Contribution from the Instituto Central de Química,
Universidad de Concepción Casilla 3-C, Concepción, Chile

Some Nickel(II) Complexes of N-(2-Aminoethyl) Heterocyclic Derivatives

G. Contreras and E. Astigarrabia

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A series of dichloro bis(N-2-aminoethyl heterocyclic derivatives) nickel(II) complexes have been prepared in which the cyclic substituents are piperazine, pyrrolidine, and morpholine. The spectral and magnetic data indicate that the complexes possess an octahedral structure.

Derived ligand field parameters, 10Dq and B lead to the following order for the ligands in the spectrochemical and nephelauxetic series, respectively, NAPir >NAPip>NAMor and NAPip>NAMor>NAPir. The variations of the ligand field parameters are discussed in terms of the metal-ligand π *bonding.*

From i.r. spectra it can be inferred that the complexes possess an actual C_{2h} *symmetry.*

Introduction

There has had considerable interest during the past few years in complexes formed between amines and nickel(II) salts particularly with regard to stereochemistry.[1-6] The complexes formed with the ethyelenediamine derivatives have received special interest. Pavkovic and Meek reported the preparations and spectral properties of some secondary and tertiary N-Alkylethylenediamine nickel(II) complexes. They deduced that the steric interactions are of greater magnitud than the inductive effects of the substitutent.

In this paper we discuss the electronic and infrared spectra of the complexes of the type $[Ni(ligand)_2Cl_2]$ where the ligand is N–(2–aminoethyl)piperazine (NAPip), N–(2–aminoethyl) pyrrolidine (NAPir) or N–(2–aminoethyl) morpholine (NAMor).

Experimental Section

The electronic spectra were performed in formamide and recorded in the range of 7,000-30,000 cm^{-1} with a Zeiss PMQ II spectrophotometer by using 1 cm matched quartz cells with the solvent as the reference.

The i.r. spectra were done in KBr disks and recorded on a Perkin-Elmer 457 spectrophotometer. The electrolytic conductancies were measured in a WTW type LBR wis-techn-werkstatten conductimeter. Table I shows that the complexes exhibit a typical behaviour of non-electrolites.

The magnetic measurements were performed by the Gouy method using $Hg[Co(CNS)_4]$[7] as the standard. The magnetic moments were corrected for the diamagnetic contributions of the ligands. Melting point determinations were done in an Electrothermal apparatus and in a Kofler microscope.

Preparation of the Complexes. The complexes were prepared by a general method. The stoichiometric amount of the ligand (0.02 mole) was added to the calculated anhydrous nickel(II) chloride (0.01 mole) dissolved in absolute ethanol or methanol. Few minutes later a solid was precipitated then filtered and washed with abundant anhydrous ethanol. In the complex with N–(2–aminoethyl)morpholine was necessary to warm the solutions previously.

Attempt to prepare Chromium(III) complexes. In an attempt to prepare the chromium(III) complexes, differents methods of preparations were used; however in all the cases the resulting products were soft solids. The analyses of those solids were not reproducible.

Analyses. The compounds were analysed in the Merck laboratory of Darmstadt (Germany). The analytical, conductivity and magnetic data are given in Table I.

Results and Discussion

The magnetic data (Table I) demostrates that the nickel(II) ions in these complexes, have two unpaired electrons and as it can be expected have not orbital contributions. The observed deviations, the magnetic moments from the spin only value could be due to the second order Zeeman effects between the ground state and the highest ligand field terms. On the other hand, conductivity measurements indicate that the three compounds are typical non-electrolites in formamid; this is in good agreement with the analytical data which show that the complexes could be formulated as $[Ni(ligand)_2Cl_2]$.

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Table I. Analytical Conductivity and magnetic data[a]

Complex	%C	%H	%N	%Cl	%Ni	Melting Point	Molar[b] Conductivity	$\mu_{eff}^{(BM)}$ 290 K
$[Ni(NAPip)_2Cl_2]$	37.00(37.14)	7.90(7.80)	20.55(21.66)	18.35(18.28)	14.75(15.12)	255[c]	10.2	2.95
$[Ni(NAPir)_2Cl_2]$	40.50(40.26)	8.40(7.90)	15.50(15.65)	20.10(19.81)	16.20(16.40)	325	16.0	2.91
$[Ni(NAMor)_2Cl_2]$	37.20(36.96)	7.40(7.24)	14.10(14.37)	18.25(18.18)	14.50(15.05)	260[c]	11.8	2.89

[a] The calculated values are in parenthesis. [b] Molar conductivities in formamide. Concentration $10^{-3}M$. [c] Decomposed.

