*Contribution from the Anorganish-Chemisches Institut,
The University, Zürich, Rämistrasse 76, Switzerland*

Four-, Five-, and Six-Coordinate Nickel(II) in Complexes of Pseudohalide Ions and Piperidine Ligands

R. Eggli and W. Ludwig

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The preparations of the pseudohalide complexes $Ni(NCX)_2(piperidine)_4$ ($X = S, Se$), $Ni(NCO)_2(piperidine)_3$ and $Ni(NCX)_2(2,6\text{-dimethylpiperidine})_2$ ($X = O,S$) are reported. Ligand field spectra have been used to assign their coordination geometries. The stereochemistry depends on the nature of the pseudohalide ion as well as on the steric requirements of the piperidine ligands. 2,6-Dimethylpiperidine only forms planar complexes. Piperidine forms solid six coordinate complexes $Ni(NCX)_2(piperidine)_4$ ($X = S, Se$), but the shape of this ligand appears to be such as to stabilise also the coordination number five (solid $Ni(NCO)_2(piperidine)_3$ and complexes in solutions of all three pseudohalide ions) and a four coordinate planar configuration (solutions of isocyanate– and isothiocyanate complexes).

Introduction

It is well known that coordination numbers and symmetries in mixed complexes of the type NiX_2L_n ($X = Cl^-, Br^-, I^-$, L = derivatives of pyridine, n = 2,4) depend to a great extent on the steric requirements of the pyridine ligands[1]. We investigated the coordination behaviour of piperidines which are more bulky than the corresponding pyridines, in nickel(II) complexes of the pseudohalogen ions NCO^-, NCS^- and $NCSe^-$

Experimental

Nickel(II) complexes of pseudohalide ions and piperidines are sensitive to moisture. All preparations have therefor been carried out with carefully dried solvents and reagents.

$Ni(NCO)_2(piperidine)_3$: 1 gr of $Ni(NCO)_2(NH_3)_4$ was boiled with 5 ml of piperidine in 50 ml of tetrahydrofurane for 1 hr. Then, residual undissolved solid was filtered off. A green solid separated on cooling which was filtered off, washed with cyclohexane and dried over P_2O_5 at atmospheric pressure.

Anal: calcd. for $C_{17}H_{33}O_2N_5Ni$: C, 51.3% H, 8.4%
found: C, 50.8%, H, 8.2%.

$Ni(NCO)_2(NH_3)_4$ was precipitated with gaseous NH_3 from a solution of $Ni(NCO)_2(pyridine)_4$ in dichloromethane. The pyridine complex was prepared as described by Nelson and Shepherd[2].

$Ni(NCS)_2(piperidine)_4$. This complex was prepared by heating $Ni(NCS)_2$ with excess of piperidine in tetrahydrofurane as described above for $Ni(NCO)_2$-(piperidine)$_3$.

Anal: calcd. for $C_{22}H_{44}N_6S_2Ni$: C, 51.3%, H, 8.6%
found: C, 51.9%, H, 8.6%.

$Ni(NCSe)_2(piperidine)_4$. A solution containing 1 gr of $Ni(NCSe)_2$ (equivalent amounts of $Ni(NO_3)_2 \cdot 6H_2O$ and KNCSe in 50 ml of acetone) was boiled for 15 min. with 5 ml of piperidine. A bright green solid, consisting mainly of polymeric $Ni(NCSe)_2$(piperidine)$_2$ precipitated on cooling. Then, 20 ml of piperidne were added and the whole mixture was carefully heated again until the colour of the solid had changed to dark green. This solid was filtered off, washed with cyclohexane and dried over P_2O_5 at atmospheric pressure.

Anal: calcd. for $C_{22}H_{44}N_6Se_2Ni$: C, 43.4%, H, 7.3%
found: C, 42.9%, H, 7.3%.

$Ni(NCX)_2(2,6\text{-dimethylpiperidine})_2(X = O,S)$. These complexes were prepared according to the methods given above for the piperidine complexes of the corresponding pseudohalides.

