Magnetic and spectroscopic properties of tetragonal $C_{14}H_{28}N_4Ni(NCS)_2$ macrocyclic complex

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meso-3,5,10,12-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) dithiocyanate was obtained from the macroamine and nickel(II) tetraammine diisothiocyanate. The visible spectrum and the magnetic moment (3.23 ± 0.01 B.M.) of compound indicate that in a solid state the nickel cation exists in a pseudo-octahedral triplet ground state, *i.e.* with the thiocyanate anions coordinated to the nickel(II) ion. The infrared spectrum suggests the Ni—NCS coordination of the thiocyanate group.

мезо-3,5,10,12-тетраметил-1,4,8,11-тетраазациклотетрадека-4,11-диен-никель(II) дитиоцианат был получен из макроамина и тиоцианата никеля(II). Спектроскопические исследования и магнитный момент (3.23 ± 0.01 B.M.) этого соединения показали, что в твердом состоянии катион никеля(II) есть в псевдо-октаэдрическом триплетном состоянии, в котором тиоцианатные анионы координированы через ион никеля(II). О характере связи в этом соединении свидетельствуют инфракрасные спектры. Тиоцианатные группы с ионом никеля(II) вероятно связаны по типу Ni—NCS.

Our earlier papers on macrocyclic nickel(II) complexes concerned mainly the square-planar diamagnetic complexes [1—3]. The triplet ground state pseudo-octahedral coordinated nickel(II) thiocyanate derivatives of fourteen-membered macrocyclic ligands, 1,4,8,11-tetraazacyclotetradeca-4,11-dienes, are rather rare compounds. The metastable, violet 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) diisothiocyanate (*I*) obtained by *Busch et al.* [4] is an interesting example of the rare coordination number isomerism. The other isomeric nickel(II) diisothiocyanate complexes of this ligand are diamagnetic with thiocyanate anions hydrogen-bonded to the relatively acidic coordinated secondary amino groups [4, 5].

Paramagnetic nickel(II) thiocyanate derivatives are common among the complexes of larger macrocyclic ligands, *i.e.* the fifteen- and sixteen-membered ones [6, 7].

Experimental

Synthesis

meso-3,5,10,12-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) diisothiocyanate

a) *trans*-$Ni(NH_3)_4(NCS)_2$

Nickel dithiocyanate (Schuchardt) was dissolved in an excess of the saturated aqueous ammonia solution and the reaction mixture was evaporated to dryness. The dissolution in ammonia and evaporation were repeated several times until the homogeneous blue-violet product crystallized from the concentrated solution. The crystals were filtered off, washed with ether, dried *in vacuo* and used without further purification.

Infrared absorption bands (solid, paraffin oil mull): 3350, 3260, 3190 $\nu(NH_3)$; 2100—2060 $\nu(C{\equiv}N)$; 1600, 1200 $\delta(NH_3)$; 777 $\nu(C{=}S)$ (cm^{-1}) (all bands specified) [8].

b) Complex

meso-3,5,10,12-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene [9] (0.5 g; 2 mmol) and *trans*-$Ni(NH_3)_4(NCS)_2$ (0.5 g; 2.1 mmol) in anhydrous methanol (150 cm^3) were heated under magnetic stirring for 8 h at 40°C and boiled for 16 h. Gaseous ammonia evolved and the colour of the solution turned from bluish to yellow.

The unreacted solid was filtered off; the filtrate was evaporated to dryness and recrystallized from aqueous methanol (1:1). The mauve shiny crystals were dried over P_4O_{10}. The yield was 0.6 g (70% basing on starting amine).

For $C_{16}H_{28}N_6S_2Ni$ calculated: 44.99% C, 6.61% H, 19.67% N, 13.74% Ni; found: 45.09% C, 6.67% H, 19.75% N, 13.5% Ni.

Infrared absorption bands (solid, paraffin oil mull): 3210 $\nu(NH)$, 2100 $\nu(C{\equiv}N)$, 1665 $\nu(C{=}N)$, 785 $\nu(C{=}S)$ (cm^{-1}).

Physical measurements

Magnetic susceptibility measurements

Temperature dependence of the magnetic susceptibility was determined (in the range 80—300 K) using a cryostat-controlled Gouy balance. Measurements were made at two magnetic field strengths and no dependence on field strength was observed within the limits of the experimental error.

Mercury tetrathiocyanatecobaltate(II) was used as a susceptibility standard [10]. All the measured susceptibilities were corrected for diamagnetism of the constituent atoms using the Pascal constants [11]. Data were fitted to the Curie—Weiss law, $\mu_{\text{eff}} = 2.83\,(\chi_M(T - \Theta)^{1/2}$, by the least-squares fitting procedure. Correlation coefficients were calculated to determine the accuracy of fit. The calculations were performed by (BGD-1) Fortran computer program using the Odra 1305 computer.

