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ELECTRONIC SPECTRUM AND THERMAL DECOMPOSITION OF NICKEL(II) COMPLEX WITH BIS(N-γ-PYRIDYL-4-PHENYLBENZAMIDE-HYDRAZONE)

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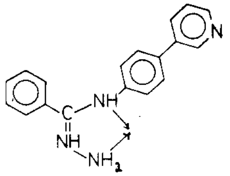
The unit cell parameters and the space group of the investigated compound were determined by means of X-ray diffraction.

Analysis of the diffusion-reflection spectra of the crystalline powder and the absorption spectra of its alcoholic solutions permitted identification and quantitative characterization of the absorption bands of the crystalline complex of $NiL_2(ClO_4)_2 \cdot 3H_2O$.

Application of differential-thermal analysis allowed determination of the mechanism of thermal decomposition of the compound. From these measurements, the expected configuration of the basic molecule was verified, involving determination of the number of non-coordinated water molecules.

The investigated complex compound contains the basic ligand L with the following structural formula:



The principle synthesis was described in a recent paper [1].

The compound itself occurs as blue-violet needle-like crystals. It is soluble in ethylalcohol, but not in ether, and is stable in air.

This paper reviews the results obtained by X-ray diffraction on the monocrystal, by reflection and absorption spectroscopy, and by thermal analysis.

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Experimental

X-ray analyses were carried by means of a PW 1120/00 generator (Philips) with the copper anticathode at 30 kV and a current of 25 mA. A nickel filter 0.012 mm in thickness was used for monochromatization of the CuK_α line (wavelength 1.5418 Å).

The periods, angles and crystallographic system were determined from oscillatory and Weissenberg photographs. The Weissenberg photographs demonstrated the systematic absence of particular reflexes, permitting determination of the space group.

Diffuse-reflection spectra were obtained with an SPM–2 quartz monochromator (ZEISS-JENA). Spectra were taken in the interval 10,000–45,000 cm^{-1} at room temperature. MgO was used as the reference compound and the reflection cell was of the R–45/0 type. These spectra were treated according to Kubelka–Munk's theory [2].

The absorption spectra of alcoholic solutions were obtained with a UNICAM SP–800 UV–VIS spectrophotometer in the 350–850 nm interval.

Thermal analysis was carried out with a Paulik–Paulik–Erdey derivatograph (MOM, Hungary). Sample size: 100 mg. Sample heating from room temperature up to 1000° was carried out at a rate of 10 deg/min, in air atmosphere, with α-Al_2O_3 as reference material in Pt crucible.

Results and discussion

Through the application of X-ray diffraction methods, the following crystallographic data were determined: $a=33.55$ Å, $b=15.44$ Å, $c=17.11$ Å, $\beta=91°$, $V = 8865.68$ Å^3, $D_0 = 1.27$, $D_c = 1.28$, $Z = 8$, space group B2/b.

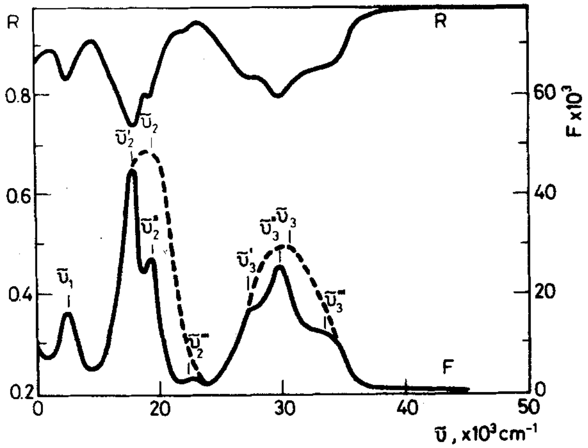


Fig. 1 Reflection spectra of $NiL_2(ClO_4)_2 \cdot 3H_2O$

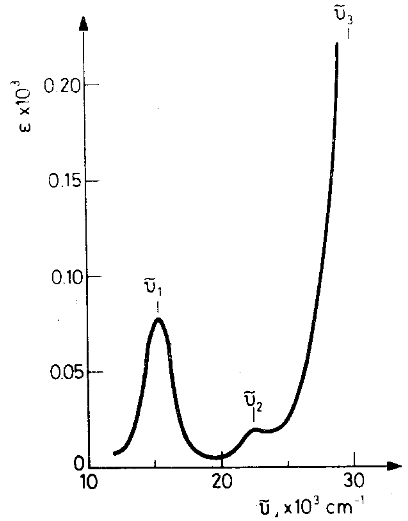


Fig. 2 Absorption spectra in ethanolic solution

The reflection spectra of the samples are given in Fig. 1, and the absorption spectra in Fig. 2.

