SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY
Vol. 33, No. 3, pp. 387–401, 2003

Metal Thiocyanato Complexes: Synthesis, Magnetic, and Spectral Studies of Some Mixed-Ligand Thiocyanato Complexes of Nickel(II) Involving Benzothiazole and Benzimidazole Derivatives

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ABSTRACT

A new series of mixed-ligand thiocyanato complexes of nickel(II) of the compositions $[Ni(NCS)_2(L)_4]$, where L = 2-mercaptobenzothiazole (2-MBZT), 2-(2′-hydroxyphenyl)-benzothiazole (2′-HPBZT), 2-(2′-tolyl)-benzothiazole (2′-TOBZT), 2-(3′-tolyl)benzothiazole (3′-TOBZT), $[Ni(NCS)_2(2\text{-AMBZT})_2]$ and $[Ni(NCS)_2(BBZLY)(H_2O)_2]$, where 2-AMBZT = 2-aminobenzothiazole and BBZLPY = 2,6-bis(benzimidazole-2′-yl)pyridine, has been synthesized by the interaction of nickel(II) thiocyanate with the respective ligands. The compounds so obtained were characterized by analytical data, molar conductances, magnetic

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DOI: 10.1081/SIM-120019992
0094-5714 (Print); 1532-2440 (Online)
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270 Madison Avenue, New York, New York 10016

measurements, infrared and electronic spectral studies. Suitable octahedral structures have been suggested for these complexes.

INTRODUCTION

In continuation of our interest to synthesize and characterize mixed-ligand thiocyanato[1−3] complexes of bipositive metal ions involving heterocyclic ligands, our studies have been extended so as to observe the ligational behaviour at some benzothiazole and benzimidazole derivatives towards nickel(II) thiocyanate.

Benzothiazole derivatives have been reported to be of medicinal importance as local anaesthestics.[4] 2-(2′-Pyridyl)benzothiazole and other benzothiazoles have been investigated as fungicidal agents.[5] The ligational behaviour of benzothiazole and its derivatives have been reported earlier from our coordination chemistry laboratory[4,6−8] by Maurya et al. and also by others.[9,10] Benzimidazole and its derivatives have been shown to possess antibacterial and antimalarial activities.[11−14] The benzimidazole moiety is reported to be toxic to fungi. A large number of benzimidazole derivatives[15] has been synthesized and patented as fungicides.

Methyl-1-butyl carbamoyl-2-benzimidazole carbonate is a novel fungicide which has been used successfully to control Losse smut (a type of plant disease caused by fungi, and characterized by the production of masses of usually black spores within host) on wheat and barley.[16]

The thiocyanate group may coordinate to the metal through either the nitrogen or the sulfur atoms or both. IR spectra have been used frequently to indicate the bonding of the thiocyanate group to the metal ions.[17,18] The thiocyanate ion should have three fundamental IR absorption frequencies: 1) a strong band due to the C–N stretch, 2) a weak C–S stretch, and 3) a weak NCS bending. In the recent past, there has been continuing interest in the synthesis and spectral studies of some mixed-ligand thiocyanato complexes.[19−27] Maurya et al.[1] recently have reported the synthesis and characterization of some mixed-ligand thiocyanato complexes of cadmium(II), mercury(II) and zinc(II) with 2- or 3-pyrazoline-5-one derivatives, viz., 3-methyl-1-phenyl-2-pyrazoline-5-one, 2,3-dimethyl-4-methylaminomethanesulfonate sodium monohydrate-1-phenyl-3-pyrazoline-5-one and 4-amino-2,3-dimethyl-1-phenyl-3-pyrazoline-5-one. However, there is no report on the synthesis and characterization of mixed-ligand derivatives of nickel(II) thiocyanate with benzothiazole and benzimidazole derivatives, viz., 2-aminobenzothiazole (2-AMBZT), 2-mercaptobenzothiazole (2-MBZT), 2-(2′-hydroxyphenyl)-benzothiazole (2′HPBZT), 2-(2′tolyl)benzothiazole (2′-TOBZT), 2-(3′-tolyl)benzothiazole (3′-TOBZT) and 2,6-bis(benzimidazole-2′-yl)pyridine (BBZLPY). As the biological activity is often augmented when the ligand forms complexes, the resulting mixed-ligand complexes may be of potential biological importance. The structures of these ligands are shown in Figure 1.

