco	(F		Molar
	weight (Calcd)		(%)	(°C)				,		Conductance ohm ⁻¹ cm ²
					C	H	z	W	×	10111
[CoL ₂ Cl ₂]		Blue	60-70	3204	54.70	3.27	13.00	6.90	7.81	18.5
[CoC40H28N8O8Cl2]	877.83				(54.68)	(3.19)	(12.76)	(6.71)	(8.08)	
[CoL ₂ Br ₂]		Greenish	80-90	280 ^d	51.42	3.02	12.12	6.23	16.74	27.2
[CoC40H28N808Br2]	966.73	blue			(49.65)	(2.89)	(11.58)	(60.9)	(16.53)	
[CoL12]		Green	60-70	280 ^d	46.65	2.89	11.08	5.09	23.53	79.2
[CoC40H28N808I2]	1060.73				(45.25)	(2.64)	(10.55)	(5.55)	(23.93)	
[CuL ₂ Cl ₂]		Greenish	80-85	280 ^d	53.75	3.10	12.51	7.67	8.34	12.5
[CuC ₄₀ H ₂₈ N ₈ O ₈ Cl ₂]	882.44	grey			(54.39)	(3.17)	(12.69)	(7.20)	(8.03)	
[CuL ₂ Br ₂]		Greenish	80-85	280 ^d	49.60	2.94	11.49	6.26.	16.79	28.4
[CuC _{to} H ₂₈ N ₈ O ₈ Br ₂]	971.34	yellow			(49.41)	(2.88)	(11.53)	(6.54)	(16.45)	
Ligand, L (NBPBI)		Yellow	45-50	139	62.88	3.86	15.45		ŀ	•
[C ₂₀ H ₁ ,N ₄ O ₄]	374.00				(64.17)	(3.74)	(14.97)			

d - decomposition temperature



Fig. 1. Structure of NBPBI

non-participation of the NO₂ group in coordination to the metal atom. In addition, all compounds show a C-N stretching vibration near 870 cm⁻¹.

Electronic Spectra

Electronic spectral data along with magnetic moments of all the complexes are shown in Table II.

All the cobalt(II) complexes exhibit two absorption bands in the region 17500-13450 cm⁻¹ which may be assigned to the ${}^{4}A_{2}$ \longrightarrow ${}^{4}T_{1}(P)$ electronic transition. An additional band observed in this region (Table II) may be due to spin-orbit coupling of the T state. The band observed in the near-IR region 7200-6900 cm⁻¹ may be attributed to the ${}^{4}A_{2} \longrightarrow {}^{4}T_{1}(F)$ transition¹³.

Substance	Absorption Maxima (cm ⁻¹)	Tentative assignments	Magnetic moment (B.M.)
{Co(NBPBI) ₂ Cl ₂]	17094	${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$	4.40
	15480		
	7050	${}^{4}A_{2} \longrightarrow {}^{4}T_{1}(F)$	
[Co(NBPBI)2Br2]	16920	${}^{4}A_{2} \longrightarrow {}^{4}T_{1}(P)$	4.20
	15850		
	14990	A A	
	6980	$A_2 \longrightarrow T_1(F)$	
{Co(NBPBI) ₂ I ₂ } 1620 1428	98, 15082 36, 13458	$^{4}A_{2} \longrightarrow ^{4}T_{1}(P)$	4.54
	6900	${}^{4}A_{2} \longrightarrow {}^{4}T_{1}(F)$	
[Cu(NBPBI) ₂ Cl ₂]	24390	$^{2}B_{1\sigma} \longrightarrow ^{2}E_{\sigma}$	2.01
	21320	<u> </u>	
[Cu(NBPBI) ₂ Br ₂]	24096	$^{2}B_{1g} \longrightarrow ^{2}E_{g}$	2.00
	15244	$^{2}B_{1g} \longrightarrow ^{2}B_{2g}$	

Electronic Spectral and Magnetic Data

The $[CuL_2Cl_2]$ complex shows broad bands in the region 24400-20000 cm⁻¹ which may be due to the ${}^2B_{1g} \longrightarrow {}^2E_{g}$ transition. $[CuL_2Br_2]$, on the other hand, exhibits two bands around 15000 cm⁻¹ and 24000 cm⁻¹ and these may be due to

 ${}^{2}B_{1g} \longrightarrow {}^{2}E_{g}$ and ${}^{2}B_{1g} \longrightarrow {}^{2}B_{2g}$ transitions, respectively. The transitions observed in this region are characteristic of square planar copper(II) complexes¹⁶. Further, all the complexes exhibit strong bands in the range 46300-29000 cm⁻¹ which may be assigned to intra-ligand transitions.

