

Synthesis of Some Octahedral Nickel(II) Complexes of One Isomer of Isomeric Me₈[14]anes: X-ray Structure of Diisothiocyanato(3,10-C-*meso*-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane, L_C)nickel(II), [NiL_C(NCS)₂]

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(Received: 4 April 2006; in final form: 19 September 2006)

Key words: axial ligand substitution derivatives, crystal structure, octahedral diisothiocyanatotetraazanicel(II) complex

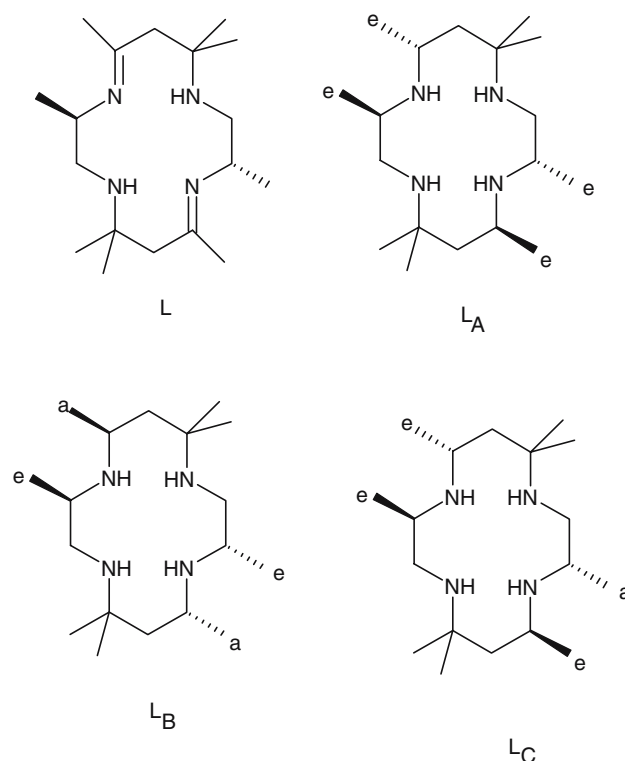
Abstract

One isomer, L_C of the isomeric Me₈[14]anes, L_A, L_B and L_C; on reaction with Ni(NCS)₂ produces a six coordinate octahedral diisothiocyanato complex, [NiL_C(NCS)₂]. This complex undergoes axial substitution reactions with the small ligands to yield corresponding monosubstituted derivatives having general formula [NiL_C(NCS)X] whereas X = Cl, Br, I, NO₂ or NO₃. The complexes have been characterized on the basis of analytical, spectroscopic, magnetic and conductance data. The structure of [NiL_C(NCS)₂] (triclinic, space group *P*-1, $\alpha = 8.0421(17)$ Å, $\beta = 8.9085(18)$ Å, $\gamma = 9.687(2)$ Å, $\alpha = 67.561(3)$ Å, $\beta = 82.896(4)$ Å, $\zeta = 598.7(2)$ Å³, $Z = 2$, $D_c = 1.352$ mg/m³, $\mu(\text{Mo } K\alpha) = 1.003$ mm⁻¹) was confirmed by X-ray crystallography.

Introduction

A number of square planar nickel(II) perchlorate complexes [1] of the isomeric ligands L_A, L_B and L_C and a variety of their axial addition reaction products (generally unstable in open air) [2] of octahedral geometry have been reported. So it was our interest to synthesize stable octahedral nickel(II) complexes of these isomeric ligands and to carry out axial substitution reactions on them which have not been carried out so far on any nickel(II) complex of macrocyclic ligands. For this purpose, a number of reactions between the different nickel(II) salts and these isomeric ligands have been carried out. But only one stable octahedral complex of formula [NiL_C(SCN)₂] has been isolated in pure state.

It has been established that stereospecific condensation of 1,2-propanediamine with acetone yields only the 3,10-C-*meso* isomer of the macrocycle 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, Me₈[14]diene, L₁, as determined by ¹H NMR [3, 4] and X-ray crystallography [5]. The reduction of L₁ with NaBH₄ yields three isomeric Me₈[14]anes, i.e. L_A, L_B and L_C (Scheme 1). In terms of the aforementioned nickel(II) chemistry, only L_C produced a stable octahedral complex, *trans*-[NiL_C(NCS)₂] on reaction with



Scheme 1.

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Ni(NCS)₂; however, each of L_A and L_B did not give any stable octahedral complex [2]. Recently a paper [6] dealing with the isomers of 3,10-*C-meso*-Me₈[14]ane and their some metal complexes has been published. The authors expected that reduction of 3,10-*C-meso*-Me₈[14]diene would give four diastereoisomeric macrocycles, L_a (SRRS), L_b (SSRR), L_c (SSRS) and L_d (SRRR). Out of them they could separate L_b (SSRR), L_c (SSRS) and L_d (SRRR) following a procedure different from ours.