EXPERIMENTAL

Materials

Nickel(II) chloride hexahydrate (B. D. H. Chemicals, Bombay), potassium thiocyanate (E. Merck, Germany), 2-aminobenzothiazole (Sisco-Chem. Industries, Bombay), 2-mercaptobenzothiazole (Aldrich Chemical Company, U. S. A.), salicylamide (E. Merck, India), *o*-toluic acid and *m*-toluic acid (Sisco-Chem Industries, Bombay) were used as supplied. Nickel(II) thiocyanate was prepared by the method of Maurya et al.[1] as reported elsewhere. All other chemicals used were of A.R. grade.

Synthesis of HPBZT, 2′-TOBZT and 2′-TOBZT

The benzothiazole derivatives were prepared by the reported method of condensation of *o*-aminothiophenol with *o*-toluic acid for 2′-TOBZT or with *m*-toluic acid for 3′-TOBZT in the presence of a sufficient quantity of polyphosphoric acid to give a suitable paste.[28] The mixture was heated slowly to 250 °C on an oil bath and the resulting solution was stirred at 250 ± 5 °C for 4–5 h, permitted to cool to about 100 °C, and then poured in a thin stream into a large volume of rapidly stirred water. The resulting solid was collected by filtration, washed with a small amount at water and reslurried in an excess at 10% sodium carbonate solution. The alkaline slurry was filtered and the product washed thoroughly with water and dried at 60 °C. The crude product was recrystallized from ethyl alcohol or an aqueous-alcohol mixture (1:1), subsequent to treatment with a small amount of activated charcoal. The purity of these compounds was checked by their literature melting points.[28] Synthesis of the benzothiazole derivatives occured as shown in the reaction scheme 1a in Figure 2.

Synthesis of 2,6-Bis(benzimidazole-2′-yl)pyridine

It was prepared by the interaction of pyridine-2,6-dicarboxylic acid and *o*-phenylenediamine as reported elsewhere.[29] The synthesis is shown in the reaction scheme 1b Figure 2.