The results obtained from the diffusion-reflection spectra permitted the calculation of Racah's parameter and the parameter 10Dq from the positions of the crystal field bands.

It was expected, and the distribution of the peaks in the absorption spectrum also indicated, that the coordination around the Ni(II) is most probably octahedral. According to the Tanabe–Sugano diagram (Fig. 3), the following transitions are present [3]:

$$^3A_{2g} \rightarrow {}^3T_{2g}$$

$$^3A_{2g} \rightarrow {}^3T_{1g}$$

$$^3A_{2g} \rightarrow {}^3T_{1g}(P)$$

The splitting parameter 10Dq and Racah's parameter were estimated according to the following relations:

$$10\mathrm{Dq} = \tilde{\nu}_1$$

$$B = \frac{\tilde{\nu}_2 + \tilde{\nu}_3 - 3\tilde{\nu}_1}{15}$$

The reflection spectra of the substance in its non-perturbed state indicated the presence of splitting for the triplet states $^3T_{1g}$ and $^3T_{1g}(P)$ at the frequencies

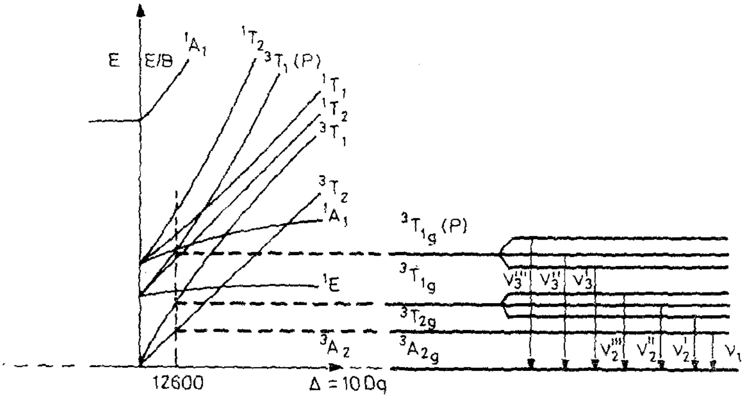


Fig. 3 The energy levels of Ni(II) d^8 configuration in the $NiL_2(ClO_4)_2 \cdot 3H_2O$ complex

Table 1 UV and visible spectra

	Peak position		Mean transition energy*, cm^{-1}		
			reflection spectra		EtOH solution
1	$\tilde{\nu}_1$		12600		15000 (80)
		$\tilde{\nu}'_2$		18000	
2	$\tilde{\nu}_2$	$\tilde{\nu}''_2$	19500	19200	22500 (20)
		$\tilde{\nu}'''_2$		22500	
		$\tilde{\nu}'_3$		27500	
3	$\tilde{\nu}_3$	$\tilde{\nu}''_3$	30500	30000	
		$\tilde{\nu}'''_3$		33400	

$$Dq \approx \frac{1}{10}\tilde{\nu} = 12600\ cm^{-1}$$

$$B = 813.33\ cm^{-1}$$

* Extinction coefficients in parentheses.

designated by $\tilde{\nu}_2$, $\tilde{\nu}'_2$, $\tilde{\nu}''_2$ and by $\tilde{\nu}_3$, $\tilde{\nu}'_3$, $\tilde{\nu}''_3$. This is a consequence of the deviation from full octahedral symmetry O_h, being a logical consequence of certain differences in electronic charge of the atoms from first coordination (as there are the atoms of oxygen and nitrogen) [4, 5].

Table 1 gives the characteristic energies of the detected transitions, the splitting parameter of the crystal field Dq and the Racah parameter B.

Figure 4 gives the characteristic diagram of the complex thermal investigations. From the DTA and DTG curves, it is obvious that the decomposition involves several complex endothermic and exothermic processes.

