

Transition-metal complexes with the hydrazides and hydrazones. I. The octahedral Ni(II) complexes with acetone 1-naphthoylhydrazone

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1990 J. Phys.: Condens. Matter 2 3611

(<http://iopscience.iop.org/0953-8984/2/15/016>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.103

The article was downloaded on 11/05/2010 at 05:52

Please note that [terms and conditions apply](#).

# Transition-metal complexes with the hydrazides and hydrazones: I. The octahedral Ni(II) complexes with acetone 1-naphthoylhydrazone

D Ž Obadović†, A F Petrović†, V M Leovac† and S Yu Chundak‡

† Faculty of Sciences, University of Novi Sad, dr Ilije Djuričića 4, 21000 Novi Sad, Yugoslavia

‡ Faculty of Chemistry, State University, Uzhgorod, USSR

Received 22 May 1989, in final form 10 November 1989

**Abstract.** The results are presented on spectral and magnetic studies of the newly synthesised Ni(II) complexes of the general formula  $\text{NiL}_2\text{X}_2$  ( $\text{L} \equiv$  acetone 1-naphthoylhydrazone,  $\text{X} \equiv \text{Cl}$ ,  $\text{Br}$ ,  $\text{NO}_3$ ,  $\text{NCS}$ ). Atoms of the first coordination sphere around the Ni(II) are identified on the basis of the IR spectral data. These data, together with those on electronic spectra and magnetic measurements, suggested an octahedral coordination of Ni(II) in these complexes. Values of the crystal-field splitting parameter  $10Dq$  served to calculate energies of the  $E_g$  and  $T_{2g}$  levels. Also, values of the orbital population on Ni(II) were calculated and, on the basis of these, the effective values of the ionisation potentials  $H_{\text{dd}}$  are determined. The most probable scheme of MOs for these complexes is proposed.

## 1. Introduction

Various important properties of carbonic acid hydrazides and hydrazones and their application in medicine, analytical chemistry and other scientific and technological fields have led to an increased interest in their complexation characteristics with transition-metal ions [1, 2]. This work is part of our studies on the complexes of 3d elements with the hydrazides and hydrazones of carbonic acids [3].

## 2. Experimental details

### 2.1. Synthesis

The ligand, acetone 1-naphthoylhydrazone, was obtained by the condensation reaction of warm ethanolic solution of 1-naphthoyl acid hydrazide with acetone. The complexes were synthesised by the reaction of the corresponding Ni(II) salt and the ligand (mole ratio 1:2), both dissolved in an ethanol–acetone solvent mixture. After filtration, the fine-grained crystals of complexes were washed with ethanol and ether, giving a yield of 50–70%. The air-dried substances were used for elemental analysis and physical measurements. Nickel was determined in the form of bis(dimethylglyoximate)nickel(II) complex, whereas C, H and N were determined by standard microanalytical methods.

**Table 1.** Elementary analyses and  $\mu_{\text{eff}}$ -values of Ni(II) complexes.

Complex	Amount (%)								$\mu_{\text{eff}}$ ( $\mu_{\text{B}}$ )
	Ni		C		H		N		
	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	
NiL <sub>2</sub> Cl <sub>2</sub>	9.96	(10.08)	57.72	(57.76)	4.99	(4.85)	9.67	(9.62)	3.24
NiL <sub>2</sub> Br <sub>2</sub>	8.75	(8.67)	50.22	(50.11)	4.43	(4.21)	8.52	(8.35)	3.21
NiL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	9.27	(9.24)	52.32	(52.94)	4.52	(4.44)	13.41	(13.22)	3.25
NiL <sub>2</sub> (NCS) <sub>2</sub>	9.34	(9.36)	56.82	(57.43)	4.8	(5.1)	13.14	(13.4)	3.18

Table 1 includes data of the elementary analysis and  $\mu_{\text{eff}}$ -values. These last indicate the presence of octahedral coordination of Ni(II) in these complexes.

### 2.2. Measurement techniques

IR spectra were recorded on a Perkin–Elmer Infracord 457 spectrophotometer using KBr discs, CHCl<sub>3</sub> and C<sub>4</sub>Cl<sub>6</sub>. Important IR bands of the ligand and the complexes are given in table 2.

