

Syntheses and Characterization of *N,N'*-Dipropyl-1,2-ethanediamine and *N,N'*-Diisopropyl-1,2-ethanediamine Complexes of Nickel(II): Thermal Studies and X-Ray Single Crystal Structure Analysis of $[\text{Ni}(\text{N,N}'\text{-Dipropyl-1,2-ethanediamine})_2(\text{NCS})_2]$

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$[\text{NiL}_2(\text{H}_2\text{O})_2]\text{X}_2$ (L = *N,N'*-dipropyl-1,2-ethanediamine; X = Cl^- , Br^- , I^- , CF_3CO_2^- , CF_3SO_3^-), $[\text{NiL}_2(\text{NCS})_2]$, $[\text{NiL}'\text{Cl}_2]$ and $[\text{NiL}'(\text{CF}_3\text{CO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (L' = *N,N'*-diisopropyl-1,2-ethanediamine) have been synthesized from solution and characterized. NiLCl_2 has been prepared in the solid state from its parent species by the temperature arrest technique. Upon heating, $[\text{NiL}_2(\text{H}_2\text{O})_2]\text{X}_2$ undergoes deauration, followed by anion coordination with a change in color: blue-violet to sky blue when X is Cl^- and Br^- ; blue-violet to green when X is I^- ; and blue-violet to greenish blue when X is CF_3CO_2^- and CF_3SO_3^- . $[\text{NiL}_2\text{X}_2]$ revert in two steps; the larger the size of X the lower is the rate of reversion. All the bis-species upon further heating decompose straightaway to unidentified end products with the exception of $[\text{NiL}_2\text{Cl}_2]$ and $[\text{NiL}_2\text{Br}_2]$, which yield mono diamine species. $[\text{NiL}_2(\text{NCS})_2]$ upon heating exhibits an irreversible endothermic phase transition (82–180 °C; $\Delta H = 8.1 \text{ kJ mol}^{-1}$) without showing any visual color change. The configuration of the complexes $[\text{NiL}_2(\text{H}_2\text{O})_2]\text{X}_2$ and $[\text{NiL}_2\text{X}_2]$ is proposed to be *trans*-octahedral on the basis of the electronic spectra in the NIR region. $[\text{NiL}_2(\text{NCS})_2]$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 9.2461(9)$, $b = 9.2633(5)$, $c = 14.4650(8)$ Å, $\beta = 92.082(5)$ and $Z = 2$. The complex possesses slightly distorted *trans*-octahedral geometry. $[\text{NiL}'\text{Cl}_2]$ and $[\text{NiL}'(\text{CF}_3\text{CO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ upon heating decompose without showing any phase transition.

Solid-state thermal properties of nickel(II) complexes of *N,N'*-dialkyl-1,2-ethanediamine, where alkyl groups are methyl and ethyl, have been studied extensively by Tsuchiya *et al.*¹ and Ray Chaudhuri *et al.*^{2–4} with the intuition that alkyl substitution on both the amino groups of the 1,2-ethanediamine moiety would be an appropriate choice for exhibiting novel thermal properties as observed in Lifschitz's salts. The novel findings reported so far are as follows: (i) configurational (*cis* \rightleftharpoons *trans*/octahedral \rightleftharpoons square-planar) isomerism; (ii) conformational isomerism; (iii) deauration followed by anion coordination; (iv) deauration without anion coordination; and (v) for-

mation of interesting intermediates which may not be prepared from solution. It is observed that the anion takes a prominent role in exhibiting any of the above transformations: e.g. complexes with the anions Cl^- , Br^- and I^- are prone to exhibit conformational isomerism and formation of novel intermediates; complexes with ClO_4^- and BF_4^- anions usually undergo deauration without anion coordination; complexes with NO_3^- are highly susceptible to exhibiting configurational isomerism, and complexes with NCS^- , CF_3CO_2^- , CF_3SO_3^- etc. generally show conformational isomerism. In order to generalise the role of alkyl groups on the thermal behavior of diamine complexes of nickel(II), further study with *N,N'*-dialkyl-1,2-ethanediamine ligands, where

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the alkyl group is propyl, isopropyl or a higher member, is relevant. With this view we report here the syntheses, characterization and solid-state thermal studies of *N,N'*-dipropyl-1,2-ethanediamine complexes of nickel(II) X_2 ($X = Cl^-$, Br^- , I^- , NCS^- , ClO_4^- , $CF_3CO_2^-$ and $CF_3SO_3^-$), *N,N'*-diisopropyl-1,2-ethanediamine complexes of nickel(II) X_2 ($X = Cl^-$ and $CF_3CO_2^-$), and a X-ray single-crystal structure analysis of *trans*-dithiocyanato(*N*)bis(*N,N'*-dipropyl-1,2-ethanediamine)-nickel(II).