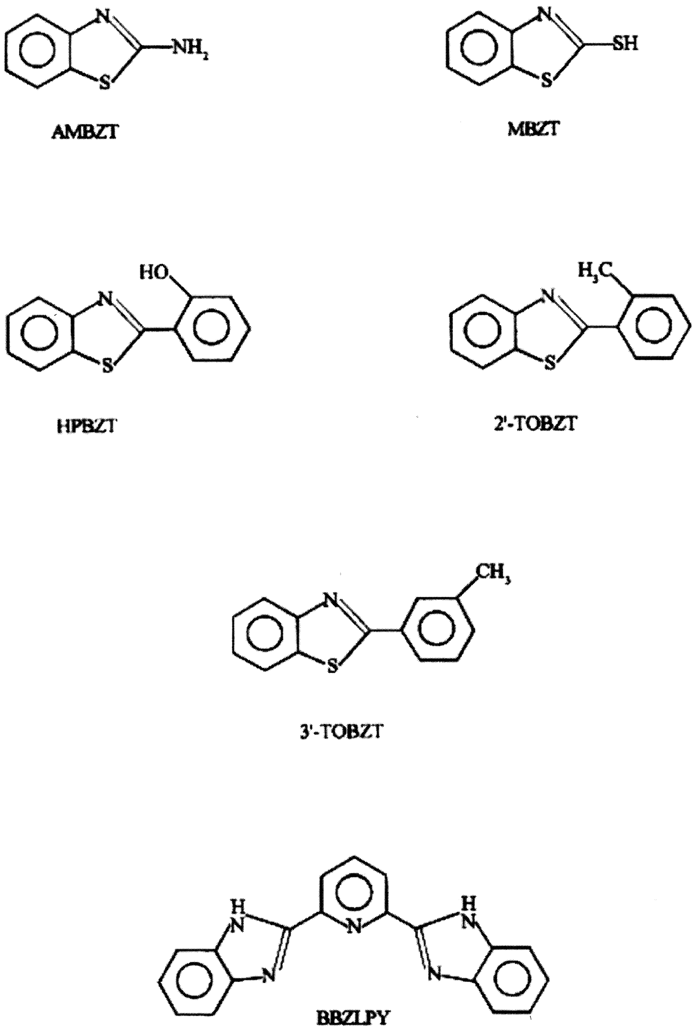
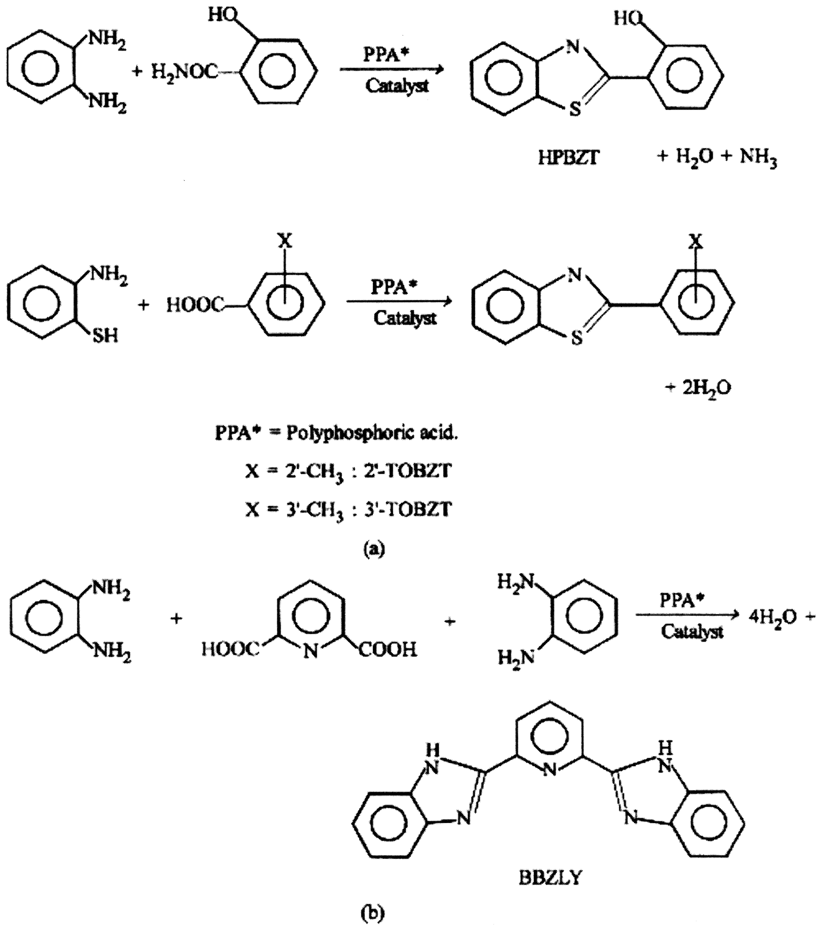


Figure 1. Ligand structures.

Synthesis of the Mixed-Ligand Complexes

A stoichiometric quantity of nickel(II) thiocyanate (0.01 M, 1.75 g) dissolved in ~30 mL of ethanol was added to the solution of the appropriate ligand (0.01 M for BBZLPY, 0.02 M for 2-AMBZT and 0.04 M for 2-MBZT, 2′-HPBZT, 2′-TOBZT or 3′-TOBZT) dissolved in ethanol (~20 mL). The resulting mixture was refluxed for 4 to 6 h at 80 °C over a hotplate. During this



PPA* = Polyphosphoric acid.
X = 2'-CH_3 : 2'-TOBZT
X = 3'-CH_3 : 3'-TOBZT

Figure 2. Reaction scheme for the preparation of the ligands.

time coloured solids separated out. They were filtered by suction, washed several times with ethanol and dried in vacuo. The analytical data are given in Table 1.

Analysis

For the determination of nickel, a weighed amount (~150 mg) of the mixed-ligand complex was decomposed by digestion with perchloric acid and nitric acid, until the resulting residue gave a transparent solution in dilute HCl. Nickel was determined as nickel dimethylglyoximate by

Table 1. Elemental analysis and some physical properties of the synthesized complexes.

