Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry, 35:101–106, 2005

ISSN: 0094-5714 print / 1532-2440 online
DOI: 10.1081/SIM-200035657

Synthesis, Spectroscopy, Cyclic Voltammetry, and Magnetic Studies on Nickel(II) Complexes with N_2S_3 and N_2S_2 Donor Macrocyclic Ligands

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Nickel(II) complexes of the general composition $Ni(L)X_2$ (where $X = Cl$, SCN and $\frac{1}{2}SO_4$) L = 2,3-dipenyl-1,4-diaza-7,10-dithia-5,6 : 11,12-dibenzo[e,k]cyclododeca-1,3-diene[N_2S_2]ane, (L^1) and L = 1,10-diaza-4,7,13-trithia-2,3 : 8,9-dibenzo-[b,h]-cyclo- pentadeca-11,15-dione[N_2S_3]ane (L^2) have been synthesized and characterized by elemental analyses, magnetic moments, IR and electronic spectral studies. The nickel(II) complexes show magnetic moments corresponding to two unpaired electrons except $[Ni(L^1)](NO_3)_2$, which is diamagnetic. Various ligand field parameters have been calculated and discussed. The electrochemical properties for Ni(II)/Ni(I) couples have been studied extensively.

Keywords IR, ^{1}H NMR, Nickel(II), macrocyclic ligands, cyclic voltammetry

INTRODUCTION

Research on diverse aspects of new macrocylic compounds has attracted world-wide interest in recent years (Arca et al. 2001; Tarafader et al., 2001). Transition metal complexes of mixed donor macrocyclic ligands constitute a potentially important class of molecules for molecular electronics and catalytic reductions (Canales et al., 2000). In a series of recent papers, the synthetic and characterization aspects of a number of transition metal complexes of different donor atoms have been described (Comba et al., 2002; Valencia et al., 2001, Vries and Reedijk, 1991). A new variety of nickel(II) complexes with N_2S_2 (L^1) and N_2S_3 (L^2) donor macrocyclic ligands have been prepared and characterized in this article. The electrochemical properties have been studied extensively for nickel(II)/nickel(I) couples.

EXPERIMENTAL

All chemicals used in the present investigation were of AR grade and were purchased from Sigma Chemical Co., U.S.A., E. Merck, Germany or Sarabhai Merck Company, India. Ethanol used was of analytical grade procured from S.D. Fine Chemicals Pvt. Ltd. It was dried by storing over clean, dried sodium wire, refluxed for 30 min and distilled using a double walled condenser at 78 °C.

Physical Measurements

The magnetic susceptibilities were measured on a Gouy balance using $Hg[Co(NCS)_4]$ as a caliberant. Infrared spectra of the complexes were recorded on a Perkin-Elmer-FTIR 1710 automatic recording spectrophotometer in KBr. Electronic spectra of the complexes were recorded on a DMR-21 automatic recording spectrophotometer in DMF solution. Conductance measurements in nitromethane were carried out on a Leeds Northup Model 4995 conductivity bridge. Analyses of carbon and hydrogen were performed at the Microanalytical Laboratory of the Central Drug Research Institute, Lucknow, India. The nitrogen contents of the complexes were determined using Kjeldahl's method. The ^{1}H NMR spectra of the macrocyclic ligands were recorded on Bruker Avance 300 spectrophotometer at 100 kHz modulation at room temperature. The voltammograms and the simultaneous current intensity-time plots for electrolysis were registered in a x-y Houston-Ommigraphic 2000 recorder. The values of E_F for reversible or quasi-reversible redox transformations were calculated as the midpoints between the anodic and cathodic peaks. The distances between peaks (ΔE) were used as the parameters for the characterization of the reversibility of the electrochemical transformation.

Received 24 September 2003; accepted 17 May 2004.

Rajiv Kumar gratefully acknowledges his younger brother Bitto for motivation. Thanks are also due to the Principal of Zakir Husain College, New Delhi, for providing laboratory facilities, to the University Grants Commission, New Delhi for financial assistance and the University Science Instrumentation Center, Delhi University, for recording IR spectra. Thanks are also due to the Solid State Physics Laboratory India for recording magnetic moments.