Reflection spectra were measured in the 10 000–45 000 cm<sup>-1</sup> range at room temperature using a monochromator SPM-2 (Veb Zeiss, Jena) with a R-45/0-type reflection cell. MgO was used as the ‘white’ standard.

The reflection spectra are illustrated later in figure 3. The electronic spectral data for the nickel(II) complexes are given in table 3.

Magnetic susceptibilities were measured by the Faraday method at room temperature, using Hg|Co(NCS)<sub>4</sub>| as the calibrant.

## 3. Results and discussion

The reaction of warm ethanol–acetone solutions of Ni<sub>2</sub>X<sub>2</sub> · nH<sub>2</sub>O (X ≡ Cl, Br, NO<sub>3</sub>, NCS) and acetone 1-naphthoylhydrazone C<sub>10</sub>H<sub>7</sub>—C(=O)—NH—N=C(CH<sub>3</sub>)<sub>2</sub> (L) in the mole ratio 1:2, yielded the paramagnetic bis(L) complexes of the general formula NiL<sub>2</sub>X<sub>2</sub>, whose values of magnetic moments are characteristic of the hexacoordinated Ni(II) [4]. It is known [5–7] that the ligands of this class are coordinated via the oxygen atom and terminal nitrogen atom. On the basis of a comparison of the  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}=\text{N})$  bands, which in the IR spectrum of the ligand (KBr) (figure 1) are observed at 1650 cm<sup>-1</sup> and 1605 cm<sup>-1</sup>, respectively, with their positions in the spectra of complexes, it can be concluded that they are in the latter case shifted towards lower energies by about 20–30 cm<sup>-1</sup> and 10–15 cm<sup>-1</sup>. This shift is even larger in the case of the  $\nu(\text{C}=\text{O})$  if the position of this band in the spectrum of the ligand recorded in CHCl<sub>3</sub> (where it is located at 1675 cm<sup>-1</sup>) is taken for comparison; this could be due to the absence of hydrogen bonds which are present in the crystalline ligand. On the basis of the above, it can be concluded that the oxygen and nitrogen atoms of the bidentate ligand occupy four coordination sites. The remaining two sites are in the halide complex occupied by Cl and Br, and by N and O of the isothiocyanate and nitrate group [8], respectively, in the other two complexes.

Table 2. Important IR spectral data Ni(II) complexes with L and force constants.

Compound	$\nu(\text{C}=\text{O})$ ( $\text{cm}^{-1}$ )	$\nu(\text{C}=\text{N})$ ( $\text{cm}^{-1}$ )	$\nu(\text{anion})$ ( $\text{cm}^{-1}$ )	$\nu(\text{Ni}-\text{N})$ ( $\text{cm}^{-1}$ )	$\nu(\text{Ni}-\text{O})$ ( $\text{cm}^{-1}$ )	$c(\text{Ni}-\text{N})$ ( $10^2 \text{ N m}^{-2}$ )	$c(\text{Ni}-\text{O})$ ( $10^2 \text{ N m}^{-2}$ )
L	1650 <sup>a</sup> 1675 <sup>b</sup>	1605					
NiL <sub>2</sub> Cl <sub>2</sub>	1610	1590		570	495	2.60	9.6
NiL <sub>2</sub> Br <sub>2</sub>	1610	1590		575	490	2.63	9.5
NiL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	1620	1595	1420, 1380, 1320 <sup>c</sup> , 1420, 1310 <sup>c</sup>	575	490	2.63	9.5
NiL <sub>2</sub> (NCS) <sub>2</sub>	1610	1605		570, 520	480	2.6	9.3

<sup>a</sup> In KBr.<sup>b</sup> In CHCl<sub>3</sub>.<sup>c</sup> In C<sub>4</sub>Cl<sub>6</sub>.Table 3. Electronic spectral data of Ni(II) complexes with L: R, reflection; A( $\epsilon$ ), absorption; IL1, IL2, intraligand bonds.