Experimental

Reagents. High-purity *N,N'*-dipropyl-1,2-ethanediamine (L) and *N,N'*-diisopropyl-1,2-ethanediamine (L') were purchased from Aldrich and used as received. All other chemicals used were of analytical reagent grade. Commercial nickel(II) iodide is practically insoluble in ethanol. Accordingly, an ethanolic solution of nickel(II) iodide was prepared by adding sodium iodide to nickel(II) chloride hexahydrate in a 2:1 molar ratio in ethanol as described by Goodgame and Venanzi.⁵ Nickel(II) squarate dihydrate was prepared by adding 1 g of dipotassium squarate dissolved in 10 cm³ of water to 2.2 g of nickel(II) chloride hexahydrate dissolved in 10 cm³ of water. Green colored $NiC_4O_4 \cdot 2H_2O$ precipitated immediately and was filtered and washed with hot water, acetone, and ether as described by West and Niu.⁶

Preparation of the complexes. $[NiL_2(H_2O)_2]X_2$ [$X = Cl^-$ (1), Br^- (2), I^- (3), $CF_3CO_2^-$ (5) and $CF_3SO_3^-$ (6)] (Table 1) were prepared by adding dropwise an ethanolic solution (5 cm³) of the diamine (L) (2 mmol) to an ethanolic solution (15 cm³) of the appropriate nickel(II) salts (3 mmol) with constant stirring. The resulting blue-violet solutions were kept in a $CaCl_2$ desiccator. The desired complexes were separated out after a few days. They were filtered, washed with isopropanol and dried in a $CaCl_2$ desiccator. All attempts to prepare single crystals suitable for X-ray analysis failed.

$[NiL_2(NCS)_2]$ (4) was synthesized by adopting the same procedure as described above. Here, methanol was used as a medium instead of ethanol. Single crystals suitable for X-ray analysis were obtained by recrystallizing the complex 4 from an acetonitrile-butanol mixture (1:2).

$[NiL_3](ClO_4)_2$ (7) was prepared by following the above procedure by changing the metal-ligand ratio to 1:3. Suitable single crystals of 7 could not be synthesized.

$[NiL_3]C_4O_4 \cdot 2H_2O$ (8) was made by adding the ligand to finely powdered nickel(II)squarate dihydrate contained in a stoppered conical flask. After a few days a blue-colored species was dissolved in distilled water and filtered. The filtrate was kept in a $CaCl_2$ desiccator. The desired complex was separated out after a few days. It was filtered, washed with isopropanol and dried in a $CaCl_2$ desiccator. Here also, no suitable single crystals were obtained.

NiL/Cl_2 (9) and $NiL/(CF_3CO_2)_2 \cdot 4H_2O$ (10) were prepared by adding a dry ethanolic solution (5 cm³) of the ligand (2 mmol) to a dry ethanolic solution (10 cm³) of the respective anhydrous nickel(II) salt with constant stirring. The resulting green-colored solution was kept in a $CaCl_2$ desiccator. After a few days the desired complex was separated out, and was filtered, washed with dry isopropanol and dried in a $CaCl_2$ desiccator.

Physical measurements. Thermal analyses (TG-DTA) were carried out using a Shimadzu DT-30 thermal analyzer under a flow of nitrogen (flow rate 30 cm³ min⁻¹). The sample (particle size 150–200 mesh) was heated in a platinum crucible at a rate of 10 °C min⁻¹ with inert alumina as a reference. The enthalpy changes of the phase transitions were calculated by a Perkin-Elmer DSC-7 differential scanning calorimeter using indium metal as a calibrant (rate of heating/cooling, 10 °C min⁻¹). Elemental analyses were performed using a Perkin-Elmer 240C elemental analyser. IR spectra (4000–400 cm⁻¹) were obtained at 27 °C using a Perkin-Elmer IR 783 where KBr/Nujol was used as medium/reference material. Electronic spectra (1400–200 nm) were obtained at 27 °C using a Hitachi model U 2100 spectrometer, where Nujol was used as a medium as well as a reference; X-ray powder diffraction patterns were obtained at 25 °C using a Seifert XRD-3000P instrument, where the source of X-rays was Cu radiation (30 kV/30 mA); the primary slits were 3 mm/soller/2 mm and the secondary slits were soller/0.2 mm. The magnetic susceptibility was measured at 27 °C using an EG and G PAR 155 vibrating sample magnetometer, where $[HgCo(SCN)_4]$ was used as a reference material, and diamagnetic corrections were made using Pascal's constants.