Anal: calcd. for $C_{16}H_{30}O_2N_4Ni$: C, 52.1%, H, 8.2%
found: C, 51.8%, H, 7.9%.

calcd. for $C_{16}H_{30}S_2N_4Ni$: C, 47.9%, H, 7.5%
found: C, 47.8%, H, 7.4%.

Spectral measurements were carried out with a Beckman DK-2A spectrophotometer. The samples used for recording diffuse reflectance spectra were obtained by grinding the complex with the fivefold amount of dry $BaSO_4$.

A slight amount of the appropriate piperidine ligand was usually added to the solutions prepared for recording spectra of the complexes. If no piperidine ligand is present, decomposition probably due to moisture occurs, resulting in a slow decolorisa-

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(1) W. Ludwig and G. Wittmann, *Helv. Chim. Acta*, *47*, 1265 (1964).

(2) S.M. Nelson and T.M. Shepherd, *Inorg. Chem.*, *4*, 813 (1965).

Table I. Characteristic properties of Ni^{II} pseudohalide complexes with piperidine (pip) and 2,6-dimethylpiperidine (dpip).

Complex		color of solid	solvent	color of solution
$Ni(NCO)_2(pip)_3$	paramagnetic	bright green	CH_2Cl_2+pip [a]	bright green
			$CHCl_3$	red
$Ni(NCS)_2(pip)_4$	paramagnetic	blue green	CH_2Cl_2+pip [a]	bright green
			$CHCl_3$	red
$Ni(NCSe)_2(pip)_4$	paramagnetic	dark green	CH_2Cl_2+pip [a]	bright green
			$CHCl_3$	bright green
$Ni(NCO)_2(dpip)_2$	diamagnetic	bright red	CH_2Cl_2	red
$Ni(NCS)_2(dpip)_2$	diamagnetic	dark red	CH_2Cl_2	red

[a] 0.1 *M* solution of piperidine.

Table II. Ligand field bands of Ni^{II} pseudohalide complexes with piperidine (pip) and 2,6-dimethylpiperidine (dpip).

Complex	solvent	band maxima, ν, kK, (ε)				
$Ni(NCO)_2(pip)_3$	R [a]	5.4	11	15.4	21.8sh	25.3
	CH_2Cl_2+pip [b]	5.9(23)	11.8sh(11)	15.2(31)		25.2(117)
	$CHCl_3$	5.4		14.9sh	20.0sh	25.8
$Ni(NCS)_2(pip)_4$	R [a]		8.9	16.1		25.3sh
	CH_2Cl_2+pip [b]	6.5(39)	11sh(9)	15.5(49)		24.5(190)
	$CHCl_3$	6.6	11.6sh	16.4	19.6	25.6sh
$Ni(NCSe)_2(pip)_4$	R [a]		9.8	16.6		26.6
	CH_2Cl_2+pip [b]	6.7(13)		16.0(29)		
	$CHCl_3$	6.6		16.0		
$Ni(NCO)_2(dpip)_2$	R [a]				19.6	
	CH_2Cl_2+dpip [c]				19.1(170)	
$Ni(NCS)_2(dpip)_2$	R [a]				19.1	
	CH_2Cl_2+dpip [c]				19.0(240)	

[a] diffuse reflectance. [b] large excess of piperidine (0.1 *M* solution of piperidine). [c] slight excess of piperidine (0.01 *M* solution of 2,6-dimethylpiperidine).

tion of the solution and the formation of white precipitates. Exact measurements of band intesities were not possible under such conditions, but band maxima could still be evaluated with sufficient precision. The magnetic properties of all complexes were checked qualitatively.

Results and Discussion

The metal complexes which have been prepared are listed in Table I together with their characteristic properties.

The pseudohalides NCO^-, NCS^- and $NCSe^-$ are potential ambidentate ligands. However, since only N-bonded NCX^- has yet been observed in mononuclear nickel(II) complexes, all pseudohalides in the prepared complexes are expected to be bonded through their nitrogen end.