Table II. Electronic Spectra for the Nickel(II) complexes (cm^{-1})[a]

Complex	(cm^{-1})	Assignment
$[Ni(NAPip)_2Cl_2]$	9.800(7.3)	$^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1)$
	16.400(8.7)	$\rightarrow {}^3T_{1g}(F)(\nu_2)$
	27.100(22.0)	$\rightarrow {}^3T_{1g}(P)(\nu_3)$
	29.600(20.4)	
$[Ni(NAPir)_2Cl_2]$	10.000(9.0)	$^3A_{2g} \rightarrow {}^3T_{2g}$
	16.200(7.4)	$\rightarrow {}^3T_{1g}(F)$
	26.700(14.3)	$\rightarrow {}^3T_{1g}(P)$
$[Ni(NAMor)_2Cl_2]$	9.600(3.1)	$^3A_{2g} \rightarrow {}^3T_{2g}$
	15.900(2.8)	$\rightarrow {}^3T_{1g}(F)$
	26.400(5.5)	$\rightarrow {}^3T_{1g}(P)$

[a] The extinction coefficients are given in parenthesis following the and maxima.

Table III. Ligand Field Parameters for the Nickel(II) Complexes.

Complex	νDq (cm^{-1})	B(cm^{-1})	β[a]	ν_2/ν_1	$\nu_2$calc (cm^{-1})
$[Ni(NAPip)_2Cl_2]$	980	940	0.90	1.67	15.850
$[Ni(NAPir)_2Cl_2]$	1000	860	0.83	1.62	16.150
$[Ni(NAMor)_2Cl\ ]$	960	900	0.86	1.65	15.900

[a] The β values were calculated from the ratio B/B_0, where $B_0 = 1041\ cm^{-1}$.

Table II lists the electronic spectral bands in solution for the previously mentioned complexes. The very low intensities of the spectral bands may indicate a centrosymmetrical configuration and the positions of the spectral bands are all consistent with an octahedral arrangement of the ligands. Because of insolubility of the complexes in most of the usual solvents used in visible and ultraviolet spectroscopy the spectra were performed, in formamide, at different times in order to detect any gross change in the electronic or geometrical structure which might occur on dissolution.

The spectra of the complexes consist of three principal bands with maxima at about 10,000 cm^{-1}, 16,000-18,000 cm^{-1}, and 26,000-29,000 cm^{-1}. The NAPip complex, in the highest energy band presents a shoulder located at 29,000 cm^{-1}. The energies of the spin-allowed transitions $^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1)$ at 10,000 cm^{-1}; $^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$ at about 16,000-18,000 cm^{-1} and $^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$ at about 26,000-29,000 cm^{-1} agree well with those predicted from the Liehr and Ballhausen[8] energy level diagram for nickel(II) ions in O_h symmetry.

The ligand field parameter, 10Dq, was taken directly from the first energy transition (ν_1) while the Racah parameter, B, was calculated by substituting the energy values of ν_1, ν_2, and ν_3 in the diagonalized secular equation. The calculations includes the mutual interaction between terms of equal symmetry but ignores the spin-orbit coupling which must be negligible as can be inferred from the magnetic data.

The ligand field parameters Dq,B,β, the calculated value for ν_2, and the ratio ν_2/ν_1 are given in Table III. Jorgensen[9] had sugested that a value in the range 1.60-1.80 for the ratio ν_2/ν_1 is an indication of an octahedral arrangement of the ligands. All the complexes reported here have this ratio about 1.70.

On the other hand, the ratio ν_2/ν_1 is related to the T_{1g} terms interactions. An increase in Dq must produce a decrease in this ratio. An Orgel diagram for nickel(II) ions shows that if there is no interaction between the T_{1g} terms, the ratio should be 1.80. In our cases, all the ratios are below 1.80 and this would indicate that there are strong T_{1g} terms interactions.

Since the absence of splitting of the absorption bands and the differences between the calculated and observed ν_2, we can infer that the complexes are practically octahedral. However the calculated value for ν_2 is lower than the observed one. This effect could be related to a smaller interaction of the T_{1g} terms than could be expected from a pure octahedral case. Obviously NAPir will act exclusively as a bidentate N-donor ligand, however for Namor and NApip the possibility that the oxygen atom and the NH group of the ring also coordinate exists. If so, the ligands should act as terdentate and due to the analytical results they should be 1:2 electrolytes in solution. On the other hand, conductivity measurements in formamide indicate their typical non-electrolyte behaviour.