The interactions of the L_A, L_B and L_C macrocycles with other metal centres have also been investigated. In different studies [7–10], a number of copper(II) complexes have been prepared and recently [11] axial addition reactions have been carried out on some diastereoisomeric square planar copper(II) complexes. In one study [12], a number of square planar nickel(II) complexes were prepared by the reactions of these ligands with nickel(II) acetate and subsequent treatment with lithium perchlorate. In another study [13], preparation of some diastereoisomeric cobalt(III) complexes, *trans*-[CoLCl₂]ClO₄ (L = Me₈[14]anes) has been achieved. Owing to the putative steric hindrance exerted by the eight-methyl groups in these macrocyclic ligands, it was originally thought that axial substitution reactions would be difficult. However, subsequent studies proved that axial substitution reactions on *trans*-[ZnL(OH₂)₂](ClO₄)₂ complexes [14], *trans*-[CoLCl₂]ClO₄ [15] as well as on *trans*-[CuL₁(ClO₄)₂]·2H₂O [9], are feasible. Hence, it seemed likely that similar axial substitution reactions could also be carried out on *trans*-[NiL_C(NCS)₂]. In this context, synthesis of *trans*-[NiL_C(NCS)₂], its characterization including X-ray structure determination and isolation of a number of its axial substitution reaction products with unidentate ligands such as Cl⁻, Br⁻, I⁻, NO₂⁻ and NO₃⁻ and their characterization have been achieved.

Experimental

Materials and measurements

All chemicals were of analytical reagent grade and used without further purification. Microanalyses (C, H, N and S) were carried out by the combustion method at the Analytical Section of the Chemistry Department, University of Hamburg, Germany. For nickel, standard titrimetric method has been employed.

Infrared spectra were taken as KBr pellets in the range 4000–400 cm⁻¹ on a Perkin-Elmer 883 infrared spectrophotometer. Electronic absorption spectra were recorded on Shimadzu UV/Visible spectrophotometer. Mass spectra were run on a JEOL MS-DX300 gas chromatograph mass spectrometer at 70 eV using a direct inlet system. Conductance measurements of the metal complexes were done in chloroform and DMF; and in one case in aqueous solution, using a HANNA instrument equipped with a HI 8820N conductivity cell.

Magnetic measurements were carried out at room temperature with a Gouy balance, calibrated against Hg[Co(NCS)₄]; susceptibilities were corrected for diamagnetic increments.

Synthesis

Synthesis of the parent ligand 3,10-*C-meso*-Me₈[14]diene dihydroperchlorate, reduction of this diene with NaBH₄ and separation into the three isomers of Me₈[14]ane (L_A, L_B and L_C) were carried out according to literature procedures [3, 16].

The complex, *trans*-[NiL_C(NCS)₂] (1): A hot methanol solution (30 cm³) of KSCN (0.1943 g, 0.002 mol) was added to a hot solution of Ni(NO₃)₂ (0.290 g, 0.001 mol) in the ratio of 1:2 in the same solvent. A white precipitate of KNO₃ was formed immediately at the bottom of the beaker, which was removed by filtration. After sometime the cold filtrate was heated for about 10 min and 0.312 g (0.001 mol) of L_C added to the hot solution of Ni(SCN)₂. A pink–violet product was formed gradually at the bottom of the beaker. The top layer of the solution was orange in colour. The mixture was then heated for about 30 min with constant stirring for completion of the reaction. The solution was allowed to cool down. The pink–violet product of *trans*-[NiL_C(NCS)₂] was filtered off, washed with redistilled ethanol followed by diethyl ether and finally dried in desiccator over silicagel. Yield 0.4143 g (85%). Anal. calcd. (%) for C₂₀H₄₀N₆S₂Ni (1): C, 49.29; H, 8.27; N, 17.24; S, 13.16; Ni, 12.04; Found: C, 49.12; H, 8.14; N, 17.78; S, 13.06; Ni, 11.90. IR (KBr disc, cm⁻¹): ν(N–H), 3210; ν(C–H), 2968; ν(CH₃), 1380; ν(C–C), 1180; ν(Ni–N), 530; ν(CN), 2080; ν(CS), 875; δNCS, 470. UV–vis: λ_{max} in nm (ε_{max} in M⁻¹ cm⁻¹) in solid state 910, 758, 659, 519, 442, 340, 246; in chloroform 914 (12), 745 (23), 540 sh, 250; in DMF 471(119), 257; in water 452 (103), 235. Colour, molar conductance Ω (ohm⁻¹ cm² mol⁻¹): in chloroform pink–violet, 0; in DMF orange, 102; in water yellow, 225. Magnetic moment μ_{eff} (BM): 2.89. EIMS: *m/z* [M⁺] 487.

