Inorganica Chimica Acta, 121 (1986) 47–51

Influence of Ligand Properties on Stoichiometry and Stereochemistry of Solid Thiocyanate Nickel(II) Complexes with Piperidine Derivatives

M. KOMAN, E. JÓNA and E. ĎURČANSKÁ

Department of Inorganic Chemistry, Slovak Technical University, 812 37 Bratislava, Czechoslovakia

(Received April 10, 1986)

Abstract

Stoichiometry and stereochemistry of the solid thiocyanate nickel(II) complexes with various piperidine ligands have been studied. The prepared complexes can be arranged into three groups by their composition: the first group includes the compound $Ni(NCS)_2(pip)_4$ (pip = piperidine) with monomeric pseudooctahedral configuration; the second one contains pentacoordinated complexes $Ni(NCS)_2L_3$ (L = 4-Mepip; 3,5-Me_2pip); the third group includes the complexes $Ni(NCS)_2L_2$ with the polymeric pseudooctahedral configuration (L = pip, 4-Mepip and 3,5-Me_2pip) or with the square-planar configuration (L = 2-Mepip and 2,6-Me_2pip). These results are discussed in relation to the corresponding complexes with pyridine ligands.

Introduction

Piperidine and its derivatives can be regarded as biogenetic amines since they are formed by activity of some enzymes (karboxylyases). On the other hand, some derivatives of piperidine are used as plastic additives (they cause quenching of the reactions of singlet oxygen [1, 2]). Known quenchers include also various nickel(II) complexes [3].

From this aspect our attention has been paid to the study of stoichiometry and stereochemistry of the thiocyanate nickel(II) complexes with piperidine ligands. It was expected that a change of the position of methyl substituents on the piperidine ligand would cause a change in the stereochemistry and stoichiometry of the complexes. The present results should contribute to preparations of complexes with expected geometry and properties (analogously to the pyridine complexes [4]).

Experimental

Starting Materials

The liquid piperidine derivatives (Reachim, Koch or Janssen) were distilled under reduced pressure. $Ni(NCS)_2$ was prepared by isothermal heating of $Ni(NCS)_2$(pyridine)$_4$ at 493 K.

Analysis

Nickel was determined by EDTA titration; carbon, hydrogen and nitrogen by microanalysis (Carlo Erba Model 11-02).

Physical Measurements

Magnetic moments were measured with a Gouy balance for the powder solids at 293 K. Electronic (d–d) spectra of the solid samples in nujol mulls were recorded with a Unicam SP 700 C spectrophotometer and infrared absorption spectra with a UR Model 20 spectrophotometer in the range of 4000 to 400 cm^{-1} at room temperature.

Preparation of the Complexes

The preparation of the complex compound $Ni(NCS)_2(pip)_4$ has been described by Eggli and Ludwig [5]. This synthesis was modified as follows: 0.02 mol of $Ni(NCS)_2$ was suspended in 50 cm^3 of benzene and 0.1 mol of piperidine was added. This system had been boiled with stirring under reflux for 5 h. Then the suspension was poured into a crystallizing dish and allowed to crystallize freely for 15–20 h. Blue crystals resulted, the chemical analysis of which led to the formula $Ni(NCS)_2(pip)_4$ (**I**). Additional complexes with the composition $Ni(NCS)_2$(4-Mepip)$_3$ (**II**), $Ni(NCS)_2$(3,5-Me_2pip)$_3$ (**III**), $Ni(NCS)_2$(2-Mepip)$_2$ (**VII**) and $Ni(NCS)_2$(2,6-Mepip)$_2 \cdot C_6H_6$ (**VIII**) were prepared analogously. The $Ni(NCS)_2(pip)_2$ (**IV**), $Ni(NCS)_2$(4-Mepip)$_2$ (**V**) and $Ni(NCS)_2 \cdot$(3,5-Me_2pip)$_2$ (**VI**) complexes were prepared by isothermal heating of starting complexes at 363 K (on the basis of the thermogravimetric curves).

Results and Discussion

The nickel(II) complexes described above are listed in Table I together with their characteristic properties. Relevant conclusions concerning the stereochemistry of the complexes were drawn from stoichiometry, electronic absorption spectra, infrared

0020-1693/86/$3.50

TABLE I. Magnetic Moments, Electronic and Infrared Absorption Spectra of Ni(II) Complexes with Piperidine Ligands