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Preparation of the Ligands

Preparation of 1,2-di(o-aminophenylthio)ethane

This diamine was prepared by heating *o*-$HSC_6H_4NH_2$ (0.01 mole, 1.25 g) with absolute (99%) EtOH (3 mL) containing Na (0.46 g, 0.02 g atom); $BrCH_2CH_2Br$ (0.372 mL, 0.02 mole) in ethanol (1 mL) was added drop-wise with constant stirring (nitrogen atmosphere) to the refluxing solution. The mixture was then cooled to 25 °C and poured into water (300 mL). The solid mass so obtained was filtered washed with H_2O and dried. The product was recrystallized from EtOH. A yellowish colored solid was obtained. Yield 2.19 g (70%); m.p. 75 °C. ^1H NMR: ($CDCl_3$) δ: 6.3 (2H, d, J = 6.8), 7.1 (2H, m), 6.6 (2H, m), 5.35 (4H, s), 7.2 (2H, d, J = 7.5), 2.8 (4H, m, S-CH_2).

Ligand L^1

To an ethanolic solution (25 mL) of 1,2-di(*o*-aminophenylthio)-ethane (0.005 mol, 0.723 g) was added to an ethanolic solution (25 mL) of benzil (0.005 mol, 1.05 g) in the presence of 1 mL conc. HCl and the resulting solution was boiled under reflux for 3–4 h. On cooling, light yellowish crystals separated out which were filtered, washed with ethanol and dried under vaccum over P_4O_{10}. Yield 1.24 g (70%); m.p. 182 °C. ^1H NMR: ($CDCl_3$) δ: 7.2–7.24 (10H, m), 6.9 (2H, d, J = 7.2), 7.1 (24H, m), 6.6 (2H, m), 7.27 (2H, d, J = 7.4), 4.0 (4H, m, S-CH_2).

Ligand L^2

To an ethanalic solution (25 mL) of thiodiglycolic acid (0.02 mole, 2.89 g), an ethanolic solution (25 mL) of 1,2-di(*o*-aminophenylthio)ethane (0.02 mole, 5.53 g) in absolute ethanol (25 mL) was added drop-wise with constant stirring at a temperature of 65 °C. The solution was then concentrated to half of its volume under reduced pressure and kept for two days at room temperature. Light yellowish crystals separated out. The resulting crystals were filtered, washed with ethanol and dried over P_4O_{10}. Yield 5.47 g (65%); m.p. 195 °C. ^1H NMR: ($CDCl_3$) δ: 7.2 (4H, m), 6.8 (2H, d, J = 7.1), 6.5 (2H, d, J = 6.8), 3.0 (4H, m), 2.8 (4H, s).

Preparation of the Complexes

A general method has been adopted for the preparation of the complexes. A hot (65–70 °C) aqueous ethanol solution (25 mL, 1:1 v/v) of the hydrated metal salt (0.01 mole) and a hot ethanol solution (25 mL) of the respective ligand (0.01 mole) were mixed. The mixture was refluxed for about 3–4 h at 75–80 °C. Upon cooling to 6 °C, the complexes separated out. They were filtered, washed with 98% ethanol and dried over P_4O_{10}.

RESULTS AND DISCUSSION

Both ligands were synthesized by the scheme in Figure 1.

Nickel(II) Complexes with the Ligand L^1 (2,3-Diphenyl-1,4-diaza-7,10-dithia-5,6 : 11,12-dibenzo[e,k]cyclododoca-1,3-diene[N_2S_2]ane)

All of the nickel(II) complexes have the composition $[Ni(L^1)X_2]$ (where X = Cl, SCN and $\frac{1}{2}SO_4$) and $[Ni(L^1)](NO_3)_2$. Condensation between the NH_2 group of diamine and the CO group of the diketone formed a new C=N group. The infrared spectrum shows a sharp band at 1590 cm^{-1} due to the C=N group (Mandal and Nag, 1983; Rao and Zacharias, 1977).