Compound	Transition ( $10^3 \text{ cm}^{-1}$ )					10Dq ( $10^3 \text{ cm}^{-1}$ )	B ( $10^3 \text{ cm}^{-1}$ )	Detection
	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$	IL1 ( $10^3 \text{ cm}^{-1}$ )	IL2 ( $10^3 \text{ cm}^{-1}$ )			
L				IL1	IL2			
				32.0	37.5			R
				32.0(153)	40.0(116)			A( $\epsilon$ )
				31.0	39.0		0.446	R
				31.5	40.0			A( $\epsilon$ )
				(158)	(124)			
				29.5	37.0		0.573	R
				31.5	39.0			A( $\epsilon$ )
				(170)	(159)			
				29.6	36.0		0.606	R
				30.4	38.5			A( $\epsilon$ )
				(1480)	(1120)			
				31.8	36.5		0.546	R
				33.2	39.5			A( $\epsilon$ )
				(1580)	(1250)			
NiL <sub>2</sub> Cl <sub>2</sub>	11.5 12.0(0.8)	15.0 16.0(2.1)	26.2 26.3(8.5)					
NiL <sub>2</sub> Br <sub>2</sub>	11.0 11.0(6)	15.8 15.8(5.5)	25.8 25.8(32)					
NiL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	11.2	16.1	26.3					
NiL <sub>2</sub> (NCS) <sub>2</sub>	11.5	17.0	25.4					

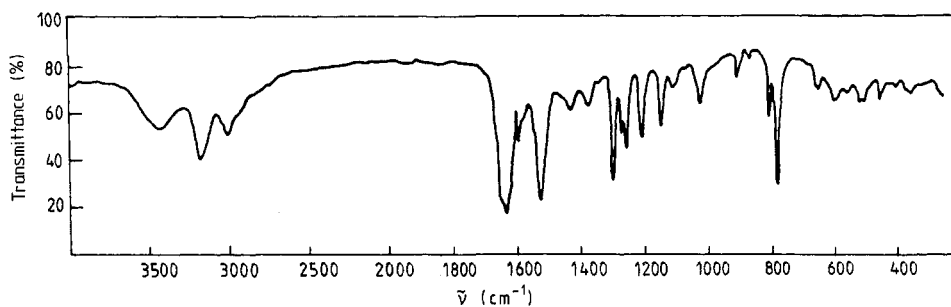


Figure 1. IR spectra of L.

The coordination of the NCS group through the N atom is also suggested by the presence of a very strong band in the IR spectrum of the  $\text{NiL}_2(\text{NCS})_2$  complex at  $2080\text{ cm}^{-1}$  which corresponds to the  $\nu(\text{C}=\text{N})$  of the coordinated isothiocyanate (figure 2). The bands of asymmetric vibrations of the coordinated  $\text{NO}_3$  group of  $\text{NiL}_2(\text{NO}_3)_2$ , in the IR spectrum recorded in hexachlorobutadiene are observed at  $1420$  and  $1310\text{ cm}^{-1}$  (table 2). Finally, it should be noticed that the IR spectrum of this complex, taken in KBr, contains also a strong band at  $1380\text{ cm}^{-1}$ , characteristic of the non-coordinated  $\text{NO}_3$  group, whose appearance can be explained by partial replacement of the coordinated nitrate with the bromide.

The calculation of the vibrational energies

$$E_1 = \hbar\omega_1 = \hbar\sqrt{c/2m} \quad (1)$$

$$E_2 = \hbar\omega_2 = \hbar\sqrt{c/m_r} \quad (2)$$

(where  $m$  is the mass of the surroundings and  $m_r$  the reduced mass) of the octahedral molecule in the nearest-neighbour approximation [9] enabled us to determine the valence band positions for the vibrations of the Ni(II) ion and its surrounding atoms. The experimental values of oscillatory frequencies were the basis for the calculation of the force constants for the investigated octahedral Ni(II) complexes (table 1). In the case of the halide complexes the bands of the Ni—Cl and Ni—Br valence vibrations should be observed at about  $310\text{ cm}^{-1}$  and  $250\text{ cm}^{-1}$ , respectively. These predicted values agree quite well with the experimentally obtained values for some similar compounds [9, 10].