Axial ligand substitution reaction products of *trans*-[NiL_C(NCS)₂]

The axial substitution products were prepared from octahedral complex, *trans*-[NiL_C(NCS)₂] by modifying the methods adopted for axial addition reaction by Bembi and co-workers [17].

The complex, *trans*-[NiL_C(NCS)Cl] (2): 0.243 g (0.0005 mol) *trans*-[NiL_C(NCS)₂] suspended in 30 cm³ of distilled methanol and 0.3870 g (0.006 mol, large excess) KCl dissolved in 30 cm³ of distilled methanol were mixed together. Then the mixture was stirred on a magnetic stirrer for about 1.5 h. After stirring, the mixture was refluxed for 1 h on a water bath while orange–yellow colour developed immediately. The yellow–orange mixture was completely dried by heating on a steam bath. The dry product was extracted with

chloroform and undissolved white product rejected. The pink chloroform extract was heated to dryness on a steam bath. The pink product *trans*-[NiL_C(SCN)Cl] was collected and dried in a vacuum desiccator over silicagel. Yield 0.1111 g (48%). Anal. calcd. (%) for C₁₉H₄₀N₅SCNi (2): C, 49.22; H, 8.70; N, 15.12; S, 6.90; Ni, 12.51; Found: C, 48.15; H, 8.13; N, 15.08; S, 6.72; Ni, 12.23. IR (KBr disc, cm⁻¹): ν(N–H), 3221; ν(C–H), 2968; ν(CH₃), 1370; ν(C–C), 1188, ν(Ni–N), 528; ν(CN), 2079; ν(CS), 883; δNCS, 473. UV–vis: λ_{max} in nm (ε_{max} in M⁻¹ cm⁻¹) in chloroform 939 (22), 528, 283; in DMF 470 (108), 326, 257. Colour, molar conductance Ω (ohm⁻¹ cm² mol⁻¹): in chloroform pink, 0; in DMF orange, 73. Magnetic moment μ_{eff} (BM): 2.00.

The complexes *trans*-[NiL_C(NCS)Br] (3) (pink), *trans*-[NiL_C(NCS)I] (4) (pink), *trans*-[NiL_C(NCS)(NO₂)] (5) (violet) and *trans*-[NiL_C(NCS)(NO₃)] (6) (violet) were prepared from reactions of the complex 1 (0.0005 mol) with the corresponding potassium salts, KX (X = Br, I, NO₂ or NO₃) (0.006 mol) according to the procedure described above. For C₁₉H₄₀N₅SBrNi (3): Yield 0.1319 g (52%). Anal. calcd. (%): C, 44.96; H, 7.95; N, 13.81; S, 6.30; Ni, 11.42; Found: C, 44.68; H, 7.80; N, 13.59; S, 6.38; Ni, 11.63. IR (KBr disc, cm⁻¹): ν(N–H), 3250; ν(C–H), 2980; ν(CH₃), 1380; ν(C–C), 1170; ν(Ni–N), 540; ν(CN), 2080; ν(CS), 875; δNCS, 475. UV–vis: λ_{max} in nm (ε_{max} in M⁻¹ cm⁻¹) in chloroform 954 (09), 678 (13), 524, 235; in DMF 475 (109), 325 (14), 296. Colour, molar conductance Ω (ohm⁻¹ cm² mol⁻¹): in chloroform pink, 0; in DMF orange, 85. Magnetic moment μ_{eff} (BM): 1.64. For C₁₉H₄₀N₅SINi (4): Yield 0.1721 g (62%). Anal. calcd. (%): C, 41.07; H, 7.26; N, 12.61; S, 5.76; Ni, 10.44; Found: C, 40.82; H, 7.22; N, 12.24; S, 5.54; Ni, 10.14. IR (KBr disc, cm⁻¹): ν(N–H), 3200; ν(C–H), 2950; ν(CH₃), 1370; ν(C–C), 1170; ν(Ni–N), 530; ν(CN), 2080; ν(CS), 875; δNCS, 470. UV–vis: λ_{max} in nm (ε_{max} in M⁻¹ cm⁻¹) in chloroform 953 (14), 678 (25), 529, 298; in DMF 493(123), 325, 272. Colour, molar conductance Ω (ohm⁻¹ cm² mol⁻¹): in chloroform pink, 0; in DMF orange, 145. Magnetic moment μ_{eff} (BM): 1.89. For C₁₉H₄₀N₆O₂SNi (5): Yield 0.1541 g (65%). Anal. calcd. (%): C, 48.08; H, 8.50; N, 17.72; S, 6.74; Ni 12.22; Found: C, 47.92; H, 8.22; N, 17.57; S, 6.63; Ni, 12.30. IR (KBr disc, cm⁻¹): ν(N–H), 3245; ν(C–H), 2968; ν(CH₃), 1371; ν(C–C), 1187; ν(Ni–N), 529; ν(CN), 2078; ν(CS), 884; δNCS, 473; ν(sNO₂), 1371; ν(aNO₂), 1473; δNO₂, 825. UV–vis: λ_{max} in nm (ε_{max} in M⁻¹ cm⁻¹) in chloroform 979 (11), 661 (19), 531, 229; in DMF 490(120), 325, 296. Colour, molar conductance Ω (ohm⁻¹ cm² mol⁻¹): in chloroform violet, 0; in DMF orange, 79. Magnetic moment μ_{eff} (BM): 2.08. For C₁₉H₄₀N₆O₃SNi (6): Yield 0.1304 g (55%). Anal. calcd. (%): C, 48.08; H, 8.50; N, 17.72; S, 6.74; Ni, 12.22; Found: C, 48.32; H, 8.50; N, 16.99; S, 6.53; Ni, 11.39. IR (KBr disc, cm⁻¹): ν(N–H), 3244; ν(C–H), 2950; ν(CH₃), 1375; ν(C–C), 1188; ν(Ni–N), 529; ν(CN), 2078; ν(CS), 884; δNCS, 479; ν(NO₃), 1329 and 1452. UV–vis: λ_{max} in nm (ε_{max} in M⁻¹ cm⁻¹) in chloroform 956 (17), 660 (20), 528, 229; in DMF 474(122), 325, 296. Colour, molar conductance Ω