The Dq values (Table III) lead to the following spectrochemical series:

$$NAPir > NAPip > NAMor$$

In the MO theory, 10Dq is related to the energy difference between the σ and π bonding. So, an increase in 10Dq is due to: i) a strong σ interaction ($L \rightarrow M$) because of destabilization of the molecular orbital σ^* (d) or ii) a strong interaction π ($M \rightarrow L$) because of destabilization of a π^* (d) molecular orbital. On the other hand, a decrease of 10Dq could be due to a strong π ($L \rightarrow M$) interaction because of destabilization of π^* (d) molecular orbital. Therefore the spectrochemical series relates reasonably to the ability to form π bonding.

From the position of the ligands in the spectrochemical series it can be inferred that they are weak π acceptors. This ability as π-acceptor must decrease

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Table IV. Infrared Spectra of the Nickel(II) Complexes

Complex	Symmetry of environment	NH_2stret(a)	NH_2stret(s)	NH_2def(a)	NH_2def(s)	NH_2rock	CN stret	Ni-Nstret
[Ni(NAPip)$_2$Cl$_2$]	C_{2h}	3300vs	3240vs	1585m	1370w 1360m	765m 745w	1045sh 1038	498m
[Ni(NAPir)$_2$Cl$_2$]	C_{2h}	3300vs	3273vs	1595s	1370s 1350s	663m	1020s 1005m	525m
[Ni(NAMor)$_2$Cl$_2$]	C_{2h}	3280vs	3230vs	1585s	1355s 1330s	770s 750m	1015sh 1010s	495m

Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

Table V. Infrared Bands of the Organic Ligand

Complex	Symmetry	CH_2street	CH_2bend	CH_2wag	CH_2 twist	CH_2rock
[Ni(NAPip)$_2$Cl$_2$]	C_{2h}	2935vs	1450s 1440sh	1310sh 1300m 1280s	1120s 1105s	905m
[Ni(NAPir)$_2$Cl$_2$]	C_{2h}	2940vs	1465vs 1455s	1323m	1110vs 1095s	905m
[Ni(NAMor)$_2$Cl$_2$]	C_{2h}	2950vs	1452vs 1440s	1310w 1298s 1285sh	1120vs 1110s	898m

Abbreviation: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

in the same order of the spectrochemical series, and it is very probable that the complex with NMor does not have π bonding.

The nephelauxetic series, based on β, is more sensitive to the presence of different kinds of cyclic ring on the ligand. However an appropriate explanation for the β values is rather difficult because of the presence of the chloride ions in the coordination sphere.

The i.r. spectra of the complexes are given in Table IV. Table IV shows the NH_2 stretching frequencies, the asymmetric and symmetric deformation frequencies, the rocking mode of the NH_2, the C–N stretching mode an the Ni–N vibration frequencies. Table V shows the stretching, rocking, bending, twisting and wagging modes of CH_2.

The NH_2 stretching frequencies are in the region of 3300 cm^{-1}. This region includes both the asymmetric and symmetric modes. The asymmetric deformation vibration occurs at about 1600 cm^{-1}, and the symmetric one at about 1350 cm^{-1}. The i.r. spectra were performed in order to assign the symmetry of the complexes. It is well known that in the *trans* isomer (C_{2h}) only the vibrations are infrared active. Therefore the i.r. spectra of the latter must be more complex. In the assignment of the symmetry of the environment four criteria were used: a) the NH_2 asymmetric deformation frequencies are split in the *cis* isomers, while a strong and symmetric band is exhibited by a *trans* derivative.[9,10] Table IV shows that the complexes exhibit a single and strong band at about 1600 cm^{-1}, b) the CH_2 twisting mode appears as two bands in the region of 1110-1120 cm^{-1} for a *trans* isomer and as four bands for the *cis*.[11] From Table V it can be inferred that the complexes show two bands in good agreement with a *trans* formulation, c) only one band is observed for a *trans* isomer in the region of 900 cm^{-1} which corresponds to the CH_2 rocking frequency,[12] and d) the band located at about 500 cm^{-1} has been assigned to the metal-nitrogen vibration and provides a good evidence to distinguish between *cis* and *trans* isomers. A single band of medium intensity is an indication of the presence of a *trans* isomer. Our complexes show a single band about that frequency. This supports the above assignment. The assignment of this band was done by comparison with known Ni–N frequencies. Adams[13] indicates that in ethylenediamine complexes the M–N vibrations are located in the range 590-506 cm^{-1}. On the other hand, in the [Ni(en)$_3$][PtCl$_4$] this vibration is in the range 515-480 cm^{-1}, while in some Pt^{II} and Pd^{II} complexes it is in the range 570-560 cm^{-1}. We have not intended to assign the conformational form of the chelate ring and the *trans* designation of the complexes is related to the position of the amine with respect to the chloride ions in the complex.

Ni–Cl stretching vibrations were not assigned because they are located about 260 cm^{-1}, a region in which the spectra are not well resolved.

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