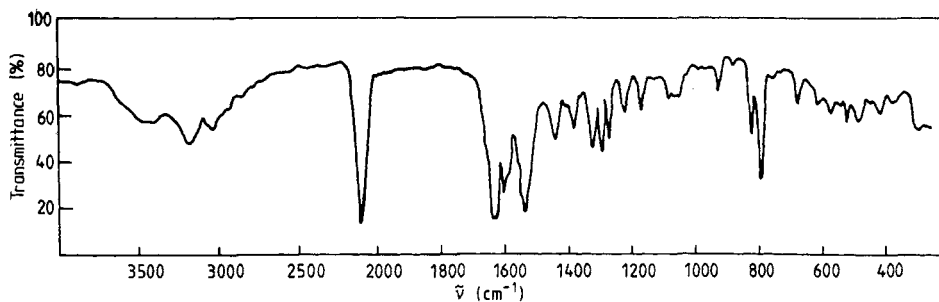


Figure 2. IR spectra of the  $\text{NiL}_2(\text{NCS})_2$  complex.

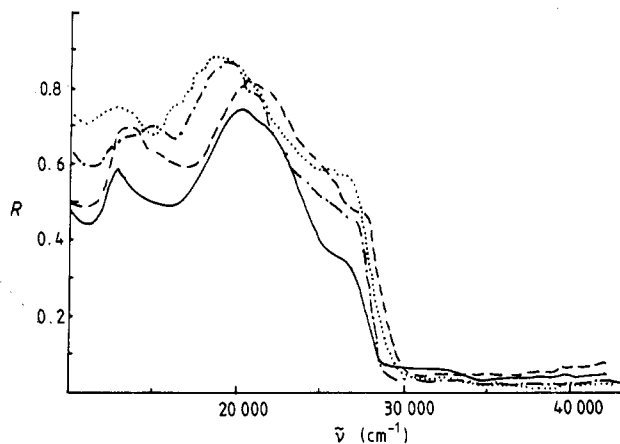


Figure 3. Reflection spectra of  $\text{NiL}_2(\text{NCS})_2$  (---),  $\text{NiL}_2(\text{NO}_3)_2$  (—),  $\text{NiL}_2\text{Br}_2$  (-·-·-) and  $\text{NiL}_2\text{CL}_2\text{Cl}_2$  (····).

The reflection spectra of the complexes (figure 3) were evaluated according to the Kubelka–Munk [11] theory. On the basis of their position and intensity, as well as of the comparison with the spectrum of the ligand itself, it can be supposed the weak bands at lower wavenumbers correspond to d–d transitions, whereas the partly split strong bands in the 30000–42000  $\text{cm}^{-1}$  range may be ascribed to intra-ligand transitions. The absorption coefficients obtained from the spectra recorded for the ethanolic solutions of the complexes indicate that the intra-ligand transitions occur most probably from the non-bonding  $n$  to the anti-bonding  $\pi^*$  ligand orbitals. The d–d transitions were detected on the basis of the diagrams of Tanabe–Sugano type for the  $d^8$  system, to which the Ni(II) ion belongs. The results are presented in table 3. A somewhat lower  $B$ -value indicates the presence of covalent character of these type of complex.

The energies of the  $E_g$  and  $T_{2g}$  levels were obtained by solving the secular equation [12]

$$|H_{ij} - WG_{ij}| = 0 \quad (3)$$

where  $G_{ij}$  are the integrals of the group overlaps, calculated on the basis of the integral for diatomic overlaps [13, 14].

The Coulomb integral  $H_{jj}$  was approximated as the ionisation potential of the valence state of the surrounding atoms, whereas the Coulomb integral  $H_{ii} \equiv H_{dd}$  was calculated from the relation

$$H_{ii} \equiv H_{dd} = (1 - s - p) (\text{d vsIE} : d^n) + S(\text{d vsIE} : d^{n-1} + \text{d vsIE} : d^{n-1}p). \quad (4)$$

where  $\text{vsIE}_s^1$  = valence state ionisation energies. Data for the constants of partial population of energy levels  $s$ ,  $p$  and  $q$  from the literature [12] were used as a first approximation. Using the above procedure, the matrix elements of the secular equations (3), i.e. the energies of the  $E_g$  and  $T_{2g}$  levels, were calculated. The orbital partial population of the Ni(II) level was obtained on the basis of introducing the experimental values for the crystal-field splitting parameter. These data were used to obtain the more exact values of the ionisation energy  $H_{dd}$ , as well as the matrix elements  $H_{ijE_g}$  and the energies of the  $E_g$  and  $T_{2g}$  levels. The process was repeated until the results obtained gave values for the parameters of crystal-field splitting which agree within the experimental error. The results are presented in table 4.