(ohm⁻¹ cm² mol⁻¹): in chloroform violet, 0; in DMF orange, 106. Magnetic moment μ_{eff} (BM): 2.05.

X-ray structure determination

The pink-violet single crystal for X-ray analysis was obtained by slow evaporation of dichloromethane–methanol (3:1) solution of the complex. Preliminary examination and data collection for crystal of diisothiocyanatonickel(II) complex were performed with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) on an Enraf–Nonius CAD4 computer controlled k -axis diffractometer equipped with a graphite crystal, incident-beam monochromator. Cell constants and orientation matrices for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections. The data were collected for Lorentz-polarization and absorption corrections were applied to the data. The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least-squares calculations with SHELX-97 [18, 19].

Crystallographic data for the octahedral diisothiocyanatonickel(II) complex; C₂₀H₄₀N₆S₂Ni $F_w = 487.42$, triclinic, space group $P\bar{1}$, $a = 8.0421(17) \text{ \AA}$, $b = 8.9085(18) \text{ \AA}$, $c = 9.687(2) \text{ \AA}$, $\alpha = 67.561(3)^\circ$, $\beta = 82.896(4)^\circ$, $\gamma = 598.7(2)^\circ$, $Z = 2$, $D_c = 1.352 \text{ mg/m}^3$, $\mu(\text{Mo } K\alpha) = 1.003 \text{ mm}^{-1}$, crystal dimensions $0.40 \times 0.40 \times 0.20 \text{ mm}^3$, 3664 reflections collected, 2669 [$R(\text{int}) = 0.0180$] independent reflections, $R1 [I > 2\sigma(I)] = 0.0632$, $wR2 [I > 2\sigma(I)] = 0.2063$.

Results and discussion

The *trans*-[NiL_C(NCS)₂] complex undergoes axial ligand substitution reactions to give monosubstituted derivatives, *trans*-[NiL_C(NCS)X] complexes, where X = Cl, Br, I, NO₂ or NO₃ as detailed in the *Experimental*. Physical data are also summarized in experimental section. Though the precursor complex, *trans*-[NiL_C(NCS)₂] was found to be stable in open atmosphere, but the derivatives were found to change their geometry from octahedral to square planar in the same atmospheric condition. Since ¹H NMR could not be measured on these octahedral nickel(II) complexes due to their paramagnetic behaviour, the exact stereochemistries could not be determined with absolute certainty, except in the case of *trans*-[NiL_C(NCS)₂], for which a crystal structure analysis has been carried out, assignments are made on the assumption that axial substitution [9, 20, 21] takes place with retention of configuration and conformation. Characterization of the complexes was achieved by UV/VIS and IR, Mass spectroscopic data as well as by magnetochemical and conductance measurements (Table 1). The magnetochemical study showed all complexes paramagnetic. Moreover structure of *trans*-[NiL_C(NCS)₂] has been confirmed by X-ray crystallography.