X-Ray data collection. A single crystal of complex 4 suitable for X-ray data collection was mounted on a Siemens P4 diffractometer equipped with a graphite monochromator. Mo K α ($\lambda = 0.71073$) radiation was employed. The unit-cell parameters and the crystal orientation matrix were determined by least-squares refinements of the setting angles of 28 reflections. The crystal and instrument stabilities were monitored with a set of 3 standard reflections measured over 97 reflections; in all cases no significant variations were found. Crystal data are summarized in Table 2. The intensity data were corrected for Lorentz and polarisation effects, and an empirical absorption correction⁷ based on a Ψ -scan was applied ($T_{min}/T_{max} = 0.5674/0.6927$). The structure was solved by the Patterson method and successive Fourier syntheses, and was refined on F^2 by full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. The H atoms were located from a difference map and were refined isotropically. Complex neutral scattering factors⁸ were used throughout. Refinement converged to $R1 = 0.0381$ and $wR2 = 0.0835$. The largest feature in the final difference map

Table 1. Data of the elemental analyses, magnetic moments, some selective bands of electronic spectra and molar conductance of *N,N'*-dipropyl-1,2-ethanediamine (L) and *N,N'*-diisopropyl-1,2-ethanediamine (L') complexes of nickel(II).

Complex	Color	Analyses (%) ^a				$\mu_{\text{eff}}/\text{BM}$	$\lambda_{\text{max}}/\text{nm}$	$\Delta_{\text{m}}/\text{cm}^2 \text{ mol}^{-1}$
		Ni	C	H	N			
$[\text{NiL}_2(\text{H}_2\text{O})_2]\text{Cl}_2$	1 Blue-violet	12.9 (12.9)	43.3 (43.2)	9.7 (9.7)	12.3 (12.3)	3.1	1205, 956, 578, 375	206
NiL_2Cl_2 ^b	1a Pink	14.1 (14.1)	45.9 (45.9)	9.6 (9.5)	13.4 (13.4)	3.2	598, 354 ^c	35
NiLCl_2 ^b	1b Light green	21.4 (21.4)	35.1 (35.1)	7.3 (7.3)	10.2 (10.2)	3.2	585, 365 ^c	35
$[\text{NiL}_2(\text{H}_2\text{O})_2]\text{Br}_2$	2 Blue-violet	10.8 (10.8)	35.3 (35.4)	8.0 (8.1)	10.3 (10.3)	3.1	1165, 855, 575, 358	185
$[\text{NiL}_2(\text{H}_2\text{O})_2]\text{I}_2$	3 Blue-violet	9.2 (9.2)	30.1 (30.1)	6.7 (6.9)	8.7 (8.8)	3.1	1150, 860, 555, 345	170
$[\text{NiL}_2(\text{NCS})_2]$	4 Blue-violet	12.7 (12.7)	46.7 (46.7)	8.7 (8.7)	18.1 (18.1)	3.1	1125, 955, 570, 360	40
$[\text{NiL}_2(\text{H}_2\text{O})_2](\text{CF}_3\text{CO}_2)_2$	5 Blue	9.6 (9.6)	39.5 (39.4)	7.0 (7.2)	9.0 (9.2)	3.1	1200, 895, 580, 365	155
$[\text{NiL}_2(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_2$	6 Blue-violet	8.6 (8.6)	31.5 (31.7)	6.4 (6.5)	8.1 (8.2)	3.1	1185, 900, 575, 355	140
$[\text{NiL}_3](\text{ClO}_4)_2$	7 Blue	8.5 (8.5)	41.4 (41.8)	8.5 (8.7)	12.0 (12.1)	3.1	575, 365 ^c	175
$[\text{NiL}_3]\text{C}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$	8 Blue	9.2 (9.2)	52.5 (52.6)	10.0 (10.0)	13.2 (13.1)	3.1	585, 370 ^c	150
$[\text{NiLC}_4\text{O}_4]$ ^b	8a Yellow	18.6 (18.6)	45.8 (45.8)	6.2 (6.4)	8.8 (8.9)	D	448	45
$[\text{NiL}'\text{Cl}_2]$	9 Light green	21.4 (21.4)	35.1 (35.1)	7.3 (7.3)	10.2 (10.2)	3.2	570, 345 ^c	30
$[\text{NiL}'(\text{CF}_3\text{CO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	10 Green	11.7 (11.7)	28.6 (28.7)	5.5 (5.6)	5.4 (5.6)	3.1	565, 355 ^c	