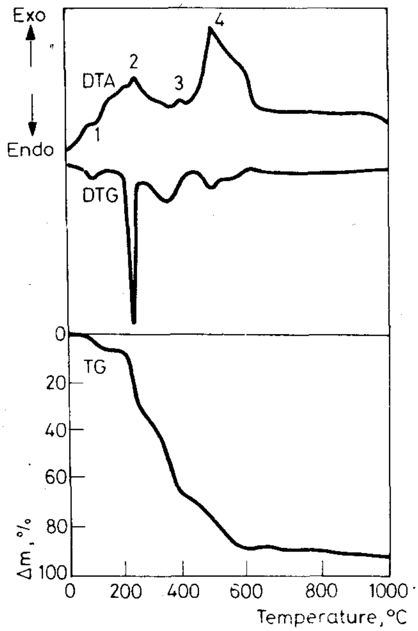


Fig. 4 DTA, TG and DTG curves of $NiL_2(ClO_4)_2 \cdot 3H_2O$

The first endothermic process is registered at 363 K (90°). This is accompained by a mass loss of 6% (TG curve) and represents the loss of the molecules of crystalline water. The calculated mass loss for the water molecules is 6.06%, in good agreement with the observed value.

Exothermic processes with maxima in the DTA curve at 503 K (230°) and 553 K (260°) are characterized by mass losses of about 21%, which corresponds to the loss of the ClO_4 groups from the basic molecule.

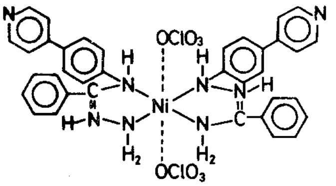
The next exothermic process in the temperature interval from 593 K (320°) up to 883 K (610°), is complex; the total mass loss here is 64%, which is in agreement with the loss of both ligand molecules. From the TG and DTG curves it is possible to separate the processes of the particular fragments leaving the ligand. The loss of 35% relates to the molecular weight of γ-pyridylbenzene ($\Delta m_{cal} = 34.8\%$), and the following 29% to the rest of the ligand itself ($\Delta m_{cal} = 30.5\%$). This last process is accompanied by the bonding of oxygen atoms to the Ni(II) ion. In this way, NiO is obtained as the final product of decomposition; this was proved by X-ray analyses of the residue of the thermal treatment. The residue at the end of this process comprises 8%, in agreement with the calculated value for this oxide ($\Delta m_{cal} = 8.3\%$).

Table 2 gives the characteristics of the thermal decomposition of $NiL_2(ClO_4)_2 \cdot 3H_2O$.

Table 2 Thermal decomposition characteristics

T, K	Effect type	Fragment liberation	Δm, %	
			obs.	calcd.
363	endo	$3H_2O$	6	6.1
473–593	exo	$2ClO_4$	21	22 3
593–703	exo	γ-pyridyl-benzene	35	34.8
703–883	exo	benzamide-hydrazone	29	30.5

From the given results and discussion, it could be concluded that the most probable structural formula of the complex is as follows:



The central Ni(II) ion proved to be hexacoordinated. Four coordination sites are occupied by nitrogen atoms from two ligand molecules, and the remaining two sites by oxygen atoms from two ClO_4 groups. The effectively present dotted group of symmetry proved to be O_h, with approximation of the equivalent effects of the N and O atoms to the central ion.

References

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Zusammenfassung — Mittels Röntgendiffraktionsmethoden wurden Gitterzellenkonstanten sowie die Raumgruppe der untersuchten Verbindung bestimmt. Durch Analyse der erhaltenen Diffusions-Reflexionsspektren von kristallinem Pulver und des Absorptionsspektrums einer alkoholischen Lösung der Verbindung war es möglich, die Absorptionsbanden des Kristallkomplexes $NiL_2(ClO_4)_2 \cdot 3H_2O$ zu identifizieren und quantitativ zu charakterisieren. Anwendung von Differentialthermoanalyse ermöglicht die Bestimmung des Mechanismus der Zersetzungsreaktion der Verbindung. Durch diese

Messungen, einschliesslich der Bestimmung der Anzahl nichtkoordinierter Wassermoleküle, wurde die erwartete Konfiguration des Grundmoleküles überprüft.

Резюме — Методом рентгеноструктурного анализа определены параметры крисаллической решетки и пространственная группа для комплекса $NiL_2(ClO_4)_2 \cdot 3H_2O$, где L–N–γ-пиридил-4-фенил-бензамидгидразон. Анализ полученного спектра диффузного отражения кристаллического порошкообразного комплекса, а также спектра его поглощения в спирте, представил возможность идентифицировать и количественно охарактеризовать полосы поглощения кристаллического комплекса. Применения дифференциального термического анализа позволило определить механизм термического разложения этого комплекса. Исходя из проведенных измерений была подтверждена конфигурация основной молекулы, включая определение числа молекул некоординированной воды.