Complex	μ_{eff} (BM)	Electronic absorption spectra, maxima of electronic bands (cm^{-1})					Infrared spectra		
							ν_{CN}	ν_{CS}	ν_{NCS}
$Ni(NCS)_2(pip)_4$ (I)	3.29	9000	15000	26000			2090	800	475
$Ni(NCS)_2(4\text{-}Mepip)_3$ (II)	3.23	6200	11500br[a]	15400	21500sh[b]	24750	2080 2070	810	480
$Ni(NCS)_2(3,5\text{-}Mepip)_3$ (III)	3.20	6000	11700br	15400	21500sh	25000	2080 2065	798	470
$Ni(NCS)_2(pip)_2$ (IV)	3.20	8200	10600	16100	29900[c]		2120	800	465
$Ni(NCS)_2(4\text{-}Mepip)_2$ (V)	3.17	8100	10600	16000	29600		2120	810	460
$Ni(NCS)_2(3,5\text{-}Me_2pip)_2$ (VI)	3.22	8200	10800	16100	29900		2120	785	470
$Ni(NCS)_2(2\text{-}Mepip)_2$ (VII)	0.62	19600					2108	860	480 470
$Ni(NCS)_2(2,6\text{-}Mepip)_2 \cdot C_6H_6$ (VIII)	0.70	19100					2107	853	485 475

[a] br = broad. [b] sh = shoulder. [c] Partial overlap with charge transfer band.

absorption spectra and magnetic moments. Stoichiometry of the complexes arranges them into the three groups: $Ni(NCS)_2L_4$, $Ni(NCS)_2L_3$ and $Ni(NCS)_2L_2$ complexes.

$Ni(NCS)_2L_4$ Complexes (L = pip)

The effective magnetic moment and the maxima of the absorption bands for these complexes are within the region usually found for paramagnetic pseudo-octahedral nickel(II) complexes [6]. The NCS groups are terminally coordinated (ν_{CN} below 2100 cm^{-1}), through the nitrogen atom only (the absence of ν_{CS} in the region 690–730 cm^{-1}) [7].

Thus the three bands observed in the electronic absorption spectra (Table I) can be assigned to the three spin allowed transition ${}^3T_{2g} \leftarrow {}^3A_{2g}$, ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$ and ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$ in O_h symmetry. However, the energy difference between the levels ${}^3T_{1g}(P)$ and ${}^3T_{1g}(F)$ calculated from the appropriate secular equations [8] is about 5500 cm^{-1} higher than the difference $\nu_3 - \nu_2$ included in Table I. This difference indicated a considerable distortion from O_h symmetry. It is likely that in order to minimise inter-ligand repulsion, the Ni–N(pip) bonds are lengthened, thus leading to a distortion of the octahedral polyhedron and the unusually low value of 10 *Dq* for piperidine [5]. This assumption has been confirmed by the X-ray structure analysis (Fig. 1) [9]. The equatorial plane of the $Ni(NCS)_2(pip)_4$ is formed by four N atoms from the piperidine molecules ($Ni–N_1$ = 228 pm, $Ni–N_2$ = 236 pm) and the axial positions are occupied by two N atoms from the NCS groups (Ni–N(NCS) = 200 pm). Thus, structural data of $Ni(NCS)_2(pip)_4$ complex indicate the significant increase of Ni–N(pip) interatomic distances in comparison with those for the analogous pyridine complexes (Table IV).

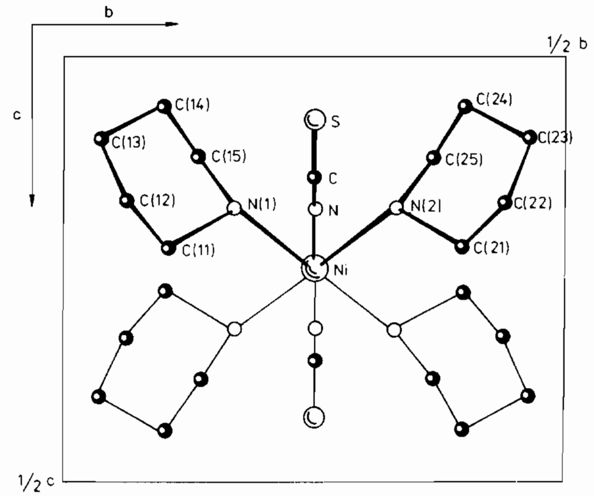

Fig. 1. The scheme of the molecular structure of $Ni(NCS)_2(pip)_4$.