The formation of the complexes may be represented by the following equation.

$$NiX_2 \cdot nH_2O + L^1 \longrightarrow Ni(L^1)X_2 + nH_2O$$

The above complexes may be four-coordinate, five-coordinate or six- coordinate depending upon the nature of the anions involved in coordination. Magnetic moments (Table 1) of the complexes, discussed below, suggest six-coordinate octahedral geometry for the chloro and thiocyanato complexes, four-coordinate square-planar geometry for $[Ni(L^1)](NO_3)_2$ and five-coordinate square-pyramidal geometry for $[Ni(L^1)SO_4]$.

The magnetic moments of the complexes at room temperature (300 K) lie in the range 2.89–3.01 B.M (Chandra and Singh, 1986) corresponding to two unpaired electrons, except for $[Ni(L^1)](NO_3)_2$, which is diamagnetic. The molar conductance measurements lie in the range 6–18 Ω^{-1} cm^2 mol^{-1} for all the complexes expect for $[Ni(L^1)](NO_3)_2$, which shows molar conductance of 205 Ω^{-1} cm^2 mol^{-1} corresponding to a 1:2 electrolyte (Bentini and Sabatini, 1966).

$[Ni(L^1)Cl_2]$ and $[Ni(L^1)(NCS)_2]$

The ν(C=N) bands in the infrared spectra of $[Ni(L^1)Cl_2]$ and $[Ni(L^1)(NCS)_2]$ appear at 1590 and 1592 cm^{-1}, respectively (Lever, 1968). This indicates that the ligand is macrocylic in nature. No IR bands are observed for free CO or NH_2 groups. However, four new bands appeared corresponding to amide groups in the IR spectrum of the ligand at 1680, 1620, 1520, and 1335 cm^{-1}indicate that complete condensation has taken place. The IR spectrum of $[Ni(L^1)(NCS)_2]$ shows a ν(CN) band at 2089 cm^{-1} corresponding to coordinated NCS. The infrared spectrum of the $[Ni(L^1)Cl_2]$ shows bands at 390–410 cm^{-1} corresponding to coordinated chloro groups. The electronic spectrum of $[Ni(L^1)Cl_2]$ complex displays three bands at 10,080, 16,806 and 27,580 cm^{-1}. $[Ni(L^1)(NCS)_2]$ displays (Livingstone and Nolan, 1969) bands at 11,325, 16,994, and 28,089 cm^{-1}. These bands may be assigned to the following transitions $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2), and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3), in order of increasing energy, respectively, characteristic of an octahedral geometry (Chandra, 1982) (Figure 2).