Table 1. Crystal data and structure refinement for *trans*-[NiL_C(NCS)₂]

Empirical formula	C ₁₀ H ₂₀ N ₃ Ni _{0.50} S
Formula weight	243.71
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions	<i>a</i> = 8.0421(17) Å <i>α</i> = 67.561(3) <i>b</i> = 8.9085(18) Å <i>β</i> = 82.896(4) <i>c</i> = 9.687(2) Å <i>γ</i> = 68.984(4)
Volume	598.7(2) Å ³
<i>Z</i>	2
Density (calculated)	1.352 mg/m ³
Absorption coefficient	1.003 mm ⁻¹
<i>F</i> (000)	262
Crystal size	0.40 × 0.40 × 0.20 mm ³
Theta range for data collection	2.27–28.24°
Index ranges	−8 ≤ <i>h</i> ≤ 10, −11 ≤ <i>k</i> ≤ 11, −12 ≤ <i>l</i> ≤ 11
Reflections collected	3664
Independent reflections	2669 [<i>R</i> (int) = 0.0180]
Completeness to theta = 28.24°	90.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8246 and 0.689
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2669/0/165
Goodness-of-fit on <i>F</i> ²	1.309
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0632, <i>wR</i> 2 = 0.2063
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0649, <i>wR</i> 2 = 0.2068
Largest diff. peak and hole	2.171 and −0.485 eÅ ⁻³

Synthesis

The complex *trans*-diisothiocyanatonickel(II) of L_C (1): The compound *trans*-[NiL_C(NCS)₂] was prepared by the reaction of nickel(II) thiocyanate with the free base ligand L_C. Since nickel(II) thiocyanate is not readily available, it was prepared by the reaction of KSCN with Ni(NO₃)₂ in the molar ratio 2:1 in methanol. The by-product KNO₃ came out of the reaction medium as a white precipitate and nickel(II) thiocyanate remained in the solution. To the solution in heated condition equimolar amount of the ligand L_C was added. Within 30 min the reaction was completed and the desired product *trans*-[NiL_C(NCS)₂] was isolated pure by extraction with chloroform and subsequent removal of chloroform by evaporation.

Axial substitution reaction products of complex (I): SCN[−] is a stronger ligand in comparison to other weak ligands like Cl[−], Br[−], I[−], NO₂[−] or NO₃[−], so it was doubtful whether these ions may substitute thiocyanate ligand from the axial sites of the nickel(II) ion in the complex [NiL_C(NCS)₂]. To test this possibility the reactions of [NiL_C(SCN)₂] (1) with KX in the ratio of 1:12 were carried out in refluxing methanol. Evaporation of methanol, subsequent extraction by chloroform of the reaction product and evaporation of chloroform extract yielded monosubstituted products. It was interesting to note that if only the excess amount of KX was

used then only mono substituted derivatives were prepared. However, equimolar or double amount of KX did not work to substitute even one NCS group by X from the compound (1). Rather the original complex (1) was isolated in solid state in each case. This phenomenon may be explained by the fact that since NCS[−] is a strong ligand compared to X[−], so it was difficult to replace NCS[−] by X[−]; only excess amount of X[−] could replace one NCS[−] instead of two.

All the analytical and experimental data were consistent with their formulation.

Spectral properties

The infrared spectra of these complexes show all characteristic ν_{N–H}, ν_{C–C}, ν_{C–H}, ν_{Ni–N} and ν_{CH₃} bands in expected regions. As described in the experimental section, the appearance of distinct and sharp ν(CN) at 2078–2080 cm^{−1}, ν(CS) at 875–884 cm^{−1}, and ν(NCS) at 470–479 cm^{−1} bands in their IR spectra, is consistent with the coordination of NCS and further, the positions of the bands support N-bound thiocyanate groups [22–26]. This assignment is in good agreement with the fact that, generally, first row transition metal complexes of thiocyanate contain M–N bonds [9]. In addition, the spectrum of complex [NiL_C(SCN)(NO₂)] (5) further shows the bands at 1473 and 1371 cm^{−1} due to ν_{asym}(NO₂) and ν_{sym}(NO₂), respectively. Appearance of a very weak band at 825 cm^{−1} may be attributed to δ_{NO₂} stretching frequency and the band at 448 cm^{−1} due to ν_{Ni–N} (Ni–N bond between Ni(II) ion and N of NO₂[−] ion) supports the unidentate mode of coordination of nitro group through N-atom. Though NO₂[−] can also coordinate as chelating bidentate ligand, this is not possible in this case at ordinary condition, because it needs the macrocycle to be folded, which is difficult due to steric hindrance of eight peripheral methyl (−CH₃) groups on the macrocycle ring.