Sr.	Complex	Found (calc.), %						Decom.	Yield
no	(empirical formula)(mol. wt.)	C	H	N	S	Ni	Color	temp. (°C)	(%)
(**1**)	[Ni(NCS)$_2$(2-AMBZT)$_2$]	40.12	2.67	17.98	26.45	12.10	grey	254	40
	($C_{16}H_{12}N_6NiS_4$) (474.69)	(40.44)	(2.52)	(17.69)	(26.96)	(12.36)			
(**2**)	[Ni(NCS)$_2$(2-AMBZT)$_4$]	40.29	2.54	9.71	37.49	6.54	grey	248	35
	($C_{30}H_{20}N_6NiS_6$) (842.69)	(40.70)	(2.37)	(9.97)	(37.97)	(6.96)			
(**3**)	[Ni(NCS)$_2$(2′-HPBZT)$_4$]	59.42	3.54	7.98	17.62	5.87	grey	225	45
	($C_{54}H_{36}N_6NiO_4S_6$) (1082.69)	(59.85)	(3.32)	(7.76)	(17.73)	(5.42)			
(**4**)	[Ni(NCS)$_2$(2′-TOBZT)$_4$]	64.48	4.27	7.42	17.49	5.72	aquamarine	230	48
	($C_{58}H_{44}N_6NiS_6$) (1074.69)	(64.76)	(4.09)	(7.81)	(17.86)	(5.46)			
(**5**)	[Ni(NCS)$_2$(3′-TOBZT)$_4$]	64.92	4.35	7.48	17.52	5.31	aquamarine	243	45
	($C_{58}H_{44}N_6NiS_6$) (1074.69)	(64.76)	(4.09)	(7.81)	(17.86)	(5.46)			
(**6**)	[Ni(NCS)$_2$(BBZLPY)(H$_2$O)$_2$]	40.78	3.62	18.42	12.58	11.72	light grey	265	70
	($C_{21}H_{17}N_7NiO_2S_2$) (521.69)	(40.30)	(3.25)	(18.78)	(12.26)	(12.24)			

precipitation with a 2% ethanolic solution of dimethylglyoxime in the presence of ammonia.[30] C, H and N were determined microanalytically.

Physical Methods

The solid state infrared spectra was recorded in Nujol on a Perkin Elmer model 1620 FT-IR spectrophotometer at the National Chemical Laboratory, Pune. ESR spectra were recorded on an EPR E-112 spectrometer using powdered samples at the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras. Electronic spectra of the complexes were recorded on a Shimadzu model UV-160 spectrophotometer. Magnetic measurements were performed by Gouy's method using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant at the Central Salt and Marine Chemicals Research Institute, Bhavnagar. Conductance measurements were performed at room temperature in dimethylformamide using a Toshniwal conductivity bridge and dip-type cell with a smooth platinum electrode of cell constant 1.3. Decomposition temperatures of the complexes were determined using an electrothermal apparatus having the capacity to record temperatures up to 360 °C.

RESULTS AND DISCUSSION

The mixed-ligand nickel(II) thiocyanato complexes under investigation were prepared according to the following equations:

$$\mathrm{Ni(NCS)_2 + 2(2\text{-}AMBZT)} \xrightarrow[\text{Reflux}]{\text{Ethanol (90\%)}} \mathrm{[Ni(NCS)_2(2\text{-}AMBZT)_2]} \quad (\mathbf{1})$$

$$\mathrm{Ni(NCS)_2 + 4L} \xrightarrow[\text{Reflux}]{\text{Ethanol (90\%)}} \mathrm{[Ni(NCS)_2(L)_4]}$$

Where L = 2-MBZT (**2**), 2′-HPBZT (**3**), 2′-TOBZT (**4**) or 3′-TOBZT (**5**) and

$$\mathrm{Ni(NCS)_2 + BBZLPY} \xrightarrow[\text{Reflux}]{\text{Ethanol (90\%)}} \mathrm{[Ni(NCS)_2(BBZLPY)(H_2O)_2]} \quad (\mathbf{6})$$

The resulting products are non-hygroscopic, air-stable, coloured solids. The colours, decomposition temperatures and % yields of these complexes are given in Table 1. The compounds were characterized on the basis of the following studies.