$Ni(NCS)_2L_3$ Complexes (L = 4-Mepip; 3,5-Me_2pip)

The stoichiometry of these complexes is compatible with monomeric pentacoordinate or polymeric hexacoordinate Ni(II) complexes. All $Ni(NCS)_2L_3$ complexes show a strong absorption band ν_{CN} at about 2080 cm^{-1} and ν_{CS} at about 800 cm^{-1}; these values correspond to the terminally bonded thiocyanate groups through the N atom. The splitting of the ν_{CN} band can be associated with the nonlinearity of NCS groups or interactions in crystal structure [7]. The number of bands in the electronic absorption spectra (Table I), their width and the position of the absorption maxima of these bands are indicative of a pentacoordinated Ni(II) atom in the $Ni(NCS)_2L_3$ complexes [10]. For a five-coordinate chromophore NiN_5, two idealized geometries, square pyramid (C_{4v} symmetry) and trigonal bipyramid (D_{3h} symmetry), must be considered. The calculated band energies for high spin Ni(II) in C_{4v} and D_{3h} [11] are compared with those observed for $Ni(NCS)_2L_3$ complexes (Table II). The above considerations show that an unambiguous assignment of the local symmetry in $Ni(NCS)_2L_3$ complexes is rather difficult. On the basis of the crystal field model, C_{4v} symmetry is favoured. Stereochemical considerations support [5] D_{3h} symmetry (NCS ligands in axial positions of a trigonal bipyramid probably decrease the steric strain). In the similar complex $Ni(NCS)_2(2,4\text{-}Me_2py)_3$, five coordination (chromophore NiN_5) has been assumed [12] on the basis of d–d transition spectra, and trigonal-bipyramidal configuration was confirmed by the X-ray structure analysis [13].

$Ni(NCS)_2L_2$ Complexes

The $Ni(NCS)_2L_2$ complexes with L = pip, 4-Mepip and 3,5-Me_2pip have an effective magnetic moment and maxima of absorption bands in the interval given for hexacoordinated pseudooctahedral complexes [4, 6]. A strong absorption band at about 2120 cm^{-1} in infrared spectra (Table I) indicate a polymeric structure with bidentate NCS groups [4, 7, 14]. This band (ν_{CN}) is observed at higher frequencies (30 cm^{-1}) for the complexes under study compared with monomeric $Ni(NCS)_2(pip)_4$ complex. The first band in the electronic absorption spectra in the region 8000 to 12000 cm^{-1} exhibits pronounced splitting, analogous to similar complexes with pyridine ligands [4, 15]. With respect to the predicted NiN_4S_2 chromophore [4] a marked tetragonal distortion is considered in these complexes. (The splitting of the second band was not observed; however, the shape of this band suggests that it contains two close components.) The position of the maxima of the absorption bands in the region 27000–30000 cm^{-1} cannot be found precisely because of remarkable overlap with the charge transfer band. The red $Ni(NCS)_2(2\text{-}Mepip)_2$ and $Ni(NCS)_2(2,6\text{-}Me_2pip)_2 \cdot C_6H_6$ complexes exhibit small positive corrected molar susceptibilities. They are probably temperature independent susceptibilities conditioned by the Zeeman effect of the second order. Consequently, these complexes can be considered as monomolecular square-planar species with a basic singlet state $^1A_{1g}$. This conclusion is supported by the electronic absorption spectra (a distinct band with the maximum at 19600 cm^{-1} or 19200 cm^{-1}) [4–6], by the infrared spectra (ν_{CN} at 2800 or 2110 cm^{-1} and ν_{CS} at 860 or 862 cm^{-1}) [4, 12, 14] as well as by the X-ray structure analysis of $Ni(NCS)_2 \cdot (2,6\text{-}Me_2pip)_2 \cdot C_6H_6$ complex [22]. The last compound was found to have clathrate character; it is formed by the square-planar $Ni(NCS)_2(2,6\text{-}Me_2pip)_2$ molecules and by the benzene molecules held together by weak van der Waals bonds with the shortest contacts between the methyl groups of the 2,6-Me_2pip ligands and the benzene molecules (Fig. 2).

Comparison of the Stoichiometry and Stereochemistry of Piperidine and Pyridine Nickel(II) Thiocyanate Complexes

Based on the data collected in Table III and IV, the following conclusions can be drawn:

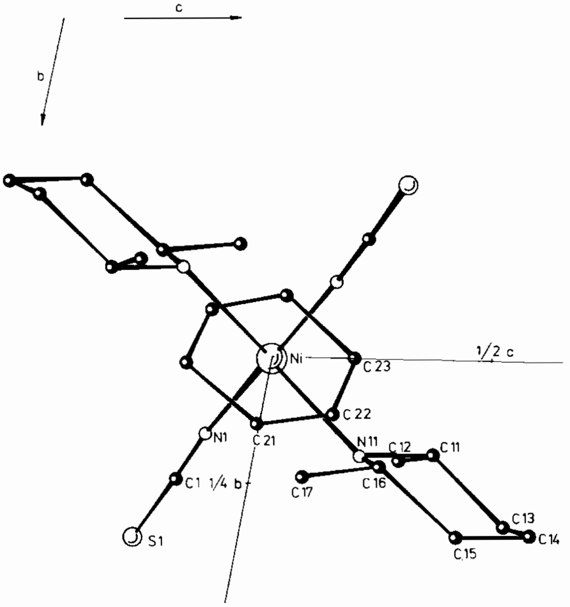

Fig. 2. The scheme of the molecular structure of $Ni(NCS)_2$-$(2,6\text{-}Me_2pip)_2 \cdot C_6H_6$.