Relevant conclusions concerning the stereochemistry of the complexes were drawn from stoichiometry and ligand field spectra. The positions of the band maxima observed in the spectra are listed in Table II. Only ligand field bands are reported.

Six coordinate complexes. The diffuse reflectance spectra of the piperidine (pip) complexes $Ni(NCS)_2(pip)_4$ and $Ni(NCSe)_2(pip)_4$ (Figure 1) resemble those displayed by the corresponding pyridine[2] and ammonia complexes[3] which in the case of NCS^- are known to have a trans octahedral structure[4] and exhibit ligand field spectra corresponding to a NiN_6 chromophore of octahedral symmetry.

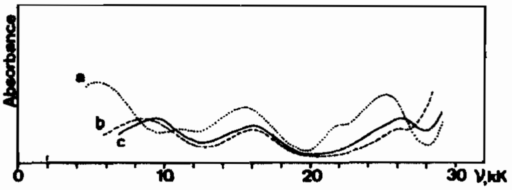

Figure 1. Diffuse reflectance spectra for: a $Ni(NCO)_2(pip)_3$, b $Ni(NCS)_2(pip)_4$), c $Ni(NCSe)_2(pip)_4$ (arbitrary scale for absorbance).

Thus the three bands observed in the visible spectra of $Ni(NCX)_2pip_4$ (X=S, Se) at approximately 9(ν_1), 16(ν_2) and 26(ν_3) kK (Table II) can be assigned to the three spin allowed transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$, ${}^3T_{1g}(F)$ and ${}^3T_{1g}(P)$ in O_h symmetry. However, the energy difference between the levels ${}^3T_{1g}(P)$ and ${}^3T_{1g}(F)$, calculated from the appropriate secular equations[5] with $10\,Dq = \nu_1$ and $15B = \nu_2 + \nu_3 - 3\nu_1$ is 2.5 kK higher than the difference ν_3–ν_2 observed in the spectrum of $Ni(NCS)_2pip_4$ (1.1 kK in $Ni(NCSe)_2(pip)_4$). This indicates a considerable distortion from O_h symmetry[5] which is more pronounced in the isothiocyanate than in the isoselenocyanate complex, but neglegibly small in the corresponding pyridine[2]

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(3) C.R. Hare and C.J. Ballhausen, *J. Chem. Phys.*, *40*, 792 (1964).

(4) E.K. Yukhno and M.A. Porai-Koshits, *Kristallografiya*, *2*, 239 (1957); M.A. Porai-Koshits and A.S. Antsyshkina, *Kristallografiya*, *3*, 694 (1958).

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and ammonia[3] complexes. Application of the "average environment rule"[5] to the spectra of both complexes, using the ligand field parameters 10 Dq = 9.6 and 10.0 kK for NCS^- and NCSe[6], places piperidine below isothiocyanate in the spectrochemical series, although the reverse position is usually observed for amines (10 $Dq(NH_3)$ = 10.8 kK). It is likely that in order to minimise interligand repulsion, the Ni-N (pip) bonds are lengthened thus leading to an unusually low value of 10 Dq for piperidine. Similar effects have been observed in the spectra of other nickel complexes with sterically hindered amines[7][8].

Five coordinate complexes. The stoichiometry of $Ni(NCO)_2pip_3$ is compatible with a mononuclear five coordinate or a polynuclear six coordinate nickel complex. The complex shows approximately identical spectra in the solid state and in a solution of dichloromethane containing a large excess of piperidine (Figure 2). The pattern of dd bands is not consistent with that expected for six coordinate Ni^{II} and tho high intensities of the main bands clearly indicate the absence of a centre of inversion in the chromophore. It can therefore be assumed that five coordinate complexes $Ni(NCO)_2pip_3$ are present in the solid state and in solutions. For a five coordinate chromophore NiN_5, two idealized geometries, square pyramid (C_{4v} symmetry) and trigonal bipyramid (D_{h3} symmetry), must be considered.