EPR Studies

The polycrystalline EPR spectra of the copper(II) complexes have been recorded at room temperature. The 'g' values were calculated using Kneubuhl's procedure¹⁷. Two 'g' values were observed for both the chloro and the bromo complexes ($g_{11} =$ 2.09; $g_{\perp} = 2.02$). The higher value for g suggests a square planar geometry for the complexes¹⁸. Further, the values are less than 2.3, which indicates covalent character of the metal-ligand bond¹⁹.

Magnetic Susceptibility Measurements

The room temperature magnetic moments of the cobalt complexes are in the range 4.1 to 4.6 B.M. (Table II) which suggest a tetrahedral geometry for these complexes. Magnetic moment values around 2.0 B.M. for the copper complexes suggest square planar structures for these complexes¹⁶.



Fig. 2. Cyclic Voltammetry of [CuL₂Cl₂] Complex

Cyclic Voltammetry of $[CuL_2Cl_2]$ Complex

The cyclic voltammetry of the $\{CuL_2Cl_2\}$ complex is shown in Fig. 2. The cyclic voltammetry of this complex (scan rate = 50 mV/s) features the reduction of Cu(II) to Cu(I) at a cathodic peak potential of -0.1540 V. Reoxidation of Cu(I) occurs upon scan reversal at 0.0500 V. The separation between the anodic peak potential (Epa) and cathodic peak potential (Epc), ΔEp = 204 mV, indicates an irreversible, one electron redox process. The formal potential $E_{1/2}$ taken as the average of Epa and Epc is -0.0520 V.

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Thermal Studies

The TG curve for the cobalt complex $[CoL_2Cl_2]$ exhibits three decomposition stages in the temperature ranges 320-460°C, 500-640°C and 700-1040°C, respectively. In the case of the Cu(II) complexes only two stages of decomposition are seen and the decomposition temperature ranges are 280-420°C and 500-950°C. In all cases, the end products, after complete decomposition of the complexes, was found to be the metal oxide, CoO and Cu₂O, respectively.

Suggested Structure

Based on the elemental analyses and various physico-chemical studies, the structures shown in Fig. 3 are tentatively proposed for the complexes.

Antibacterial Activity Studies

The prepared complexes were tested for their antibacterial activity against gram negative bacteria *Escherichia coli*, *Vibrio costicola*, and *Psuedomonas fluorescence*; gram positive *Bacillus polymyxa*, and *Streptoverticillium sp.* All complexes showed inhibition of growth of all the strains, along with an increase in concentration from 100 μ g/mL to 500 μ g/mL in a linear fashion



Fig. 3. Proposed Structure of the Complexes

(Table III). Maximal inhibition of growth was observed at 500 μ g/mL concentration. The percentage of growth inhibition varied between 88-91% for *E. coli*, 89-93% for *B. polymyxa*, 93-96% for *V. costicola*, 85-89% for *P. fluorescence* and 55-71% for *Streptoverticillium sp.* for all complexes, $[CoL_2Cl_2]$, $[CoL_2Br_2]$, $[CoL_2I_2]$, $[CuL_2Cl_2]$, and $[CuL_2Br_2]$. Interestingly, $[CoL_2Cl_2]$ and $[CoL_2I_2]$, were observed to effect inhibition of the growth around 50% of *P. fluorescence*. Among the strains, *V. costicola* was more sensitive and *Streptoverticillium sp.* relatively less sensitive to the complexes tested. Unlike other strains, *B. polymyxa* was sensitive to the complexes tested only when the