TABLE II. Calculated Band Energies for C_{4v} and D_{3h} Symmetry and Observed for $Ni(NCS)_2(R\text{-}pip)_3$ Complexes

Energies (cm^{-1})					
Calculated C_{4v}		R		Calculated D_{3h}	
		4-Me	3,5-Me_2		
$^3B_1 \rightarrow {}^3E(F)$	5900	6200	6000	5400	$^3E' \rightarrow {}^3E''(F)$
$^3B_2, A_2(F)$	11000	11500	11700	13700	$^3A''_2, {}^3A''_1(F)$
$^3E(F)$	16600	15400	15400	14200	$^3A'_2(F)$
$^3A_2(P)$	23500	21500	21500	21300	$^3E''(P)$
$^3E(P)$	26000	24800	25400	25400	$^3A'_2(P)$

TABLE III. Comparison of Stoichiometry and Stereochemistry of Solid Thiocyanate Nickel(II) Complexes with Piperidine and Pyridine Ligands

L	Stereochemistry	Complex	L	Stereochemistry
			py	monomeric-O [16]
pip	monomeric-O	$Ni(NCS)_2L_4$	4-Mepy	monomeric-O [17, 18]
			3,5-Me_2py	monomeric-O [12]
4-Mepip 3,5-Me_2pip	P	$Ni(NCS)_2L_3$	4-Mepy	dimeric-O [19]
pip	polymeric-O	$Ni(NCS)_2L_2$	py	polymeric-O [20]
4-Mepip	polymeric-O		4-Mepy	polymeric-O [20]
3,5-Me_2pip	polymeric-O		3,5-Me_2py^a	polymeric-O [12]
2-Mepip	Sq		2-Mepy	Sq [20]
2,6-Me_2pip^b	Sq		2,6-Me_2py	Sq [12]

[a] $Ni(NCS)_2(3,5\text{-}Me_2py)_{1.5}$; O = octahedral, P = pentacoordinated, Sq = square-planar complex. [b] $Ni(NCS)_2(2,6\text{-}Mepip)_2 \cdot C_6H_6$.

TABLE IV. Structural Data for Solid $Ni(NCS)_2L_4$ Complexes with Piperidine and Pyridine Ligands

Complex	R_a^{a} (pm)	R_e^{b} (pm)	$R_a - R_e$	Reference
$Ni(NCS)_2(pip)_4$	200.0	232.0	32	9
$Ni(NCS)_2(py)_4$	206.0	216.0	10	16
α-$Ni(NCS)_2(4\text{-}Mepy)_4$	206.8	212.8	6	17
β-$Ni(NCS)_2(4\text{-}Mepy)_4$	206.4	212.8	6.4	18
$Ni(NCS)_2(3\text{-}Etpy)_4$	205.0	212.7	7.7	21
$Ni(NCS)_2(3\text{-}Etpy)_4$	205.0	216.2	11.2	21

[a] R_a = The mean value of Ni–N(NCS) distances (in the axial position). [b] R_e = The mean value of Ni–N(pipe or py) distances (in the equatorial plane.

(i) The influence of 2-methyl-substituted heterocyclic ligands on the stoichiometry and stereochemistry of the complex is evident. Owing to the steric and electronic properties of the ligands [4], complexes of the composition $Ni(NCS)_2L_2$ with a square-planar configuration have been isolated in the solid state.

(ii) The 3- or 4-methylpiperidine ligands form either five-coordinated complexes $Ni(NCS)_2L_3$ or pseudooctahedral complexes $Ni(NCS)_2L_2$ while the similar pyridine complexes are always pseudooctahedral.

(iii) A comparison of the mean values of Ni–N-(pip or py) distances in the equatorial plane (R_e) with those of Ni–N(NCS) in the axial position (R_a) found for $Ni(NCS)_2L_4$ complexes shows a smaller tetragonal distortion for pyridine complexes compared with that found for the piperidine complex. It is evident from Table IV that the values of ($R_a - R_e$) differences (32 pm) in the pyridine complexes are considerably changed (from 6.0 to 11.2 pm) in comparison with the piperidine complex. Thus, the properties of heterocyclic ligands play an important role in the tetragonal distortion of these complexes.

(iiii) Increase of the Ni–N(piperidine) distances in the equatorial plane (in comparison with pyridine ligands) results in decreasing of the axial Ni–N(NCS) distances. Thus, the central atom–axial ligand distances depend on the central atom–equatorial ligand distances. This is in agreement with the conception of the equatorial–axial interactions of the ligands [23.]

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