Infrared Spectra

The important IR spectral bands and tentative assignments are presented in Table 2. The thiocyanate group is known to be coordinated to the metal ion through either the sulfur atom or the nitrogen atom or both. Nickel(II), being in the 3d-transition series, has been associated with ''Class A'' metals, where the coordination of the thiocyanate group to nickel(II) is of the Ni-NCS type,[18] that is, coordination through the nitrogen atom. The appearance of ν(C−N) and ν(C−S) modes at 2080 to 2115 cm^{-1} and 780 to 812 cm^{-1} indicates that the bonding of the thiocyanate group towards nickel(II) ion is of the Ni−NCS type.[19]

The ligands 2-MBZT, 2′-TOBZT and 3′-TOBZT used in the present study possess two potential donor sites: 1) the benzothiazole nitrogen and 2) the benzothiazole sulfur, while the ligands 2-AMBZT and 2′-HPBZT are potentially tridentate: 1) the benzothiazole nitrogen, 2) the benzothiazole sulphur, and 3) the amino nitrogen in the case of AMBZT or the phenolic oxygen in the case of 2′-HPBZT. The benzimidazole derivative BBZLPY contains five potential donor sites: 1) and 2) the imidazole tertiary nitrogens, 3) and 4) the imidazole NH-nitrogens, and 5) the pyridine ring nitrogen.

The ν(OH) band at 2540 cm^{-1} in the free 2′-HPBZT is unaffected after complexation suggesting that the phenolic OH group is not involved in the bonding. The possibility of amino nitrogen ($-NH_2$) coordination in the ligand 2-AMBZT towards nickel was also examined. The appearance of $\nu_{as}(N-H)$ and $\nu_s(N-H)$ modes of the amino group at 3376 and 3283 cm^{-1}, respectively, in the complex (**1**), suggests coordination of this amino nitrogen towards nickel. It is observed that the CSC band of the ligands 2-AMBZT, 2-MBZT, 2′-HPBZT, 2′TOBZT and 2′-TOBZT occurring at 700–720 cm^{-1} is not affected appreciably in the respective complexes. This indicates that the benzothiazole sulfur is not taking part in the coordination. The appearance of a band at 1620–1640 cm^{-1} assignable to ν(C=N) + ν(C=C) modes indicates the bonding of the benzothiazole tertiary nitrogen[2,8] to nickel in the complexes (**1**)–(**5**).

The NH stretching and bending vibrations of the ligand BBZLPY which occur at 3100 and 1455 cm^{-1}, respectively, remain almost unchanged, suggesting that the NH nitrogen of the imidazole nucleus[30] is not involved in coordination. The ν(C=N) band which occurs at 1635 cm^{-1} in the ligand undergoes a shift to lower energy and then appears at 1608 cm^{-1} after complexation. This suggests the coordination of at least one of the tertiary nitrogens of the benzimidazole moiety. An additional band observed at 1635 cm^{-1} for the uncomplexed ν(C=N) mode (imidazole tertiary nitrogen) indicates that one of the imidazole tertiary nitrogens is reluctant to coordinate in the compound (**6**). The assignment of bands due to ν(C=N) (pyridine

Table 2. Important IR spectral bands (cm^{-1}), molar conductances, and magnetic moments of the synthesized complexes.

Sr. no.	Complex	ν(C−N)	ν(C−S)	ν(C=N) + (C=N)	ν(NH)	Λ_M ($Ohm^{-1}cm^2$-$mole^{-1}$)	μ_{eff} (B.M)
(**1**)	$[Ni(NCS)_2(2\text{-}AMBZT)_2]$	2085 s	795 m	1634 s	3576-3283 br	7.8	3.02
(**2**)	$[Ni(NCS)_2(2\text{-}MBZT)_4]$	2080 s	782 m	1630 s	-	9.9	3.18
(**3**)	$[Ni(NCS)_2(2'\text{-}HPBZT)_4]$	2090 s	795 m	1640 s	-	8.5	3.15
(**4**)	$[Ni(NCS)_2(2'\text{-}TOBZT)_4]$	2095 s	795 m	1620 s	-	11.3	3.27
(**5**)	$[Ni(NCS)_2(3'\text{-}TOBZT)_4]$	2100 s	780 m	1625 s	-	10.9	3.11
(**6**)	$[Ni(NCS)_2(BBZLPY)(H_2O)_2]$	2115 s	812 m	1608, 1640 s	-	12.8	3.16

Table 3. Solubility of the synthesized complexes in different solvents.