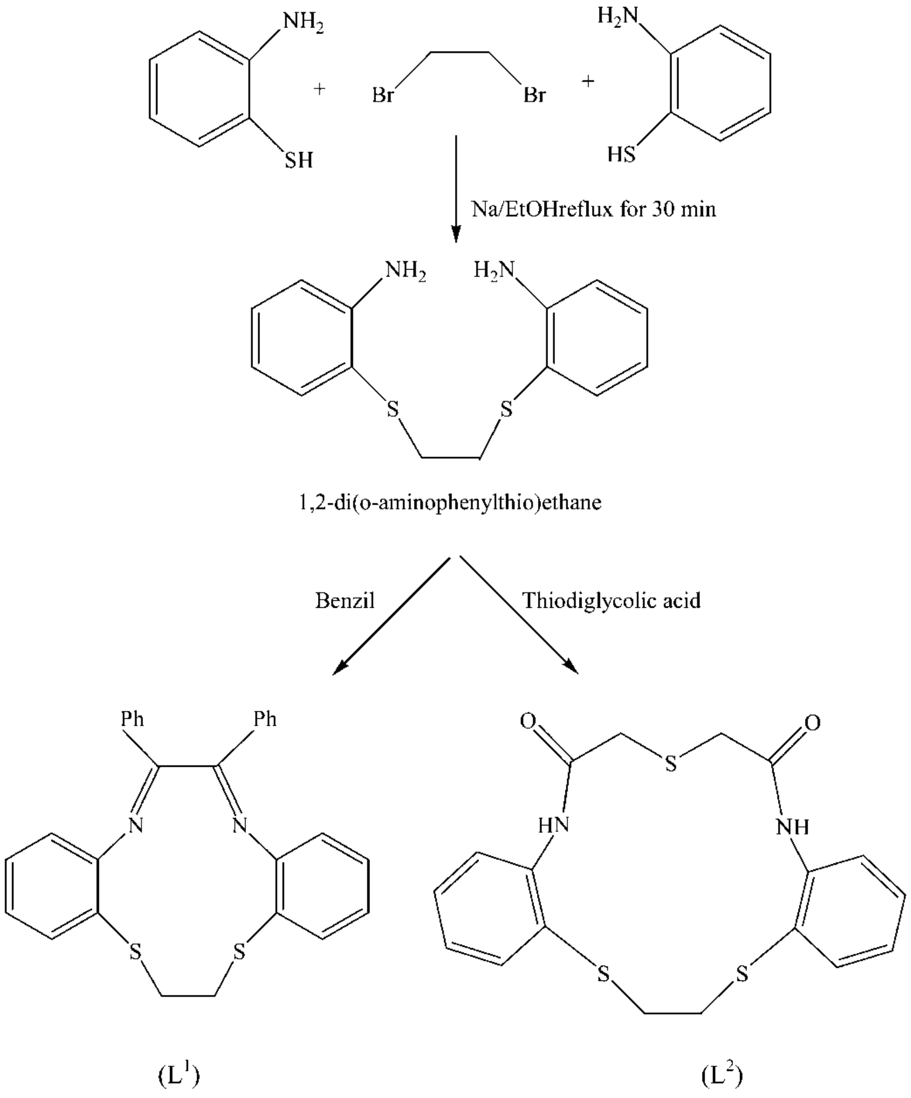

FIG. 1. Synthesis and structure of macrocyclic ligand L^1 and L^2.

[Ni(L¹)](NO₃)₂

The infrared spectrum of the nitrato complex shows a band at 1385 cm^{-1} corresponding to an uncoordinated nitrate group. Further, the complex was found to be diamagnetic (no unpaired electrons) in the solid as well as in benzene solution. This suggests a square-planar geometry around nickel(II) (Chandra and Singh, 1986). The electronic spectrum of this complex displays three well-defined bands at 18,115, 22,540, and 26,240 cm^{-1}, which may be assigned, respectively, to $^1A_{1g} \rightarrow {}^1A_{2g}$ (ν_1), $^1A_{1g} \rightarrow {}^1B_{1g}$ (ν_2), and $^1A_{1g} \rightarrow {}^1E_g$ (ν_3) transitions corresponding to square-planar geometry (Figure 3). The first two bands are purely d-d transitions, whereas ν_3, obviously is enveloped by strong charge transfer (Chandra and Singh, 1986).

[Ni(L¹)SO₄]

The infrared spectrum of the complex shows bands at 940 (ν_1), 1050 (ν_2) and 1150 (ν_3) cm^{-1}, which indicate that the sulfato group acts as unidentate (Bentini and Sabatini, 1966). Thus, a five-coordinate structure (square-pyramidal or trigonal-bipyramidal) may be suggested for this complex.

The electronic spectrum of the complex shows two absorption bands at 10,425 and 12,475 cm^{-1}, which may be assigned to $^3E \rightarrow {}^3A_2$ (F) (ν_1) and $^3E \rightarrow {}^3B_2$ (F) (ν_2) transition respectively, corresponding to five-coordinate square-pyramidal geometry (Livingstone and Nolan, 1969) (Figure 4).

Nickel(II) Complexes with the Ligand L^2 (1,10-Diaza-4,7,13-trithia-2,3:8,9-dibenzo[b,h]-cyclopentadeca-11,15-dione[N_2S_3]ane)

All the complexes have the composition $[Ni(L^2)X]X$ (X = Cl, NO_3 or NCS) and $[Ni(L^2)SO_4]$. The formation of the complexes may be represented by the following equation.

