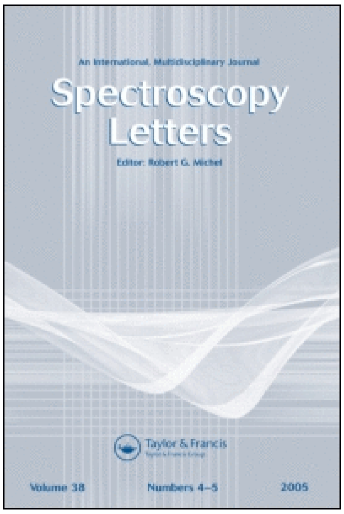

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Spectroscopic and Structural Studies of Clathrate Compound of Bis(Ethylenediamine)-Diisothiocyanatonickel(II)-Benzene

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SPECTROSCOPIC AND STRUCTURAL STUDIES OF CLATHRATE COMPOUND OF BIS(ETHYLENEDIAMINE)-DIISOTHIOCYANATONICKEL(II)-BENZENE

key words: electronic absorption spectrum, bis(ethylenediamine)-diisothiocyanato-nickel (II), ligand field theory, structural studies

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ABSTRACT

The electronic absorption spectrum of the title crystal of the clathrate compound of $[Ni(en)_2(NCS)_2]\cdot C_6H_6$ has been measured. The experimental results are discussed quantitatively with ligand field theory(LFT) and the radial wave function of non-free nickel(II) ion. The calculation value coincides well with the experimental results. In particularly, it provides significant correlation between the electronic absorption spectrum and the crystal structure of the compound.

INTRODUCTION

Trans-bis(ethylenediamine)-diisothiocyanatonickel(II) was first prepared by Wernner as a red violet precipitate by a metathesis of bis(ethylenediamine)-nickel(II). After that, much work has been investigated in this field by many researchers(1-3). Recently, the crystal synthesis and crystal structure of bis-(ethylene-diamine)-diisothiocyanatonickel(II)-benzene was reported(4) as a special structure of the first member of a new family of inclusion compounds based on a bidenateamine complex host.

The electronic absorption spectra of the crystal complexes combined with the spectroscopic properties of the complexes may act as a bridge to reveal links between the crystal structure and the electronic structure. Much work about the correlation between the spectrum and coordination structure has been done in our lab for many years. Some work on complexes of Ni(II) ion and amino acid have been reported(5-7), but the studies of electronic absorption spectrum of the clathrate compound was very limited. We have been very interested in the special structure of inclusion compounds based on a bidenateamine complex host. In order to obtain more information on nickel complexes and to study the characteristics of mixed ligand complexes, as they relate to the known crystal structure(4), we have determined its electronic absorption spectrum. In this paper we discuss the electronic absorption spectrum of $[Ni(en)_2(NCS)_2]$ crystal and explain them reasonably with the scaling radial wave function theory of non-free ions which was first proposed by us(8,9). Using this theory, we have received a series of results which are very well in agreement with the experimental values.

EXPERIMENTAL

The compound of $[Ni(en)_2(NCS)_2]\cdot C_6H_6$ was prepared as follows: two kinds of water solution(each 10 ml) of $Ni(NO_3)_2.6H_2O$(2.92 g) and KSCN(4.05 g) were mixed. To the stirring emerald green solution were added dropwise 1.5 ml of neat ethylenediamine. After most of the ethylenediamine had been added , a fine light purple precipitate formed. The pH of the solution was 10, then 2- aminoethanol was added, until the precipitate had completely dissolved, raising the pH to 11.2. The dark blue-purple solution was diluted with water to a total volume of approximately 45 ml. Solid citric acid was added in small portions until the pH fell to 7.9. A 15 ml sample of this solution was placed into a 50 vial and 2 ml benzene was placed on the top of the aqueous layer at room temperature, the crystal was obtained.

Elemental analysis was carried out with a Perkin-Elmer 240 C and found: C, 36.86; H, 5.67; N: 22.79. Calc. for $C_{12}H_{22}N_6S_2Ni$: C, 38.45; H, 5.94; N, 22.52%.

The electronic absorption spectrum(diffuse reflection spectrum) of [Ni(en)$_2$(NCS)$_2$]·C_6H_6 crystals was recorded at room temperature in the range 200-2500nm with (HITANCHI)V-34100 UV/VIS made by ANHUI INSTITUTE OF OPTICS AND FINE MECHANICS, CHINESE ACADEMY OF SCIENCE. The results measured and the computer resolution of overlapping electronic absorption bands are curved and shown in FIG. 1.

