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On the Electronic Spectra of Nickel(II) Polynuclear Coordination Compounds with Pyridine and Its Derivatives

M. ANDRUH, C. I. LEPADATU and MARIA BREZEANU

Chair of Inorganic Chemistry, Faculty of Chemical Technology, Polytechnical Institute of Bucharest, str. Dumbrava Rosie nr. 23, Bucharest, Roumania

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Abstract

The electronic spectra of NiL_2Cl_2-type polynuclear coordination compounds are discussed. Considering the in-plane ligand field strength lower than the axial one, the electronic parameters for L = pyridine and 4-benzoyl-pyridine are calculated in the strong field approach and the Angular Overlap Model, taking into account the complete configuration interaction.

Introduction

In the coordination chemistry of nickel(II), complexes of composition NiL_2X_2 (L is a heterocyclic amine and X a halide ion) belong to the following structural types: complexes with square-planar or (pseudo)tetrahedral configurations and polymeric with an octahedral stereochemistry of the nickel(II) ion (D_{4h} symmetry).

The steric configuration adopted by the NiL_2X_2 complexes appears to be determined both by the electronic factors (*i.e.* the donor properties of the ligand and the anion) and by the steric ones (steric hindrance to the organic ligand) [1, 2].

NiL_4X_2 and NiL_2X_2-type coordination compounds (where L is pyridine and its substituted derivatives) and their magnetic and spectrochemical properties have been extensively studied [3–8].

The polymeric complexes of Ni(II) containing pyridines as organic ligands and bridging halide ions have been characterized by electronic and infrared spectroscopy [9–11] and magnetic measurements [12, 13].

The electronic parameters for $NiPy_4X_2$ were calculated using both weak and strong field approaches [14] and the Angular Overlap Model (AOM) [15].

The aim of this paper is to calculate the empirical energy parameters for polymeric NiL_2Cl_2 complexes (L = pyridine, Py, and 4-benzoyl-pyridine, 4Bz-Py).

Experimental

Dichlorodipyridine nickel(II) was prepared as described by Goodgame *et al.* [10].

Dichlorodi(4-benzoyl-pyridine)nickel(II) was obtained by controlled thermal decomposition of dichlorotetra(4-benzoyl-pyridine) nickel(II):

$$[Ni(4Bz\text{-}Py)_4Cl_2] \xrightarrow{180°C} Ni(4Bz\text{-}Py)_2Cl_2 + 2(4Bz\text{-}Py)$$

(Weight loss: found, 42.60%; calc., 42.46%)

In a preceding paper [16] we reported the nonisothermal kinetic study of thermal decompositions of the coordination compounds containing 4-benzoyl-pyridine as ligand.

Dichlorotetra(4-benzoyl-pyridine)nickel(II) was obtained as follows. A solution of 4-benzoyl-pyridine (0.73 g) in 5 ml methanol was added to a solution of nickel chloride hexahydrate (0.24 g) in 5 ml methanol. The green precipitate formed was filtered off, washed with methanol containing a small amount of ligand and dried *in vacuo*. *Anal.* Found: Ni, 11.80; C, 58.05; H, 3.70; N, 5.91; Cl, 14.60. Calc. Ni, 11.96; C, 58.65; H, 3.63; N, 5.65; Cl, 14.31%.

Results and Discussion

The electronic spectra of the two compounds were recorded by the reflectance technique within 4000–28 000 cm^{-1} (Table I). For dichlorodipyridine nickel(II) the spectrum is the same as that reported by Goodgame *et al.* [10].

The spectra of these compounds show obvious deviations from octahedral symmetry and the bands have been assigned to D_{4h} symmetry.

Goodgame *et al.* [10] assigned in their paper the bands occurring at 13.9 and 24.1 kK to the transitions $^3B_{1g} \rightarrow {}^3E_g^b$ and $^3B_{1g} \rightarrow {}^3E_g^c$, respectively. Using their assignment scheme, or another differing

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TABLE I. Diffuse Reflectance Spectral Data (kK)