$$NiX_2 \cdot nH_2O + L^2 \longrightarrow [Ni(L^2X]X + nH_2O$$

TABLE 1
Elemental analyses and magnetic moments of nickel(II) complexes

S. no.	Compound	Formula weight	Color	M. p. (°C)	Yield (%)	Elemental analyses (%) found/(calcd.) Ni	C	N	H	μ_{eff} (B.M.)
(1)	L^1	450.62	White	180	70	—	74.12	6.0	4.32	—
	$C_{28}H_{22}N_2S_2$						(74.60)	(6.20)	(4.90)	
(2)	[Ni(L^1)Cl$_2$]	580.23	Light green	240	43	10.0	57.40	40.6	3.63	3.02
	$C_{28}H_{22}Cl_2N_2NiS_2$					(10.12)	(57.96)	(4.83)	(3.83)	
(3)	[Ni(L^1)(SCN)$_2$]	625.45	Purple	216	48	9.10	57.21	8.51	2.94	2.89
	$C_{30}H_{22}N_4NiS_4$					(9.37)	(57.61)	(8.95)	(3.55)	
(4)	[Ni(L^1) (NO$_3$)$_2$]	633.27	Dark green	235	52	9.01	52.71	8.52	3.14	Diamagnetic
	$C_{28}H_{22}N_4NiO_6S_2$					(9.27)	(53.10)	(8.84)	(3.51)	
(5)	[Ni(L^1)SO$_4$]	605.35	Green	224	58	9.35	55.41	4.45	3.55	2.96
	$C_{28}H_{22}N_2NiO_4S_3$					(9.70)	(55.55)	(4.63)	(3.67)	
(6)	L^2	390.52	White	195	65	—	55.30	7.10	4.50	—
	$C_{18}H_{18}N_2O_2S_3$						(55.36)	(7.17)	(4.66)	
(7)	[Ni(L^2)Cl]Cl	520.13	Blackish green	226	48	11.00	41.20	5.20	3.11	3.00
	$C_{18}H_{18}Cl_2N_2NiO_2S_3$					(11.29)	(41.57)	(3.47)	(3.47)	
(8)	[Ni(L^2)(NCS)](NCS)	565.35	Green	217	50	10.10	42.24	9.80	3.00	2.91
	$C_{20}H_{18}N_4NiO_2S_5$					(10.39)	(42.49)	(9.90)	(3.22)	
(9)	[Ni(L^2)(NO$_3$)](NO$_3$)	573.17	Light green	235	52	10.00	37.00	9.71	2.91	2.95
	$C_{18}H_{18}N_4NiO_8S_3$					(10.25)	(37.71)	(9.77)	(3.18)	
(10)	[Ni(L^2)SO$_4$]	545.25	Black green	221	57	10.65	39.00	4.90	3.15	2.98
	$C_{18}H_{18}N_2NiO_6S_4$					(10.77)	(39.65)	(5.14)	(3.30)	

The magnetic moments of the complexes lie in the range 2.90–3.01 B.M. corresponding to two unpaired electrons. The molar conductivity of Ni(L^2)X$_2$ (X = Cl, NO$_3$ or NCS) in nitrobenzene was found in the range 80–95 Ω^{-1} cm^{-1} mol^{-1}, which indicates that the complexes are 1:1 electrolytes and may be formulated as [Ni(L$_2$)X]X (X = Cl, NO$_3$ NCS).

The IR spectrum of the ligand (L^2) shows moderate-intensity absorptions in the range 1600–1630 cm^{-1} attributable to the imine ν(C=N) (Mandal and Nag, 1983; Rao and Zacharias, 1977) but no bands are observed for free COOH or NH$_2$ groups and four new bands corresponding to amide groups (Rosokha et al., 1993) at 1680, 1620, 1520, and 1325 cm^{-1} appeared, indicating that complete condensation has occurred. A single, sharp band observed in the region 3340–3380 cm^{-1} may be assigned to ν(N-H) of a secondary amino group (Nakamoto, 1978).

The IR spectrum of the thiocyanate complex shows two ν(CN) absorptions at 2085 and 2052 cm^{-1} indicating two types of thiocyanato linkages, one corresponding to coordinated and the other to uncoordinated NCS (Bentini and Sabatini, 1966; Lever, 1968; Chandra et al., 2003).