Similarly appearance of bands at 1452 and 1329 cm^{−1} in [NiL_C(SCN)(NO₃)] (6), is attributed to coordinated NO₃[−] group. The separation of these bands by 123 cm^{−1} is accounted for unidentate mode of coordination [27]. Though NO₃[−] can also coordinate as bidentate ligand, this is not possible as explained above. Since IR-spectrum of this complex could not be run at a range lower than 400 cm^{−1}, so the band at around 350–250 cm^{−1} for Ni–O stretch could not be recorded. For the same reason, the stretching frequency of Ni–X' (X' = Cl, Br or I) at around 260 cm^{−1} in derivatives 2, 3 and 4 could not be detected.

The electronic spectra of the complexes in solid state and in chloroform exhibit d–d bands at 910–979 nm (ν₃) and 758–657 nm (ν₂) and 342–340 nm (ν₁), and low molar extinction coefficient (ε) values in the range of 9–23 dm³ mol^{−1} cm^{−1} as expected for six-coordinated octahedral nickel(II) complexes [28, 29]. However, all bands are not clear in some of the complexes. On the other hand, the electronic spectra of these complexes in DMF solution show d–d bands at 452–490 nm, which can be assigned for square planar nickel(II) complexes

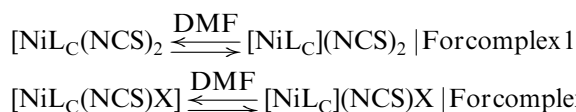
to the ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition [30–32]. The higher ϵ value $103\text{--}123\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ in the visible region is also an indication of square planar configuration.

Molar conductance

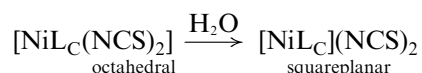
The conductance value of $0\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ for these complexes in CHCl_3 strongly supports the non-electrolytic nature of these complexes, i.e. two anions (two NCS^- ions for complex 1 and NCS^- and X^- for complexes 2–6) are coordinated to nickel(II). No change of colour of these compounds in this solvent from the solid state indicates that the complex does not change its geometry and conformation in this solvent.

On the other hand, the DMF solutions of the complexes are conducting, which indicates that the anionic ligands come out of the coordination sphere in DMF solution. However, the conductance values of $73\text{--}125\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ are little for 1:2 electrolytes. This may be explained as follows.

In DMF solution both anionic ligands come out of the coordination sphere and the 1:2 electrolytes, $[\text{NiL}_C](\text{SCN})_2$ for complex 1 or $[\text{NiL}_C](\text{SCN})\text{X}$ for complexes 2–6 are produced. However, the conversion is not complete and there exists an equilibrium between the octahedral nonelectrolyte $[\text{NiL}_C(\text{SCN})_2]$ and square planar 1:2 electrolyte $[\text{NiL}_C](\text{SCN})_2$.



The change of colour from pink–violet or violet in solid state (and also in chloroform solution) to orange in DMF solution is a strong evidence in favour of change in molecular structure, specially in favour of formation of square planar complex. But the yellow aqueous solution of complex (1) (the solution was made by heating the sample in water for long) showed a conductance value of $209\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ corresponding to 1:2 electrolyte. This may be attributed to complete conversion of octahedral complex (1) to square planar one [29] as expressed by the following expression



The above mentioned anomalies were also noted for analogous nickel(II) complexes [29] and corresponding copper(II) complexes of the same ligand [7].

Crystal structure of complex 1

The molecular structure of diisothiocyanato(3,10-C-meso-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane, L_C)nickel(II), $[\text{NiL}_C(\text{NCS})_2]$ is illustrated in Figure 1. Crystal data and refinement parameters are listed in Table 1. The selected geometric parameters are presented in Tables 2–4. The nickel(II) cation exists in a distorted octahedral geometry defined

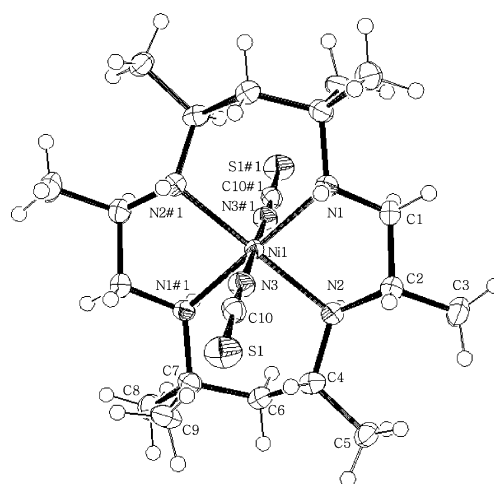


Figure 1. Crystal structure of diisothiocyanato(3,10-C-meso-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane, L_C)nickel(II), $[\text{NiL}_C(\text{NCS})_2]$.