^aCalculated values are in parentheses; D, diamagnetic. ^bIsolated pyrolytically in the solid state (*vide* Table 5). ^cElectronic spectra in NIR region are not shown.

was a residual of $0.278 \text{ e} \text{ \AA}^{-3}$. All calculations were carried out using SHELXS86,⁹ SHELXL93,¹⁰ PARST¹¹ and ORTEPII¹² programs. The final fractional coordinates, selected bond distances and angles of complex **4** are listed in Tables 3 and 4, respectively. Additional material available from Cambridge Crystallographic Data Centre comprises thermal parameters, hydrogen atom coordinates, hydrogen bonding geometry, structure factor tables, and complete bond distances and angles.

Results and discussion

Elemental analyses reveal that *N,N'*-dipropyl-1,2-ethanediamine (L) produces complexes of the type $\text{NiL}_2\text{X}_2 \cdot 2\text{H}_2\text{O}$ ($\text{X} = \text{Cl}^-$, Br^- , I^- , CF_3CO_2^- and CF_3SO_3^-); $\text{NiL}_2(\text{NCS})_2$; and $\text{NiL}_3\text{X}_2 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{ClO}_4^-$, $n = 0$ and $0.5\text{C}_4\text{O}_4^{2-}$, $n = 2$), whereas *N,N'*-diisopropyl-1,2-ethanediamine (L') yields only $\text{NiL}'\text{Cl}_2$ and $\text{NiL}'(\text{CF}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ (Table 1). All efforts to prepare the complexes of L' with other nickel(II) salts failed due to hydrolysis. All the complexes exhibit IR bands due to $\nu(\text{NH}_2)$ and $\nu(\text{CH}_2)$, which are comparable to those of diamine systems, whose chelate character has been established by X-ray single-crystal analyses.³ The magnetic and electronic spectral data (Table 1) of the complexes correspond to octahedral nickel(II). Thus, $[\text{NiL}_3]\text{X}_2 \cdot 2\text{H}_2\text{O}$ and $[\text{NiL}_2\text{X}_2]$ should have N_6 and N_4X_2 chromophores,

respectively, around nickel(II), whereas the chromophore around nickel(II) in the case of $\text{NiL}_2\text{X}_2 \cdot 2\text{H}_2\text{O}$ may be either N_4X_2 or N_4O_2 . All $\text{NiL}_2\text{X}_2 \cdot 2\text{H}_2\text{O}$ have molar conductance values (in dry methanol) typical of 1:2 electrolytes (Table 1), and all of them exhibit an IR band at ca. 700 cm^{-1} due to $\rho_{\text{w}}(\text{H}_2\text{O})$ ¹³ suggesting the coordination of two water molecules and an N_4O_2 chromophore around nickel(II). On the other hand, in $\text{NiL}'\text{Cl}_2$, chloride ions should act as bridging ligand and in $\text{NiL}'(\text{CF}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$, at least two water molecules should be in the coordination sphere to satisfy octahedral geometry. It is documented that octahedral bis(diamine)nickel(II) complexes may have either a *cis*- or *trans*-configuration. To determine the exact configuration electronic spectra of the complexes in the NIR region have been studied. All the complexes show a further splitting of d-d band in that region, suggesting a *trans*-configuration.^{14,15}

X-Ray single-crystal structure analysis. An ORTEP view of complex **4** with the atom numbering scheme is shown in Fig. 1. The nickel atom occupies the centre of inversion. The coordination polyhedron of the metal atom is a distorted octahedron. The four nitrogen atoms (N1, N2 and the centrosymmetrically related ones N1*, N2*) of the two bidentate diamine (L) ligands define the equatorial plane, and the two nitrogen atoms (N3 and

Table 2. Crystallographic data for complex **4** and **4a**.