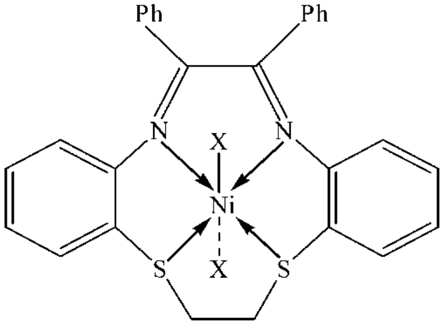

FIG. 2. Suggested structure of [Ni(L^1)X$_2$ where X = Cl and NCS.

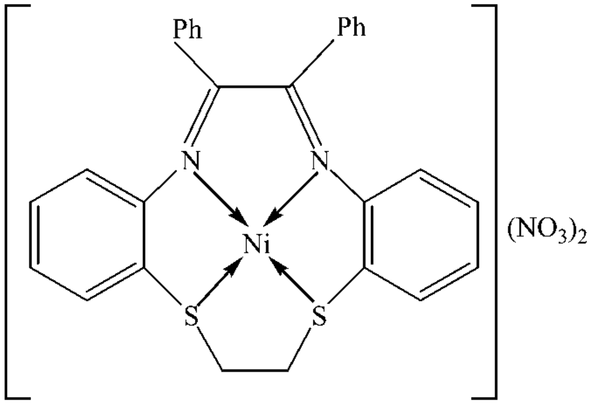

FIG. 3. Suggested structure of [Ni(L^1] (NO$_3$)$_2$.

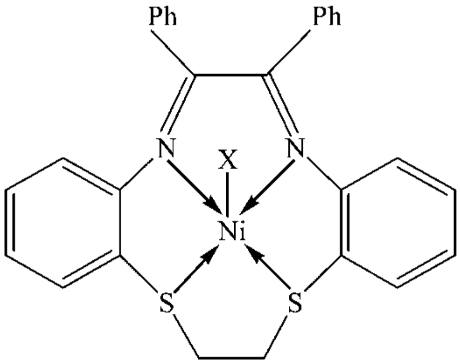

FIG. 4. Suggested structure of [Ni(L^1)SO4], X = OSO$_3$.

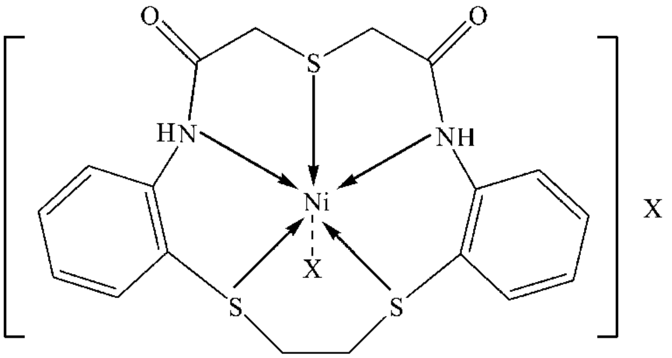

FIG. 5. Suggested structure of [Ni(L^1)X]X, where X = Cl, SCN, NO$_3$ and $\frac{1}{2}$SO$_4$.

The IR spectrum of nitrate complex exhibits bands at 1425 (ν_1), 1375 (ν_3), 1201 (ν_5), 1010 (ν_2), μ and 836 (ν_6) cm^{-1}. The difference between ν_1 and ν_5 is $\sim$125 cm^{-1}, which indicates that the nitrate groups act as unidentates in this complex. A broad band at 1385 cm^{-1} corresponding to uncoordinate nitrate group is also present in the IR spectrum of the complex (Chandra, 1982).

The sulfate complex shows IR spectral bands at 935 (ν_1), 1040 (ν_2), and 1145 (ν_3) cm^{-1} indicating that the sulfate group acts as a unidentate (Chandra and Gupta, 2002).

The electronic spectra of the nickel(II) complexes exhibit three strong bands at 9,945–10,666 (ν_1), 12,455–15,321 (ν_2), and 25,461–30,426 (ν_3) cm^{-1}, well within the range for the six-coordinate octahedral geometry for the complexes as reported earlier (Lever, 1968). The first two bands result from the splitting of one band, and can be assigned to $^3B_{1g} \rightarrow {}_3E_g$ (ν_1) and $^1B_{1g} \rightarrow {}^3B_{2g}$ (ν_2) transitions, assuming the effective symmetry to be D_{4h} (originating from $^3T_{2g}$ in O_h symmetry). The other two higher frequency bands can be assigned to $^3B_{1g} \rightarrow {}^3A_{2g}$(F) and $^3B_{1g} \rightarrow {}^2A_{2g}$(P) on the basis of symmetry arguments (Figure 5).