Table 2. The selected bond distances [\AA] and angles [$^\circ$] for *trans*- $[\text{NiL}_C(\text{NCS})_2]$

Ni(1)–N(1)	2.096(4)	Ni(1)–N(1)#1	2.096(4)
Ni(1)–N(2)	2.104(5)	Ni(1)–N(2)#1	2.104(5)
Ni(1)–N(3)	2.115(5)	Ni(1)–N(3)#1	2.115(5)
S(1)–C(10)	1.635(6)	N(1)–C(1)	1.475(7)
N(2)–C(2)	1.494(7)	N(2)–C(4)	1.509(11)
N(3)–C(10)	1.158(7)	C(1)–C(2)	1.533(8)
C(2)–C(3)	1.528(8)	C(4)–C(5)	1.534(12)
C(4)–C(6)	1.596(12)	C(6)–C(7)	1.540(8)
C(7)–C(8)	1.544(8)	C(7)–C(9)	1.522(8)
N(1)#1–Ni(1)–N(1)	180.0(3)	N(1)–Ni(1)–N(2)	84.68(18)
N(2)#1–Ni(1)–N(2)	180.0(3)	N(1)–Ni(1)–N(3)	84.95(18)
N(2)–Ni(1)–N(3)	91.96(19)	N(1)–Ni(1)–N(2)#1	95.32(18)
N(2)–Ni(1)–N(3)#1	88.04(19)	N(1)#1–Ni(1)–N(3)	95.05(18)
N(3)–Ni(1)–N(3)#1	180.0(2)	C(1)–N(1)–Ni(1)	105.3(3)
C(2)–N(2)–C(4)	116.0(5)	C(2)–N(2)–Ni(1)	107.3(3)
C(2)–N(2)–Ni(1)	109.6(5)	C(10)–N(3)–Ni(1)	174.7(5)
N(1)–C(1)–C(2)	110.6(4)	N(2)–C(2)–C(3)	116.2(5)
N(2)–C(2)–C(1)	107.3(4)	C(3)–C(2)–C(1)	107.8(5)
N(2)–C(4)–C(5)	115.7(8)	C(5)–C(4)–C(6)	107.6(7)
N(2)–C(4)–C(6)	105.1(7)	C(7)–C(6)–C(4)	114.9(6)
N(1)#1–C(7)–C(9)	111.6(5)	C(9)–C(7)–C(6)	112.2(5)
N(1)#1–C(7)–C(6)	107.4(4)	C(9)–C(7)–C(8)	108.5(5)
N(1)#1–C(7)–C(8)	109.8(5)	C(6)–C(7)–C(8)	107.3(5)
N(3)–C(10)–S(1)	177.6(5)		

by N_6 donor set with all equatorial chiral methyl group where two NCS groups occupied two axial positions of nickel(II) ion and both of them are bound through N atoms forming N-bonded diisothiocyanato complex. The Ni(1)–N(1) and Ni(1)–N(2) separations of 2.096(4) and 2.104(5) \AA , respectively, are equal to each other and the independent Ni(1)–N(3), N(3)–C(10), and S(1)–C(10) separations are 2.115(5), 1.158(7) and 1.635(6) \AA , respectively. Each bond angle of N(1)#1–Ni(1)–N(1), N(2)#1–Ni(1)–N(2) and N(3)#1–Ni(1)–N(3), is 180° as expected for octahedral geometry. However, though each of other N–Ni–N bond angles is supposed to be 90° as expected for perfect octahedral geometry but they are