Sr. no.	Compound	Acetone	CCl_4	$CHCl_3$	DMF	Ethanol	Methanol	Ethyl acetate
(**1**)	$[Ni(NCS)_2(2\text{-}AMBZT)_2]$	PS	IS	IS	S	IS	PS	IS
(**2**)	$[Ni(NCS)_2(2\text{-}MBZT)_4]$	PS	IS	IS	S	IS	PS	IS
(**3**)	$[Ni(NCS)_2(2'\text{-}HPBZT)_4]$	S	IS	IS	S	PS	PS	IS
(**4**)	$[Ni(NCS)_2(2'\text{-}TOBZT)_4]$	PS	IS	IS	PS	PS	S	IS
(**5**)	$[Ni(NCS)_2(3'\text{-}TOBZT)_4]$	S	IS	IS	S	PS	S	IS
(**6**)	$[Ni(NCS)_2(BBZLPY)H_2]$	PS	IS	IS	S	PS	S	PS

Abbreviation: S = soluble (80–100%); PS = partially soluble (~50%); IS = Insoluble (5–10%). Solubility was tested by taking 100 mg of each compound in 5 mL of the solvent.

moiety) of the ligand and complex is somewhat difficult due to the appearance of this band along with the bands of the tertiary nitrogen of the benzimidazole moiety. However, the appearance of a band at 1044 cm^{-1} due to the ring breathing mode of the pyridine moiety indicates the coordination of the pyridinic nitrogen.[31,32] These observations suggest the bidentate coordination of BBZLPY. This is due to the rigidity and non-planarity of the two benzimidazole moieties. The appearance of a band at 3392 cm^{-1} due to the ν(OH) mode suggests the presence of coordinated water in this complex.

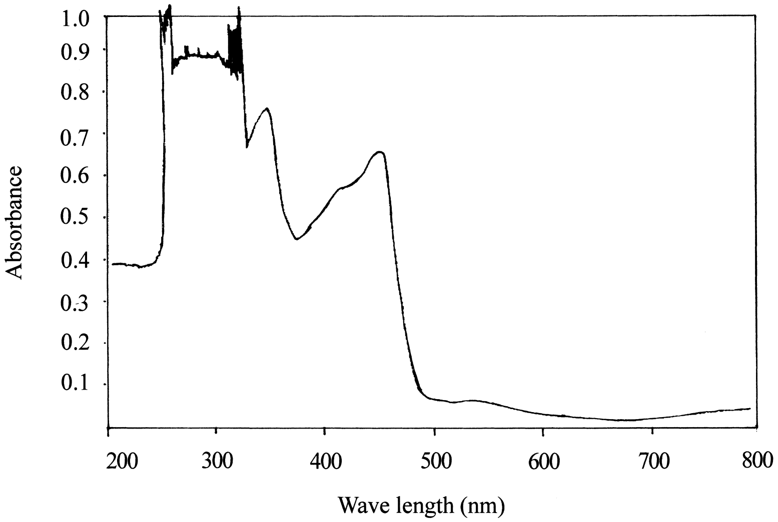
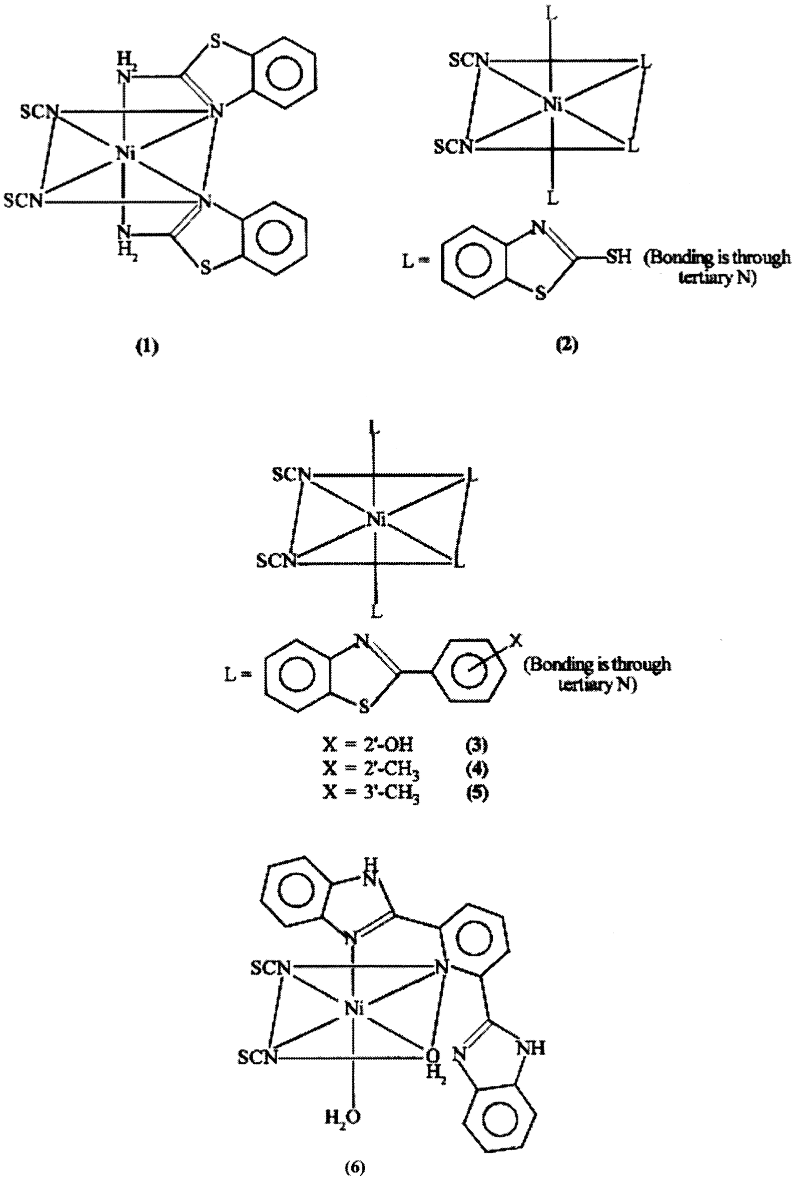