RESULTS AND DISCUSSIONS

The crystal structure of [Ni(en)$_2$.(NCS)$_2$]·C_6H_6, Nickel(II) ion coordination is a slightly distorted square bipyramid with dissothiocyanato occupying an axial position is clearly seen in FIG. 2a. The compound has two nearly linear trans-isothiocyanato ligands bound to the nickel in the modestly bent arrangement (Ni-N(1)-C(1) 166^0). The deviation from linear ligation is actually substantially less than the complex displays in its pure crystalline state (Ni-N-C 143.0^0)$^{(10)}$. The ability of the isothiocyanate ligand to vary its angle of coordination over a wide range undoubtedly plays a large role in the ability of these complexes to form inclusion compounds with many different guests. The coordination number is six. N(1) and N(6) atoms come from diisothiocyanato, the other four N atoms are provided by biethylene- diamine,. we chose N(1)-Ni as Z axis of the title crystal

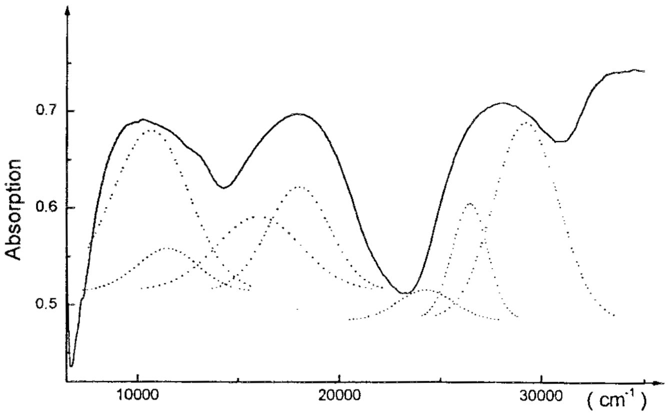
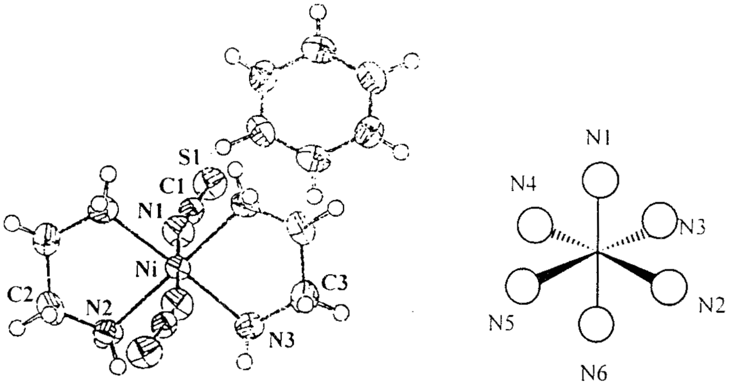


FIG.1. The electronic absorption spectra of the title complex.



(a) (b)

FIG.2. (a) Molecular structure of the complex.

(b) Coordinate structure of [Ni(en)$_2$(CNS)$_2$].

(FIG.2b) , the data of structure are listed in Table 1. As seen from the data of the crystal structure (Table 1), four N atoms provided by bipyramid are exhibited in an approximately flattened plane. So, the approximate symmetry of the coordination structure of $Ni(en)_2(NCS)_2$ is C_{2h}.

In ligand field theory, Li Jianmin et al. had suggested a non-free ions wave function radial scaling theory for which a program package(PLFT) had been developed and the radial wave function of Ni(II) can be written in double ζ (8,9) as,

$$R_{3d}(r, \Omega) = C^{-1/2}[0.534855STO(\zeta_1)+0.62500STO(\zeta_2)] = a_1STO(\zeta_1)+a_2STO(\zeta_2)$$

where $\zeta_1 = 6.1282(1-0.351045\Omega-0.208760\Omega^2)$

$$\zeta_2 = 2.4250(1-1.584119\Omega+0.322824\Omega^2)$$

$$C = 1-0.668569\{0.483577-[2(\zeta_1\zeta_2)^{1/2}/(\zeta_1+\zeta_2)]^7\}$$

where Ω is the so called scale of non-freedom, which is the parameter determined by the number of ligands, average bond length, the ratio of dipole length and bond length $\{\bar{t}\}$, and the average dipole moments of ligands$\{\bar{\mu}\}$, to describe the deviation free ion. It is given by the expression:

$$\Omega = N\bar{\mu}/R$$

$$\bar{\mu}^2 = kN\bar{\mu}/R^2\,(1-\bar{t}/2)^2$$

where N is the number of ligand atoms ,

R is the average bond length,

k=0.393427, where $\bar{\mu}$ can be estimated by the atomic parameter method

$$\bar{\mu} = k_0q\alpha/\,(r_c^+ + r_c^-)$$

where $k_0 = 1.442$, q is the ratio of the charge and radius of the central ion,

α is the electronic polarization rate of the ligand ion,

r_c^+ and r_c^- are the radii of the positive and negative ions.