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for *trans*-[NiL_C(NCS)₂]U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Ni(1)	0	10000	0	18(1)
S(1)	1542(2)	13473(2)	2187(2)	37(1)
N(1)	2283(6)	9998(6)	-1304(5)	23(1)
N(2)	1719(6)	7744(6)	1554(5)	25(1)
N(3)	701(6)	11596(6)	803(5)	26(1)
C(1)	3578(7)	8240(8)	-647(6)	29(1)
C(2)	3581(7)	7628(8)	1062(6)	28(1)
C(3)	5004(8)	5839(9)	1664(8)	38(1)
C(4)	1281(14)	7754(14)	3112(11)	24(2)
C(5)	2568(11)	6301(10)	4353(9)	28(2)
C(6)	-626(8)	7527(9)	3444(7)	35(2)
C(42)	1310(30)	7010(40)	3180(30)	27(5)
C(52)	2010(30)	7730(30)	4020(20)	34(6)
C(62)	-626(8)	7527(9)	3444(7)	35(2)
C(7)	-2223(7)	9227(8)	2983(6)	27(1)
C(8)	-3920(8)	8766(8)	3561(7)	33(1)
C(9)	-2103(9)	10471(9)	3661(7)	33(1)
C(10)	1041(7)	12404(7)	1349(6)	24(1)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for *trans*-[NiL_C(NCS)₂]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	18(1)	19(1)	17(1)	-7(1)	-2(1)	-4(1)
S(1)	51(1)	34(1)	35(1)	-17(1)	-1(1)	-21(1)
N(1)	22(2)	27(2)	19(2)	-10(2)	1(2)	-7(2)
N(2)	24(2)	25(2)	22(2)	-7(2)	-1(2)	-5(2)
N(3)	31(2)	25(2)	25(2)	-12(2)	1(2)	-10(2)
C(1)	21(3)	32(3)	27(3)	-10(2)	0(2)	-2(2)
C(2)	23(3)	30(3)	27(3)	-11(2)	-2(2)	-4(2)
C(3)	29(3)	36(3)	38(3)	-14(3)	-8(3)	4(3)
C(4)	33(5)	19(5)	21(4)	-6(4)	-1(3)	-12(4)
C(5)	27(4)	25(4)	25(4)	-3(3)	-4(3)	-6(3)
C(6)	27(3)	43(4)	22(3)	-5(2)	-2(2)	-3(3)
C(42)	26(10)	33(14)	20(10)	-11(11)	-4(7)	-7(11)
C(52)	38(12)	48(15)	29(11)	-21(10)	-1(9)	-22(10)
C(62)	27(3)	43(4)	22(3)	-5(2)	-2(2)	-3(3)
C(7)	24(3)	35(3)	22(3)	-11(2)	3(2)	-10(2)
C(8)	26(3)	38(3)	31(3)	-9(3)	1(2)	-12(2)
C(9)	36(3)	47(4)	23(3)	-17(3)	7(2)	-19(3)
C(10)	24(3)	20(2)	25(3)	-8(2)	4(2)	-7(2)

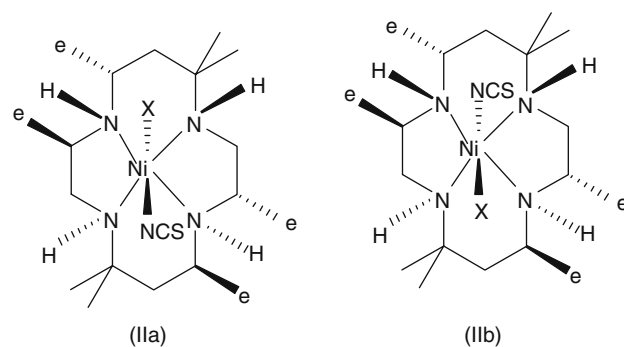
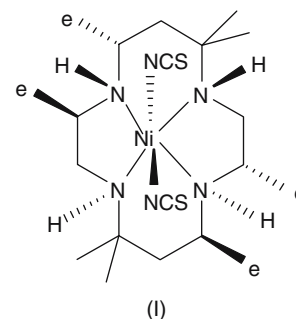
The anisotropic displacement factor exponent takes the form: $-2^2[h^2 a^* U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

deviated, rather summation of each neighbouring pair of bond angles is 180° as evident from Table 3. For example bond angle of N(1)#1-Ni-N(2)#1 is, $84.6(18)^\circ$ and that of N(1)-Ni-N(2)#1 is $95.32(18)^\circ$.

It is noted that on the four chiral N-centres, two NH groups are above N4 equatorial plane and the other two below. This *trans* III form as shown in Figure 1 has been established as the most thermodynamically stable form [12, 26]. As a whole the conformation and configuration of the ligand of this complex is same as that of one diastereois-

meric square planar nickel(II) complex of the same ligand L_C, [NiL_Cβ](ClO₄)₂ [11].

On the basis of above evidences the following a planar *trans*-structure (I) has been assigned to the complex 1 in the solid state.



Since it has been known that axial substitution [20, 21] takes place without change of conformation and configuration of original ligand of the parent complex, so a common structure (IIa) or (IIb) for complexes 2–6 have been assigned.

Supplementary material

Crystallographic data for the structural analysis have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number CCDC 297511. Copies of this information can be obtained free of charge via E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>; Telephone: +44-01223-762910. Facsimile: +44-01223-336033. Postal Address: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

Acknowledgement

TGR is thankful to KOSEF for providing a post-doctoral fellowship. Also Kims and Park wish to acknowledge the support of Korea Research Foundation Grant (KRF-2004-005-C0009).

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