	Complex 4	Complex 4a
Empirical formula	NiC ₁₈ H ₄₀ N ₆ S ₂	NiC ₁₈ H ₄₀ N ₆ S ₂
Color	Royal blue	Blue-violet
Formula weight	463.39	463.39
Temperature/K	293(2)	293(2)
Wavelength $\lambda/\text{\AA}$	0.71073	1.5406
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$
$a/\text{\AA}$	9.2461(9)	8.248(4)
$b/\text{\AA}$	9.2633(5)	10.279(4)
$c/\text{\AA}$	14.4650(8)	14.929(6)
$\beta/^\circ$	92.082(5)	92.57(1)
$V/\text{\AA}^3$	1238.1(2)	1264.4(10)
Z	2	2
$\rho_{\text{calcd}}/\text{g cm}^{-3}$	1.243	1.217
μ/mm^{-1}	0.967	0.970
$F(000)$	500	500
Crystal size/mm	0.26 × 0.41 × 0.68	Powder
Data collection		
Diffractometer	Siemens P4	
Scan mode	ω -Scan	
Absorption correction	Empirical	
T_{max}	0.6927	
T_{min}	0.5674	
θ range/ $^\circ$ for data collection	2.20–25.00	
Reflections collected	2947	
Independent reflections	2172 [$R(\text{int})=0.0269$]	
Refinement		
Refinement on	F^2	
No. of parameters	204	
Final R [$I > 2\sigma(I)$]	$R1^a=0.0381$, $wR2^b=0.0835$	
Final R (all data)	$R1=0.0606$, $wR2=0.0947$	
Weighting parameters (A , B) ^c	0.0459, 0.000	
Goodness-of-fit on S^d	1.071	
Maximum Δ/σ	0.019	
$\rho_{\text{max}}/e \text{\AA}^{-3}$	0.278	
$\rho_{\text{min}}/e \text{\AA}^{-3}$	−0.363	

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR2 = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)^2\}]^{1/2}$. ^c $w = 1 / [\sigma^2(F_o^2) + (AP)^2 + BP]$, where $P = (F_o^2 + 2F_c^2) / 3$. ^d $S = [\sum \{w(F_o^2 - F_c^2)^2\} / (N - P)]^{1/2}$, where N is the number of data and P is the total number of parameters refined.

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**.

Atom	x	y	z	$U(\text{eq})^a$
Ni	0	0	0	33(1)
S	1701(1)	4177(1)	1668(1)	64(1)
N(1)	−2129(3)	903(3)	51(2)	40(1)
N(2)	170(3)	1454(3)	−1166(2)	39(1)
N(3)	768(3)	1551(3)	928(2)	45(1)
C(1)	−2240(4)	2085(4)	−636(2)	51(1)
C(2)	−1365(4)	1693(5)	−1463(2)	49(1)
C(3)	1144(3)	2637(4)	1246(2)	39(1)
C(4)	−2677(4)	1332(4)	963(2)	46(1)
C(5)	−4286(5)	1575(7)	987(3)	71(1)
C(6)	−4753(7)	1825(11)	1960(4)	103(2)
C(7)	967(4)	2850(4)	−1107(2)	48(1)
C(8)	2586(4)	2685(4)	−950(3)	51(1)
C(9)	3324(6)	4150(5)	−908(4)	70(1)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

N3*) of the isothiocyanate groups coordinate in *trans* axial positions. The N3–Ni–N3* axis is nearly orthogonal to the equatorial plane [angle ranges from 87.7 (1) to 92.3(1) $^\circ$]. In-plane distortion is introduced by a ligand bite angle N1–Ni–N2 82.9(1) $^\circ$. The NCS group is almost linear, with an N3–C3–S angle of 178.3(3) $^\circ$. The bonding between the Ni atom and the NCS group is bent, with a C3–N3–Ni angle of 162.3(3) $^\circ$. The Ni–N distances in complex **4**, in the range 2.074–2.168(2) \AA , are consistent with the corresponding values for nickel(II)–amine complexes with octahedral metal coordination.^{3,16–20} The five-membered chelate ring N1–C1–C2–N2–Ni displays an open envelope geometry with a C2 atom on the flap, 0.620(5) \AA away from the least-squares plane through the remaining endocyclic atoms. The conformation of the diamine chelate ring is $\delta\lambda$, as the molecule has a centre of inversion. Sulfur atoms play an important role in the molecular packing; N2...Sⁱ ($i=x, -y+1/2, z-1/2$) contact of 3.534(3) \AA may be considered as a

Table 4. Selected bond lengths (in Å) and angles (in °) for 4.