Table 4. Calculated energy data of Ni(II) complexes.

Complex	$G_{Eg}$ ( $2p\sigma, 3d\sigma$ ) ( $10^3 \text{ cm}^{-1}$ )	$G_{T_{2g}}$ ( $2p\pi, 3d\pi$ ) ( $10^3 \text{ cm}^{-1}$ )	$H_{ij} = H_{L.L.}$ ( $10^3 \text{ cm}^{-1}$ )	$H_{ii} = H_{ad}$ ( $10^3 \text{ cm}^{-1}$ )	$E_g$ energy ( $\sigma$ ) ( $10^3 \text{ cm}^{-1}$ )	$T_{2g}$ energy ( $\pi$ ) ( $10^3 \text{ cm}^{-1}$ )	$10Dq_{calc}$ ( $10^3 \text{ cm}^{-1}$ )
$\text{NiL}_2\text{Cl}_2$	0.278	0.156	-113.33	-135.6 $q = 0.327, s = 0.76, p = 0.5$	-98.7	-110.2	11.5
$\text{NiL}_2\text{Br}_2$	0.221	0.134	-113.33	-133.97 $q = 0.327, s = 0.716, p = 0.5$	-96.0	-107.5	11.0
$\text{NiL}_2(\text{NO}_3)_2$	0.256	0.144	-120.6	-143.29 $q = 0.37, s = 0.82, p = 0.5$	-100.1	-111.3	11.2
$\text{NiL}_2(\text{NCS})_2$	0.325	0.210	-113.35	-121.28 $q = 0.208, s = 0.844, p = 0.44$	-94.5	-106	11.5

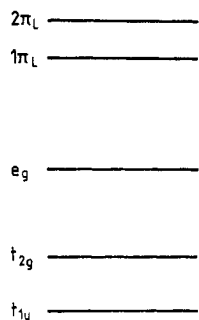


Figure 4. MO scheme for the  $\text{NiL}_2(\text{NCS})_2$  complex.

On the basis of these calculation and experimental values for the maxima of electronic spectra, the MO scheme presented in figure 4 was determined. By taking the non-bonding  $t_{1u}$  ligand orbital to be the lowest-energy orbital, then, on the basis of the intra-ligand transitions and average values of the ionisation potentials for the N and O atoms of the ligand, the energies for  $1\pi_L$  and  $2\pi_L$  ligand orbitals were calculated.

## References

- [1] Grekov A P 1966 *Organicheskaya Khima Gidrazina* (Kiev: Tekhnika) pp 133–216
- [2] Katual M and Dutt G 1972 *Talanta* **22** 151
- [3] Chundak S Yu, Leovac V M, Obadović D Ž and Petrović D M 1986 *Transition Met. Chem.* **11** 308–12
- [4] Cotton F A and Wilkinson G 1988 *Advanced Inorganic Chemistry* (New York: Wiley-Interscience) p 745
- [5] Gogorishvili P V, Kharitonov Yu Ya, Karparashvili M V and Machkoshvili R I 1969 *Zhr. Neorg. Khim.* **14** 2891
- [6] Nagano K, Hisashi K and Akiko H 1964 *Chem. Pharm. Bull.* **12** 1198
- [7] Kharitonov Yu Ya, Machkoshvili R I, Generanova N B and Schelokov R N 1974 *Zhr. Neorg. Khim.* **19** 1124
- [8] Nakamoto K 1986 *Infrared Spectra of Inorganic and Coordination Compounds* (New York: Wiley-Interscience) pp 254–87
- [9] Obadović D Ž, Carić S and Tošić B S 1990 *J. Quantum Chem.* at press
- [10] Beecroft B, Campbell M J M and Grzeszkowiak R 1972 *Inorg. Nucl. Chem. Lett.* **8** 1097
- [11] Kubelka P and Munk F 1931 *Z. Tech. Phys.* **12** 593
- [12] Balhauzen C J and Gray H B 1962 *Inorg. Chem.* **1** 111
- [13] Jaffé H H and Doak G O 1952 *J. Chem. Phys.* **21** 196
- [14] Jaffé H H 1952 *J. Chem. Phys.* **21** 258