Ligand Field Parameters

Lever (Lever, 1968) have devised normalized spherical harmonic Hamiltonian parameters applicable to molecules of D_{4h} symmetry. The values of ligand field parameters are given in Table 2. The transition energies $^3B_{2g}$ and ^3E_g of the $^3T_{2g}$ levels are used for calculating the ligand field parameters (Lever, 1968) Ds and Dt. These are the tetragonal splitting parameters, which are related to the transition energy. Dq^{xy} and Dq^z are the splitting parameters for in-plane and for axial ligands. These parameters were calculated by means of the following equations.

$$\mathrm{Dt} = 4/35(^3\mathrm{B}_{2g} - {}^3\mathrm{E}_g)$$

$$\mathrm{Dq}^z = 1/10(2\nu\mathrm{E}_g - {}^2\mathrm{B}_{2g})$$

$$\mathrm{Dq}^{xy} = 1/10(\nu\mathrm{B}_{2g})$$

$$\Delta\nu = 6\mathrm{Ds} - (5/4)\mathrm{Dt}$$

McClure's (McClure, 1961) parameters δt_{2g} and δe_g depend upon the splitting of the t_{2g} and e_g orbitals. $\delta\sigma$ and $\delta\pi$ were determined from the crystal field parameters Ds and Dt by the equations shown below.

$$\delta t_{2g} = 3\mathrm{Ds} - 5\mathrm{Dt}$$

$$\delta_{eg} = 4\mathrm{Ds} + 5\mathrm{Dt}$$

$$\delta\sigma = -(1/8)(15\mathrm{Dt} + 12\mathrm{Ds})$$

$$\delta\pi = (1/2)(5\mathrm{Dt} - 3\mathrm{Ds})$$

The value of the Ds parameter is found be greater than Dt for all complexes. The ratio of these parameters, Dt/Ds,

TABLE 2
Ligand field parameters and NSH parameters for nickel(II) complexes

S. no	Compound	Dt	D_q^z	D_q^{xy}	Ds	δt_{2g}	δ	δ
(**2**)	[Ni(L^1)CI$_2$]	532	601	1245	529	1013	210	536
(**3**)	[Ni(L^1)(NCS)$_2$]	490	640	1490	690	380	106	655
(**5**)	[Ni(L^1)SO$_4$]	350	620	1310	710	380	408	190
(**7**)	[Ni(L^2)CI]CI	290	710	1295	560	230	785	115
(**8**)	[Ni(L^2)(NCS)](NCS)	310	690	1390	770	860	108	380
(**9**)	[Ni(L^2)(NO$_3$)](NO$_3$)	470	650	1450	650	400	930	575
(**10**)	[Ni(L^2)SO$_4$]	286	743	1532	832	1066	711	—

provides information about r^2/R^2, where r is a average radius of the d-shell and R the average metal ligands distance. σ-bonding along the xy-plane is strong. It is related to the negative sign of the σ parameters values. But the $\delta\pi$ values are positive in our result. It indicates that the π bonding effect is relatively more important along the axial direction than σ-bonding.

Cyclic Voltametry

The electrochemical behavior of the nickel(II) complexes was studied in acetonitrile. A quasi-reversible redox process, assigned to the Ni(III)/Ni(II) couple was observed. E_F (Gobi and Uhsaka, 1998) (binding constant) = 1.085 V ($\Delta E = 86\,\text{mV}$). An irreversible process where $E_{cat} = -1.45\,\text{V}$ is attributed to the Ni(II)/Ni(I) couple. A small additional peak at ca. 0.59 V is assigned to adsorption effects. A peak, which may be assigned to the ligand oxidation, was observed at 1.25 V (Jing-Li et al., 2003).

The E_F values for the single quasi-reversible redox transformation of the nickel(II) complexes are strongly anion dependent and decrease in the order $SCN > NO_3 > Cl > SO_4$.

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