Ni–N(3)	2.074(3)	N(2)–C(2)	1.484(4)
Ni–N(3)*	2.074(3)	N(2)–C(7)	1.490(4)
Ni–N(1)	2.143(3)	N(3)–C(3)	1.154(4)
Ni–N(1)*	2.143(3)	C(1)–C(2)	1.512(5)
Ni–N(2)	2.168(2)	C(4)–C(5)	1.506(5)
Ni–N(2)*	2.168(2)	C(5)–C(6)	1.505(7)
S–C(3)	1.628(3)	C(7)–C(8)	1.513(5)
N(1)–C(1)	1.479(4)	C(8)–C(9)	1.519(6)
N(1)–C(4)	1.485(4)		
N(3)*–Ni–N(3)	180.0	C(1)–N(1)–C(4)	112.4(3)
N(3)*–Ni–N(1)	89.95(11)	C(1)–N(1)–Ni	107.9(2)
N(3)–Ni–N(1)	90.05(11)	C(4)–N(1)–Ni	118.6(2)
N(3)*–Ni–N(1)*	90.05(11)	C(2)–N(2)–C(7)	110.6(3)
N(3)–Ni–N(1)*	89.95(11)	C(2)–N(2)–Ni	102.8(2)
N(1)–Ni–N(1)*	180.0	C(7)–N(2)–Ni	123.0(2)
N(3)*–Ni–N(2)	87.68(11)	C(3)–N(3)–Ni	162.3(3)
N(3)–Ni–N(2)	92.32(11)	N(1)–C(1)–C(2)	109.1(3)
N(1)–Ni–N(2)	82.93(10)	N(2)–C(2)–C(1)	109.9(3)
N(1)*–Ni–N(2)	97.07(10)	N(3)–C(3)–S	178.3(3)
N(3)*–Ni–N(2)*	92.32(11)	N(1)–C(4)–C(5)	115.5(3)
N(3)–Ni–N(2)*	87.68(11)	C(6)–C(5)–C(4)	111.2(4)
N(1)–Ni–N(2)*	97.07(10)	N(2)–C(7)–C(8)	113.9(3)
N(1)*–Ni–N(2)*	82.93(10)	C(7)–C(8)–C(9)	110.9(4)
N(2)–Ni–N(2)*	180.0		

Symmetry transformations used to generate equivalent atoms: * $-x, -y, -z$

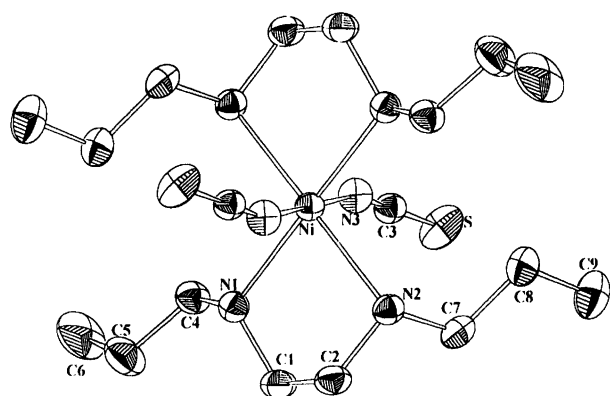


Fig. 1. ORTEP plot, *trans*-[NiL₂(NCS)₂](4) with atom numbering scheme.

hydrogen bond. The overall chelate ring conformations and the crystal packing (Fig. 2) are stabilized by van der Waal's forces.

Thermal analyses. Simultaneous TG–DTA analyses show that [NiL₂(H₂O)₂]₂X₂ upon heating loses water molecules in a single step in the temperature range ca. 100–160 °C (Table 5) and transform to NiL₂X₂. The temperature range at which the elimination of water molecules takes place also supports their coordination (*vide supra*). The value of enthalpy change for each deauration is given in Table 5, which indicates that the value decreases on increasing the size of X. NiL₂X₂ species possess *trans*-octahedral geometry, as is evident from their magnetic and electronic spectral data (Table 1). Thus, [NiL₂(H₂O)₂]₂X₂ upon heating undergoes deauration followed by an anion coordination reaction. This reaction