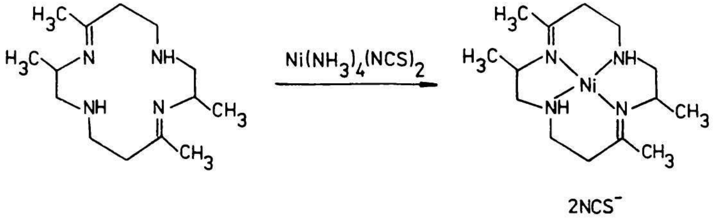
Spectroscopic studies

The electronic absorption and reflectance spectra (in the range 10 000—30 000 cm^{-1}) were measured on the Beckman ultraviolet 5240 Spectrophotometer. Reflectance spectra of the complex were made with a MgO standard and the data are collected in Table 2.

Infrared spectra in the region of 4000—400 cm^{-1} were recorded on a Perkin—Elmer 621 Model Spectrophotometer in Nujol.

Results and discussion

meso-3,5,10,12-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) dithiocyanate (*III*) was obtained from the macroamine (*II*) [9] and nickel(II) tetraammine diisothiocyanate



II *III*

The ligand (*II*) has the *meso* configuration of carbon atoms 3 and 10 [9].

Coordination compound of nickel(II) cation with ligand (*II*) has the centrosymmetric structure axial with both 3,10-methyl groups and with the *meso* *N*-configuration [9]. The *N*-enantiomeric configuration is energetically less convenient because of crowding of equatorial 3-methyl group and 5-methyl group. The thiocyanate is relatively small linear anion, which would not deform the cation of (*III*) strongly when coordinated to the nickel(II) ion. It is very likely that the conformation of ligand (*II*) in compound (*III*) is like that in diperchlorato nickel(II) complex, *i.e.* centrosymmetric [9].

The 1,4,8,11-tetraazacyclotetradeca-4,11-diene ligands in coordinated form are relatively rigid and have no tendency to exist in a folded conformation with anionic ligands *cis*-coordinated to the metal ion [12].

The visible spectrum and the magnetic moment of compound (*III*) indicate that in a solid sample the nickel(II) cation exists in a pseudo-octahedral triplet ground state, *i.e.* with the thiocyanate anions coordinated to the nickel(II) ion [13—16]. The ground state configuration of nickel(II) ion in a regular octahedral field is $^3A_{2g}$ ($t_{2g}^6e_g^2$) and it will be paramagnetic with two unpaired electrons as it follows from a simple energy level diagram. The contribution to the magnetic susceptibility is given by the spin-only term, spin-orbit coupling of the second order, and the temperature independent paramagnetism. The observed magnetic moments of the known tetragonal Ni(II) complexes are in the region of 2.83—3.4 B.M. [17—19]. Magnetic susceptibility over the temperature range 80—300 K reveals a marked temperature dependence (Table 1).

Table 1

Magnetic data of $C_{14}H_{28}N_4Ni(NCS)_2$[a]

T/K	$\chi_M \cdot 10^8$ m^3 mol^{-1}	T/K	$\chi_M \cdot 10^8$ m^3 mol^{-1}
80	20.72	201	8.09
109	15.45	216	7.40
123	13.56	229	7.12
135	12.19	246	6.63
149	11.10	260	6.24
162	10.21	271	6.04
175	9.37	285	5.80
188	8.67	295	5.48

a) Magnetic susceptibilities were corrected for diamagnetism — 0.30×10^{-8} m^3 mol^{-1}.

A Curie—Weiss behaviour was observed for this complex with the Weiss constant equal to 3.4 K and $C = 1.28$ cm^3 mol^{-1} K. The criterion used to determine the best fit is the minimization of the sum of the squares of the deviation A; its value is 7.372×10^9, where $A = \sum_i (\chi_i^{\text{calc}} - \chi_i^{\text{exp}})^2$. Magnetic moment obtained in the measured region was equal to 3.23 ± 0.01 B.M. and it was typical for tetragonal nickel(II) compounds.

In the spectra of octahedral nickel(II) compounds can be observed three bands, corresponding to the $^3A_{2g} \leftarrow {}^3T_{1g}$, $^3A_{2g} \leftarrow {}^3T_{2g}$ (*F*), and $^3A_{2g} \leftarrow {}^3T_{2g}$ (*P*) transition. The lowest energy transition, ${}^3A_{2g} \leftarrow {}^3T_{1g}$, gives an approximate value of the ligand field splitting, 10 Dq.