Compound	$\rightarrow {}^3T_{2g}$ (O_h)		$\rightarrow {}^3T_{1g}(F)(O_h)$		$\rightarrow {}^3T_{1g}(P)(O_h)$	
	$\rightarrow {}^3B_{2g}$	$\rightarrow {}^3E_g^a$ (D_{4h})	$\rightarrow {}^3E_g^b$	$\rightarrow {}^3A_{2g}^a$	$\rightarrow {}^3E_g^c$	$\rightarrow {}^3A_{2g}^b$
$NiPy_2Cl_2$	6.00	8.40	12.30	13.90	22.40	24.10
$Ni(4Bz\text{-}Py)_2Cl_2$	6.15	8.51	12.10	13.70	22.50	24.39

from that given in Table I, we get unreasonable or complex solutions. Therefore, the assignments are made assuming that the in-plane field strength is lower than the axial one (see below). Our calculation procedure is that usually employed for *trans*-$[Nia_2b_2]$ chromophores [14, 17] including all the configuration interactions between the three E_g levels and between the two A_{2g} levels. The calculations assumed the following equations:

$$\begin{array}{c|ccc|c} & {}^3E_g^a & {}^3E_g^b & {}^3E_g^c & \\ \hline {}^3E_g^a & A_{11}-E & A_{12} & A_{13} & \\ {}^3E_g^b & A_{21} & A_{22}-E & A_{23} & =0 \\ {}^3E_g^c & A_{31} & A_{32} & A_{33}-E & \end{array}$$

$$\begin{array}{c|cc|c} & {}^3A_{2g}^a & {}^3A_{2g}^b & \\ \hline {}^3A_{2g}^a & B_{11}-E & B_{12} & =0 \\ {}^3A_{2g}^b & B_{21} & B_{22}-E & \end{array}$$

Thus, with all configuration interactions included, the energies of the six transitions are given by a linear equation, a two by two secular determinant and a three by three secular determinant. The A_{ij} and B_{ij} matrix elements may be found in Lever's work [14] for the strong field approach and in other papers dealing with the Angular Overlap Model and its applications [15, 18, 19].

The calculated electronic (Δ_1, Δ_2, Δ_3, Dq^z) and Racah parameters are presented in Table II.

According to these results, the single electron energies are more likely to follow the sequence

$$d_{xy} < d_{xz} = d_{yz} < d_{x^2-y^2} < d_{z^2}$$

TABLE II. Calculated Electronic Parameters in Strong Field Approach (kK)

Parameters	$NiPy_2Cl_2$	$Ni(4Bz\text{-}Py)_2Cl_2$
Δ_1	−0.90	−1.18
Δ_2	6.00	6.15
Δ_3	−4.83	−4.74
Dq^z	1.14	1.10
B	0.81	0.84

in agreement with the effect of tetragonal distortion on the energy levels in an octahedral environment caused by elongation in the *xy* plane, or with an in-plane field strength lower than the axial one.

The set of AOM and Racah parameters were estimated by fitting the excited state energies using a computer program based on the Davidon–Fletcher–Powell optimization method [20] (Table III).

TABLE III. Angular Overlap Model Parameters (kK)

Parameters	$NiPy_2Cl_2$	$Ni(4Bz\text{-}Py)_2Cl_2$	$NiPy_4Cl_2$ [14]
e_σ^N	4.48	4.47	4.67
e_σ^{Cl}	2.13	2.14	2.98
e_π^N	0.44	0.43	0.57
e_π^{Cl}	0.17	0.12	0.58
B	0.799	0.798	0.798

In order to compare the two sets of results, we calculated the parameters dσ, dπ, Dq^{xy}, Ds and Dt, which are inter-related with those obtained by the two approaches. The data collected in Table IV show a good agreement between the two semiempirical methods used.

TABLE IV. Correlation Between Semiempirical Parameters (kK)

Parameters	$NiPy_2Cl_2$		$Ni(4\text{-}Bz\text{-}Py)_2Cl_2$	
	AOM	Strong field	AOM	Strong field
Dt	−0.33	−0.31	−0.33	−0.27
Ds	−0.76	−0.82	−0.75	−0.85
Dq^{xy}	5.93	6.0	5.93	6.15
dσ	1.76	1.81	1.75	1.67
dπ	0.32	0.45	0.31	0.59

According to the results obtained in this work, pyridine and 4-benzoyl-pyridine seem to be π-donors toward the nickel(II) ion, in agreement with other works [15, 21].

The lower values of e_σ^{Cl} and e_π^{Cl} parameters in the polymeric compounds, compared with those calculated for the mononuclear compound $NiPy_4Cl_2$, may be explained by the different nature of the chlorine ions in the two complexes: in the former complex, the chloride ions act as a bridge between two nickel ions, the bond being therefore weaker than Ni(II)–Cl bonds in the $NiPy_4Cl_2$ compound.

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