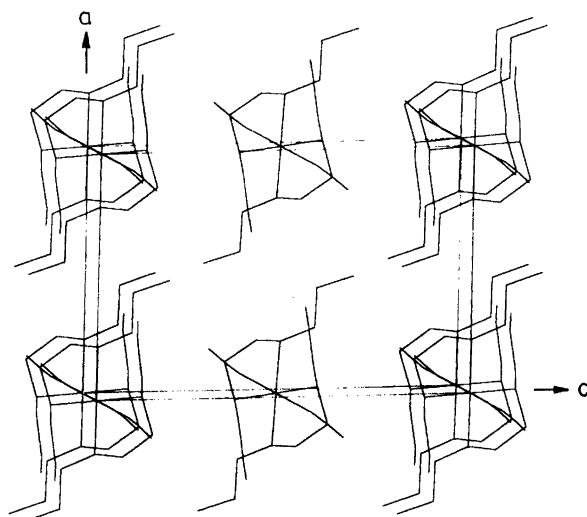


Fig. 2. Crystal packing diagram of *trans*-[NiL₂(SCN)₂](4) (L = *N,N'*-dipropyl-1,2-ethanediamine) showing the molecular arrangement.

is accompanied by color changes, blue–violet to sky blue where X is Cl[−] and Br[−]; blue–violet to green where X is I[−], and blue–violet to greenish blue where X is CF₃SO₃[−], CF₃CO₂[−]. Here, the thermochromism is proposed to be due to the change in the coordination environment around nickel(II). [NiL₂X₂] reverts on exposure to a humid atmosphere (60% or above). [NiL₂Cl₂] upon further heating undergoes a deamination reaction and transforms to NiLCl₂ with visual color change, sky blue to green. Thermochromism shown here is also proposed to be due to environmental change around nickel(II). NiLCl₂ shows two low-intensity bands

Table 5 Thermal parameters of *N,N'*-dipropyl-1,2-ethanediamine (L) complexes of nickel(II).

Thermally induced reactions	Temperature range/°C	DTA peak temp		$\Delta H/\text{kJ mol}^{-1}$
		Endo	Exo	
<i>trans</i> -[NiL ₂ (H ₂ O) ₂]Cl ₂ (1) → <i>trans</i> -[NiL ₂ Cl ₂] (1a)	108–145	133		64.5
<i>trans</i> -[NiL ₂ Cl ₂] (1a) → NiLCl ₂ (1b) ^a	201–250	240		—
<i>trans</i> -[NiL ₂ (H ₂ O) ₂]Br ₂ (2) → <i>trans</i> -[NiL ₂ Br ₂] (2a)	118–165	150		46.6
<i>trans</i> -[NiL ₂ Br ₂] (2a) → NiLBr ₂ (2b) ^a	230–287	264		—
<i>trans</i> -[NiL ₂ (H ₂ O) ₂] ₂ (3) → <i>trans</i> -[NiL ₂] ₂ (3a) ^a	130–158	156		38.7
<i>trans</i> -[NiL ₂ (NCS) ₂] (4) → <i>trans</i> -[NiL ₂ (NCS) ₂] (4a) ^a	82–180	151		8.1
<i>trans</i> -[NiL ₂ (H ₂ O) ₂](CF ₃ CO ₂) ₂ (5) → <i>trans</i> -[NiL ₂ (CF ₃ CO ₂) ₂] (5a) ^a	56–78	70		27.8
<i>trans</i> -[NiL ₂ (H ₂ O) ₂](CF ₃ SO ₃) ₂ (6) → <i>trans</i> -[NiL ₂ (CF ₃ SO ₃) ₂] (6a) ^a	123–159	142		24.5
[NiL ₃](C ₄ O ₄) ₂ · 2H ₂ O (8) → [NiLC ₄ O ₄] (8a) ^a	180–233	218		—

^aUpon further heating decomposes to unidentified end product.