			Percent	ade inhibition	of growth	
Substance	Сопс. ру/ш	E. coli	B. polymyxa	V. costicola	P. fluorescence	Streptoverticillium sp.
[CoL ₂ C1 ₂]	100	7.00	8.00	0.20	24.00	5.00
	300	54.00	23.00	68.00	41.00	29.00
	500	88.00	89.00	93.00	43.00	65.00
[CoL _Z Br ₂]	100	8.00	13.00	0.80	16.00	48.00
	300	53.00	20.00	55.00	47.00	55.00
	500	91.00	93.00	95.00	89.00	66.00
[CoL ₂ I ₂]	100	16.00	9.00	3.00	24.00	46.00
	300	51.00	25.00	56.00	45.00	48.00
	500	91.00	93.00	96.00	48.00	55.00
[CuL ₂ C1 ₂]	100	1.00	5.00	+2.00	18.00	8.00
	300	48.00	19.00	55.00	42.00	47.00
	500	89.00	91.00	94.00	85.00	66.00
[CuL ₂ Br ₂]	100	4.00	6.00	+0.70	31.00	8.00
	300	51.00	22.00	52.00	04.00	29.00
	500	88.00	90.00	93.00	91.00	71.00
L, Ligand (NBPBI)	100 300 500	+6.00 +3.00 1.00	+3.00 +5.00 +7.00	+1.00 +4.00 +6.00	12.00 19.00 22.00	8.00 42.00 43.00
DMF was used as a	control	and showed ni	l activity again	ist the above m	icroorganisms	

TABLE III

Antibacterial Activity of Co(II) and Cu(II) Complexes with NBPBI

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concentration was 500 μ g/mL. The percentage inhibition observed with this strain at 300 μ g/mL was very low (19-25%) compared to other strains, which showed inhibition around 50%. An increase in the concentration from 300 μ g/mL to 500 μ g/mL, did not show any significant effect on *Streptoverticillium sp.*, unlike in others.

The antibacterial activity of the ligand was also studied. The ligand did not show any significant effect on *E. coli*, *V. costicola*, and *B. polymyxa*. However, *P. fluorescence* and *Streptoverticillium sp.* inhibited growth at 42-43% and 19-22%, respectively, at 500 μ g/mL.

EXPERIMENTAL

Materials

m-Nitrobenzaldehyde, σ -phenylenediamine, and other chemicals used were of Analar grade purity. Solvents were purified by standard procedures²⁰. cobalt(II) bromide and copper(II) bromide salts were prepared from cobaltous carbonate and cupric carbonate (Riedel Chemicals), respectively, by reacting these carbonates with HBr. Cobalt(II) iodide was obtained in a similar way using cobaltous carbonate with HI. Cobalt(II) chloride (Merck), and copper(II) chloride (BDH) salts were used as received.

Synthesis of the Ligand

The ligand, NBPBI was prepared according to the procedure reported in the literature 21 .

Synthesis of the Complexes

 $[CoL_2Cl_2]$. A hot ligand solution of NBPBI (3.74 g, 10 mmol dissolved in 75 mL ethanol) was added to a cobalt(II) chloride hexahydrate (1.18 g, 5 mmol dissolved in 5 mL ethanol) and the resulting green colored solution was refluxed for about 3 h over a water bath. The blue crystals obtained during reflux were filtered, washed with hot ethanol and chloroform and dried *in vacuo* over anhydrous CaCl₂. Yield: 2.9 g (68%)

 $[CoL_2Br_2]$ and $[CoL_2I_2]$. A solution containing cobalt(II) bromide (1.09 g, 5 mmol) or cobalt(II) iodide (1.56 g, 5 mmol) and NBPBI (3.74 g, 10 mmol) in acetone (20 mL) was refluxed for about 2 h. Then the volume of the solution was reduced to half and the greenish blue crystals formed on cooling were collected, washed with chloroform and dried *in vacuo* over anhydrous CaCl₂. Yield: 4.1 g (86%) for $[CoL_2Br_2]$ and 3.5 g (67%) for $[CoL_2I_2]$