Figure 3. Electronic spectrum of $[Ni(NCS)_2(BBZLPY)(H_2O)_2]$.



(1)

(2)

$X = 2'\text{-}OH$ (3)
$X = 2'\text{-}CH_3$ (4)
$X = 3'\text{-}CH_3$ (5)

(6)

Figure 4. Proposed structures of the complexes.

Conductance Measurements

The molar conductances of all the mixed-ligand complexes in 10^{-3} M DMF are given in Table 2. These values are indicative of the non-electrolytic[33] nature of these complexes (Table 3).

Magnetic Measurements

The observed magnetic moments, 3.02–3.27 B.M. (Table 2), of the complexes under investigation, correspond to two unpaired electron and give no specific information about their stereochemistry.

Electronic Spectra

The electronic spectrum of one representative compound, (**6**), was recorded in 10^{-3} M DMF solution (Figure 3). This compound shows spectral peaks at 368, 418, 525 and 750 nm. The first intense UV band is attributed to ligand → metal charge transfer transition. We are unable to give any explanation for the band shapes of the two high energy signals in the electronic spectrum. The remaining three peaks at 418, 525 and 750 nm may be assigned to the spin-allowed transitions from the ground state level, $^3A_{2g} \rightarrow {}^3T_{1g}$ (P), $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{2g}$, respectively. This is in conformity with the expected d–d transitions for octahedrally coordinated Ni(II) complexes.[34]

CONCLUSIONS

The analytical data and the above physico-chemical studies suggest that the mixed-ligand complexes may be formulated as $[Ni(NCS)_2(L)_4]$, where L = 2-MBZT, 2′-HPBZT, 2′-TOBZT or 3′-TOBZT, $[Ni(NCS)_2(2\text{-}AMBZT)_2]$ and $[Ni(NCS)_2(BBZLPY)(H_2O)_2]$. Suitable octahedral structures are proposed for these complexes as shown in Figure 4.

ACKNOWLEDGMENTS

The authors are thankful to Professor S. D. Tripathi, Vice-chancellor of this University, for encouragement, and Professor K. K. Mishra, Head, Department of Chemistry, for laboratory facilities and helpful discussion. Analytical facilities provided by the Central Drug Research Institute, Lucknow, India, and the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Chennai, India, are gratefully acknowledged.

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Received: August 17, 1998 Referee I: C. M. Hockensmith
Accepted: October 28, 2002 Referee II: J. J Alexander

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