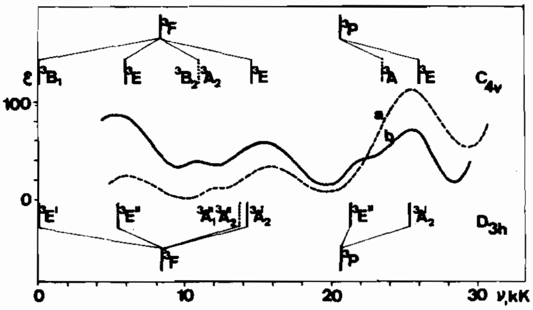

Figure 2. Ligand field spectra of $Ni(NCO)_2pip_3$ (a in 0.1 *M* solution of pip in CH_2Cl_2, b diffuse reflectance spectrum) and calculated energies of terms for spin allowed transitions in C_{4v} (calcd. for Dq(axial)=Dq(basal)=1.1 kK, angle N(axial)-Ni-N(basal)=100°) and D_{3h} symmetry (calcd. for Dq(axial) =Dq(equatorial)=1.3 kK). ——— level for symmetry allowed transition; .... level for symmetry forbidden transition.

A first attempt to evaluate the geometry of the coordination polyhedron has been based on a quantitative assignment of the dd bands using crystal field splitting diagrams which have been calculated by Ciampolini[9] for high spin Ni^{II} in C_{4v} and D_{3h} symmetry. The calculated band energies for C_{4v} and D_{3h} symmetry which give the best fit with the observed reflection spectrum of $Ni(NCO)_2pip_3$ are compared with the latter in Figure 2 and Table III. In C_{4v} symmetry, six spin allowed transitions are expected, but only the three transitions $^3B_1 \rightarrow {}^3E(F)$, $^3E(F)$ and $^3E(P)$ are symmetry allowed. In accordance with these selection rules, the three principal bands of high intensities at 5.4, 15.4, and 25.3 kK can be assigned to these transitions (calculated energies: 5.9, 14.6, and 26.0 kK). The weak band at 11 kK and the shoulder at 21.8 kK can therefore be assigned to the orbitally forbidden transitions $^3B_1 \rightarrow ({}^3A_2(F), {}^3B_2(F))$ and $^3A_2(P)$, which are expected at 11.0 and 23.5 kK. The value Dq (apical) = Dq(basal) = 1.1 kK which has been found to give the best fit is in agreement with an average Dq of 1.0 kK estimated for $Ni(NCO)_2pip_3$, if Dq(NCO) and Dq(pip) are approximated by Dq(NCS) = 9.6 kK[6] and $Dq(NH_3)$ = 10.8 kK[5]. In D_{3h} symmetry, the energies of all six spin allowed transitions calculated with Dq(axial) = Dq(equatorial) = 1.3 kK fit reasonably well to the observed band positions, but significant disagreement arises if the selection rules are considered: Within the ^3F manifold, the two allowed transitions $^3E' \rightarrow {}^3E''$ and $^3A_2'$ can be assigned to the intense bands at 5.4 and 15.4 kK (calculated energies 5.4 and 14.2 kK) and the symmetry forbidden transitions $^3E' \rightarrow ({}^3A_1'', {}^3A_2'')$, which were both expected at 13.7 kK, to the weak band at 11 kK. However, the transitions to the two levels $^3E''$ and $^3A_2'$ originating from ^3P are both orbitally allowed, but only the band at 25.3 kK has a sufficiently high intensity to confirm the assignment to the $^3E' \rightarrow {}^3A_2'$ transition, whereas the shoulder at 21.8 kK is too weak to be observed in the solution spectrum, thus making the assignment to the symmetry allowed transition $^3E' \rightarrow {}^3E''$ somewat doubtful.

Table III. Tentative band assignment in C_{4v} and D_{3h} symmetry for diffuse reflectance spectrum of $Ni(NCO)_2pip_3$.