 $\frac{[CuL_2Cl_2]}{(3.74 \text{ g}, 10 \text{ mmol in } 75 \text{ mL}}$ ethanolic solution of the ligand

solution of copper(II) chloride dihydrate (0.85 g, 5 mmol) or copper(II) bromide (1.12 g, 5 mmol in 5 mL ethanol) and the resulting solution was refluxed for about 1 h. The complexes were formed during refluxion. The greenish grey crystals obtained in the case of the chloro complex of copper(II) and the greenish yellow ones in the case of the bromo complex were filtered, washed with hot ethanol and chloroform, and dried *in vacuo* over anhydrous CaCl₂. Yield: 3.6 g (83%) for $[CuL_2Cl_2]$ and 4.0 g (83%) for $[CuL_2Br_2]$

Antibacterial Activity Studies

The antibacterial efficiency of the prepared complexes was tested against bacteria available in the culture collection of the Centre for Biotechnology, Cochin University of Science and Technology. Strains tested were Escherichia coli (CBT GS 109), Vibrio costicola (ACMR 267) and Psuedomonas fluorescence (ACMR 171), Bacillus polymyxa (CBT B 25) and Streptoverticillium sp. (CBT SA 133). B. polymyxa, V. costicola, P. fluorescence were grown in a nutrient broth, E. coli in a Luria broth and Streptoverticillium sp. in glucose-peptone-yeast extract-beef extract broth. Different concentrations of the complexes (prepared from a stock solution containing 1000 μ g/mL in DMF) were added to 5 mL of the respective media, sterilized and uniformly inoculated with 24 h old cells. The cultures were

incubated at room temperature on a rotary shaker at 150 rpm. Growth was determined by measuring the turbidity at a wave $length^{22}$ of 600 nm using a spectrophotometer after 24 h for the bacteria and 48 h for the *Streptoverticillium sp.*

Analytical Methods

Determinations of Co(II) and Cu(II) and the halogens were carried out using standard procedures²³. Microanalyses for carbon, hydrogen and nitrogen were done on a Heraeus CHN analyzer. Molar conductances of the complexes in acetone were determined by a Digital Conductivity Meter, Century CC 601 model with a dip type smooth platinum electrode. Magnetic susceptibility measurements of the complexes at room temperature were determined by the Gouy method using Hg[Co(SCN)] as calibrant. Electronic spectra of the complexes in acetone were recorded on a Shimadzu UV-160A UV-visible recording spectrophotometer in the wave length region 1100-200 nm. Near-IR spectra of the Co(II) complexes were also recorded with a Hitachi U-3410 spectrophotometer. Infrared spectra of the ligand and the complexes were taken on KBr discs in the region 4600-400 cm⁻¹ using Nujol mulls on a Shimadzu-FTIR 8101 infrared spectrophotometer. The cyclic voltammetry studies of the $[CuL_2Cl_2]$ complex were performed in DMF at 25.0 \pm 0.2°C. Voltammograms were generated with the use of an EG & G PAR model

273 Potentiostat. An IBM PS-2 computer along with EG & G M-270 software was employed to control the experiment and to acquire the data. An EPSON FX-850 Printer (DMP-40) was used to print out the cyclic voltammograms. A three-electrode system consisting of sphere electrode, a platinum plate platinum auxillary а electrode, and a reference electrode Ag(s)/AgNO, was used. Tetra(-n-butyl)ammonium perchlorate (0.1 M) was used as the supporting electrolyte. The experimental solution was deoxygenated by bubbling research grade nitrogen through it and an atmosphere of nitrogen was maintained over the solution during measurement. Polycrystalline EPR spectra were obtained using a Bruker Model ER 200-D EPR spectrophotometer at room temperature. Thermal studies were carried out with a Shimadzu TGA-50 thermogravimetric analyser at a heating rate of 20°C \min^{-1} in an air atmosphere using a platinum crucible in the temperature range between room temperature and 1050⁰C. The mass of the samples used was in the range 5-12 mg. The antibacterial activity of the complexes was tested by measuring the turbidity at 600 nm using a Shimadzu UV-160A UV-visible recording spectrophotometer.

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