in its electronic spectrum (in Nujol) in the visible region, typical of octahedral nickel(II) and the magnetic susceptibility study (Table 1) also corroborates this. IR spectra suggest that the chelating character of the diamine is retained. Therefore, to satisfy the octahedral geometry both the chloride ions should act as bridging ligands. [NiL₂Br₂] upon further heating also undergoes deamination, yielding NiLBr₂, as is evident from the plateau in its TG curve, but isolation in its pure form could not be done. [NiL₂X₂] (X = I, CF₃SO₃ or CF₃CO₂) on heating decomposes straightaway to an unidentified end product without showing any plateau in its TG curve, whereas [NiL₂(NCS)₂] upon heating shows an irreversible endothermic phase transition (82–180 °C; $\Delta H = 8.1 \text{ kJ mol}^{-1}$) with no visual change in color. IR spectra of the low- and high-temperature phase species do not differ appreciably. In order to characterize the high-temperature phase species, **4a**, we tried to synthesize its single crystals but failed. Thus, complex **4a** was examined by X-ray powder diffraction. Accurate d_{hkl} spacings (in Å) were obtained from powder patterns recorded. The initial cell parameters have been determined from powder diffraction data using the program TREOR,²¹ and accurate lattice parameters were obtained by least-squares refinements. The results are summarized in Tables 2 and 6. Though it is difficult to comment on the mechanism of phase transition from X-ray powder diffraction data, the following observations are noteworthy. There are no drastic change in the cell volume, and $0k0$ reflections show systemic absences with k odd, but all $h0l$ reflections are present, indicating the absence of any glide planes (Table 6). The likely space group of the high-temperature phase species, **4a**, is $P2_1$. In complex **4** with space group $P2_1/c$ ($Z = 2$), the Ni atom occupies the centre of inversion. However, with space group $P2_1$ the two molecules have to be distributed over two general equivalent positions. At high temperatures the steric forces are loosened. Then the molecules are no longer centrosymmetric, and this is probably due to conformational changes of the diamine chelate rings.

Owing to the explosive character of perchlorate salts, [NiL₃](ClO₄)₂ was studied up to 200 °C, and at this

Table 6. X-Ray powder diffraction data of **4a**.

h	k	l	d_{obs}	d_{cal}
0	0	2	7.512	7.464
1	0	1	7.093	7.082
1	1	0	6.410	6.431
0	1	2	6.047	6.044
0	2	0	5.120	5.140
0	1	3	4.471	4.475
-1	2	1	4.218	4.213
-2	0	1	4.013	4.018
1	1	3	3.872	3.868
-2	1	1	3.743	3.742
0	1	4	3.511	3.505
1	0	4	3.340	3.341
-1	1	4	3.278	3.276
1	1	4	3.174	3.177
0	2	4	3.014	3.018
1	3	2	2.893	2.895
0	3	3	2.820	2.821
3	0	1	2.678	2.680
-2	3	1	2.606	2.607
3	0	2	2.540	2.541
3	2	1	2.377	2.376
3	1	3	2.300	2.300
-3	1	4	2.209	2.208
-2	4	2	2.106	2.106
-4	0	2	2.009	2.009
1	5	2	1.923	1.922
3	2	6	1.702	1.702
-3	1	8	1.557	1.558

temperature range no phase transition/decomposition is observed. On the other hand, [NiL₃]C₄O₄ · 2H₂O upon heating loses two molecules of water and two molecules of diamine in a single step, and transforms to yellow-colored NiLC₄O₄ (**8a**) which is diamagnetic and exhibits only one strong band at ca. 445 nm, corresponding to square-planar nickel(II). The IR spectrum in the region 1400–1800 cm⁻¹ has been studied to assign the coordination mode of C₄O₄²⁻ ion.^{6,22} Complex **8a** exhibits a very strong and broad band at 1445 cm⁻¹ assigned to a mixture of C–C and C–O stretching vibrations and two additional bands at 1620 and 1750 cm⁻¹ assigned to C···O indicate a bidentated chelating character for the squarate ligand.

$[\text{NiL}'\text{Cl}_2]$ and $\text{NiL}'(\text{CF}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ upon heating do not exhibit any phase transition and decompose straightaway to an unidentified end product. Figures for electronic spectra, TG-DTA and DSC are deposited.

Conclusions

N,N'-Dipropyl-1,2-ethanediamine (L) produces a number of complexes with nickel(II), whereas its isomeric ligand, *N,N'*-diisopropyl-1,2-ethanediamine (L'), yields only $[\text{NiL}'\text{Cl}_2]$ and $[\text{NiL}'(\text{CF}_3\text{CO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$. The cause of such a difference in complexation is probably due to the greater steric and inductive effect of the bulky isopropyl group. It is observed that the types of complex formed and their corresponding thermal properties do not differ much on increasing the chain length of the substituted alkyl group: methyl \rightarrow ethyl \rightarrow propyl. The structure of the thiocyanate complex of L is *trans*-octahedral, as is observed in the case of the corresponding *N,N'*-dimethyl-1,2-ethanediamine analogue,³ and does exhibit an irreversible phase transition proposed to be due to conformational changes of the diamine chelate rings. Here also chloride, bromide and iodide complexes undergo deaquation followed by anion coordination, as is observed in the case of the analogous complexes of *N,N'*-dimethyl/diethyl-1,2-ethanediamine.

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