	Energies [kK]			
calcd. C_{4v} [a]		obs.	calcd. D_{3h} [b]	
$^3B_1 \rightarrow {}^3E(F)$	5.9	5.4	5.4	$^3E' \rightarrow {}^3E''(F)$
$^3B_2$, $A_2(F)$	11.0	11.0	13.7	$^3A_2''$, $^3A_1''(F)$
$^3E(F)$	14.6	15.4	14.2	$^3A_2'(F)$
$^3A_2(P)$	23.5	21.8	21.3	$^3E''(P)$
$^3E(P)$	26.0	25.3	25.4	$^3A_2'(P)$

[a] for Dq(axial) = Dq(basal) = 1.1 kK, angle N(axial)-Ni-N (basal) = 100°. [b] for Dq(axial) = Dq(equatorial) = 1.3 kK

Further information will be gained from comparison with dd spectra of appropriate nickel complexes with known sterochemistry. At the present time, quite a number of paramagnetic five coordinate high spin Ni^{II} complexes are known[10][11] but most of them are formed with polydentate ligands. The only ligands yet known to form five coordinate high spin complexes containing monodentate ligands with equal donor atoms are phosphinoxides and arsinoxides[12]. The ligand field spectrum of $[Ni(Ph_2MeAsO)_4NO_3](NO_3)$ which contains a NiO_5 chromophore of C_{4v} symmetry has been interpreted by Lewis[13] using single

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(7) S.F. Pavkovic and D.W. Meek, *Inorg. Chem.*, *4*, 20 (1965).

(8) A.B.P. Lever, S.M. Nelson, and T.M. Shepherd, *Inorg. Chem.*, *4*, 810 (1965).

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(10) L. Sacconi in «Transition Metal Chemistry», R.L. Carlin (Ed.) Dekker, New York, 1968, Vol. IV, p. 199.

(11) P. Orioli, *Coord. Chem. Revs.*, *6*, 285 (1971).

(12) A.M. Brodie, S.H. Hunter, G.A. Rodley, and C.J. Wilkins, *Inorg. Chim. Acta*, *2*, 195 (1968).

(13) M. Gerloch, J. Kohl, J. Lewis, and W. Urland, *J. Chem. Soc., A*, 3269 (1970).

crystal polarized spectra. The pattern of bands which were assigned to spin allowed transitions resembles that observed in $Ni(NCO)_2(pip)_3$, with the difference that all bands are shifted by ~ 3 kK to lower energies as is expected from the positions O<N in the spectrochemical series. However, four additional weak and sharp bands which were not observed in the spectrum of $Ni(NCO)_2pip_3$ are found and assigned to spin forbidden transitions.

The compound [Ni(tris(2–dimethylaminoaminoethyl)amine)NCS]NCS contains a NiN_5 chromophore of D_{3h} symmetry (trigonal bipyramid)[14]. Its diffuse reflection spectrum is almost identical with that of the isocyanate complex, displaying three intense bands at 7.7, 16.2 and 24.6 kK and two weak bands at 13.2 and 21 kK, to which, using single crystal polarised spectra, the same assignement[14] was given as proposed in Table III for $Ni(NCO)_2(pip)_3$ assuming D_{3h} symmetry.

The above considerations show that an unambiguous assignment of the local symmetry in $Ni(NCO)_2$-pip_3 to either C_{4v} or D_{3h} symmetry is rather difficult: On the basis of the crystal field model, C_{4v} symmetry is favoured, due to the better fit of the spectrum to the selection rules. But the comparison with spectra of five coordinate complexes having chromophores of C_{4v} and D_{3h} symmetry puts more weight on the assignment of D_{3h} symmetry to the microsymmetry of the complex. Stereochemical considerations support this assumption,the ligand arrangement of highest symmetry (NCO in axial positions of a trigonal bipyramid) probably being that of least steric strain.