The $[C_{14}H_{28}N_4Ni]^{2+}$ cation forms the pseudo-octahedral (tetragonal) dithiocyanato complex. The reflectance spectrum of the $C_{14}H_{28}N_4Ni(NCS)_2$ complex (in the range 10 000—30 000 cm^{-1}) shows six bands (Table 2). The bands at 28 700 and 20 400 cm^{-1} are intensive, broad and asymmetric. Bands observed between 10 000—15 000 cm^{-1} are rather very weak in intensity. For two energetically highest bands, corresponding to the ${}^3A_{2g} \leftarrow {}^3T_{1g}$ (P) and ${}^3A_{2g} \leftarrow {}^3T_{1g}$ (F) transitions of the octahedral field or to the ${}^3B_{1g} \leftarrow ({}^3E_g, {}^3A_{2g})$ and ${}^3B_{1g} \leftarrow ({}^3E_g, {}^3A_{2g})$ transitions of the tetragonal field [20—24], no splittings are observed, but only their asymmetry. The energetically lowest band corresponding to the ${}^3A_{2g} \leftarrow {}^3T_{2g}$ octahedral transition underwent the splitting.

Table 2

Spectra of $C_{14}H_{28}N_4Ni(NCS)_2$ complex

Reflectance spectra (band position) cm^{-1}	Absorption spectra (band position) cm^{-1}	ε_{mol}/mol^{-1} cm^{-1}
28 700	44 100	21 850
20 400	35 600	4 150
14 600	22 400	73
13 000	15 400	17
12 600		
11 600		

It seems to be likely that the bands at 11 600, 12 600, and 13 000 cm^{-1} correspond to the ${}^3B_{1g} \leftarrow {}^3E_g$ transitions while the band at 14 600 cm^{-1} corresponds to the forbidden transition of the octahedral field, ${}^3A_{2g} \leftarrow {}^1E_g$ [25] and ${}^1A_{1g} \leftarrow {}^3B_{1g}$ transition in D_{4h} symmetry.

Two transitions very close to each other at 12 600 and 13 000 cm^{-1} may suggest the splitting of the ${}^3E_g$ level in tetragonal complex due to the lowering of the symmetry of a complex below D_{4h} in solid phase.

Thus, the band at 11 600 cm^{-1} should be assigned to the ${}^3B_{1g} \leftarrow {}^3B_{2g}$ transition, while the doublet at 12 600 and 13 000 cm^{-1} would correspond to the ${}^3B_{1g} \leftarrow {}^3E_g$ transition.

Absorption spectrum of that complex in aqueous solution is markedly different from the reflectance spectrum. In the range 10 000—30 000 cm^{-1} a couple of bands are replaced by one band only at 22 500 cm^{-1}, with the molar extinction coefficient equal to 73 mol^{-1} cm^{-1}. That band should be attributed to the ${}^1A_{1g} \leftarrow {}^1B_{1g}$ transition in the square-planar nickel(II) compounds. The spectrum of that type is the obvious evidence for dissociation of the complex in aqueous solution [26] and for the change of the metallic centrum environment symmetry from octahedral to square-planar

$$\mathrm{NiN_4(SCN)_2} \rightleftharpoons \mathrm{NiN_4^{2+}} + 2\mathrm{NCS^-}$$

Since the infrared spectrum of the complex (Table 3) shows no bands in the range 690—720 $\mathrm{cm^{-1}}$ and the peak corresponding to the ν_3 vibration appears at 785 $\mathrm{cm^{-1}}$, the thiocyanate group bonding could be supposed to be of the Ni—NCS type [27—32].

Table 3

Infrared spectra of $\mathrm{C_{14}H_{28}N_4Ni(NCS)_2}$ complex ($\tilde{\nu}/\mathrm{cm^{-1}}$)

437 m	954 s	1323 m
473 w	982 m	1347 vw
480 w	997 s	1378 s
495 w	1023 m	1410 w
574 m	1066 w	1460 s, b
595 w	1093 m	1490 w
623 w	1102 w	1671 s
785 m	1133 m	2040 w
837 w	1143 m	2095 vs
848 m	1208 s	...
900 m		3225 s

m — medium, w — weak, vw — very weak, s — strong, vs — very strong, b — broad.
Values given in $\mathrm{cm^{-1}}$.

The single ν(NH) and ν(C≡N) thiocyanate bands indicate that no hydrogen bonding between NH and NCS groups exists in the compound (*III*). On the other hand, the close similarity of the absorption bands position in solid compounds (*I*) and (*III*) allows to suggest the centrosymmetric structure of the compound (*I*). For the compound (*III*) we have proposed the tetragonal structure with the symmetry centre on nickel(II) ion.

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