The six coordinate complexes $Ni(NCS)_2(pip)_4$ and $Ni(NCSe)_2(pip)_4$ also form bright green solutions in dichloromethane containing an excess of piperidine. Their spectra are similar to that of the isocyanate complex discussed above (Table II), although in the spectrum of the isoselenocyanate complex, the ligand field band of highest energy is not observed. This band is probably hidden by the low energy tail of the first electron transfer band which appears at lower energy than in the corresponding isocyanate and isothiocyanate complexes. Thus it can be assumed that these solutions contain five coordinate complexes $Ni(NCX)_2(pip)_3$ (X = S, Se) which were formed by dissociation of the six coordinate complexes upon solution.

Four coordinate complexes. The isocyanate and isothiocyanate complexes formed with 2,6-dimethylpiperidine (dpip), $Ni(NCO)_2(dpip)_2$ and $Ni(NCS)_2(dpip)_2$, have both identical spectra in the solid state and in solution Table II. They display only one ligand field band at 19-20 kK. This indicates a square planar arrangement of the four N donors which is also expected from the diamagnetism shown by these complexes. The planar configuration preferred by this ligand must be due to the steric hindrance exerted by the methyl groups located at the α-position to the donor atom. The two piperidine ligands are expected to be arranged in a position avoiding steric strain, which is achieved if the piperidine rings lie perpendicular to the NiN_4 plane, the large methyl groups thus covering the area above and below it, preventing coordination of two additional ligands. Similar nickel complexes with square planar NiN_4 configuration were formed with highly C-substituted ethylenediamines[15] $[Ni(2,3\text{-diaminobutane})_2]^{2+}$ and others). They also exhibit only one ligand field band at ~ 22 kK.

Equilibrium between five coordinate and planar four coordinate complexes. The green solutions containing $Ni(NCX_2(pip)_3$ (X = O,S) remain only stable in the presence of a large excess of piperidine. If $Ni(NCO)_2(pip)_3$ and $Ni(NCS)_2(pip)_4$ are solved in pure trichloromethane, red solutions were formed which exhibit the spectra characteristic for five coordinate complexes with one additional band of considerable intensity at ~ 20 kK (Figure 3). This band vanishes and green solutions result again if piperidine is added. This can be explained by the assumption of an equilibrium between five coordinate and four coordinate species, if the additional band at 20 kK is assigned to the ligand field transitions of planar $Ni(NCX)_2(pip)_2$. Solutions of the isoselenocyanate complex in pure $CHCl_3$ are green and show the same spectrum as that if excess piperidine is present. This, together with the fact that NCO^- does not form six coordinate nickel complexes with piperidine in the solid state, leads to the conclusion that the tendency of the pseudohalides to form complexes of high coordination number decreases in the series $NCSe^- > NCS^- > NCO^-$. This has also been observed in complexes of the type $M(NCX)_2$ (pyridine)$_4$ (M = Ni, Co, X = O, S, Se)[2)16)] where the ease of dissociation of the pyridine ligands increases in the series $NCSe^- < NCS^- < NCO^-$. The same is reflected in the spectra of the six coordinate piperidine complexes which indicate a smaller deviation from O_h symmetry for $Ni(NCSe)_2(pip)_4$ than for $Ni(NCS)_2(pip)_4$.

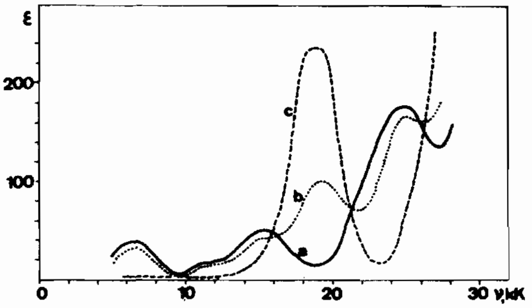

Figure 3. Ligand field spectra of nickel isothiocyanato complexes: a $Ni(NCS)_2(pip)_4$ in 0.1 *M* solution of pip in CH_2Cl_2, b $Ni(NCS)_2(pip)_4$ in $CHCl_3$ (arbitrary scale for ε), c $Ni(NCS)_2(dpip)_2$ in 0.01 *M* solution of dpip in CH_2Cl_2.

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