With the theory, the electronic structures of hundreds of complexes have been explained perfectly(11). According to the environment of Ni(II) and the coordinate

TABLE 1

The structural data of the complex

Atom	N(1)	N(2)	N(3)	N(4)	N(5)	N(6)
R(Å)	2.108	2.104	2.092	2.104	2.092	2.108
θ(deg.)	0.0	91.7	90.05	88.2	89.4	179.6
φ(deg.)	0.0	0.0	97.1	180.0	277.2	0.0

system we have taken, the original data file can be set up, the parameters of the crystal field and the electronic energy of the crystal can be calculated by using a Program Package used for the calculation of Ligand Field Theory (PLFT). The values calculated are listed in Table 2 and Table 3. The observed values in Table 3 are results of the resolved absorption.

In the absorption curve of $[Ni(en)_2(NCS)_2]\cdot C_6H_6$ in FIG. 1. there are three strong and wide absorption peaks. It is known that spectral term symbols of d^8 configuration are ^3P, ^3F, ^1S, ^1D, ^1G. In the crystal field of C_{2h} symmetry ,the ground state is $^3A_{2g}$. From the spectral selection rules in the complex the parity forbidden is canceled. So the transitions from the ground state to the triplet state are allowed and they form some strong transition absorption, which are named the normal d-d transition spectrum band . For the effect of the ligand field, the ^3F spectrum term symbol has been split into three energy levels. They are $^3A_{2g}$, $^3T_{1g}$, and $^3T_{2g}$. So added together with the ^3P spectrum term, they will form three strong transition absorption peaks evidently corresponding to the three absorption peaks in FIG.1. As for the transitions from the ground state ($^3A_{2g}$) to single states they have--because of the spin forbidden rule--some weaker absorption peaks and compose the mutual combination spectrum band that is also the central ion spectrum band. The

TABLE 2

The crystal field parameters of the complex

$\bar{\mu}$ (Debye)	1.18700	a1	0.56886
Ω (Hartree)	0.18862	a2	0.66474
$\tilde{N}$	0.910	$<r^2>$(a.u.)	2.45124
$p^{(2)}$	1.82121	$<r^4>$(a.u.)	16.09335
$p^{(4)}$	2.31044	$<r^{-3}>$(a.u.)	4.89256
ζ_1	5.67690	B (cm^{-1})	911
ζ_2	1.72825	C (cm^{-1})	3135
$\bar{t}$	0.05880	ζ_{3d} (cm^{-1})	459

where B and C are Recah's parameters, ζ_{3d} represents spin-orbital coupling constant, and $p^{(2)}$and $p^{(4)}$ are polarization factors defined by us.

TABLE 3

Data of the electronic absorption spectrum

energy levels	Cal	Obs
$^3F(^3A_{2g}, e^2)$	0.	0.
$^3F(^3T_{2gb}, te)$	10910	10643
$^3F(^3T_{2gc}, te)$	11348	11486
$^3F(^3T_{1ga}, te)$	11895	
$^3F(^3T_{1gx}, te)$	16328.	16006
$^3F(^3T_{1gz}, te)$	17079	
$^3F(^3T_{1gy}, t^2)$	17955	17987
$^3P(^3T_{1gx}, t2)$	24286	24257
$^3P(^3T_{1gz}, t2)$	26679	26445
$^3P(^3T_{1gy}, t2)$	28865	29237

strength of transitions of this kind is only about one hundredth of that of the normal d-d transition band. For the C_{2h} symmetry, in the electronic absorption spectrum of $[Ni(en)_2(NCS)_2]\cdot C_6H_6$, we can not see a weak absorption peak. From octahedral field to C_{2h} field, the degenerate energy states of the spectral term are further split , absorption spectrum of the transitions from the ground state (${}^3A_{2g}$) to the higher energy state are seen , which is seven strong peaks lying at 10643, 11486, 16006, 17987, 24257, 26445, 29237 cm^{-1} and assigned as transition ${}^3T_{2gb}(te)$--${}^2A_{2g}(e^2)$, ${}^3T_{2gc}(te)$- -${}^2A_{2g}(e^2)$, ${}^3T_{1gx}(te)$--${}^3A_{2g}(e^2)$, ${}^3T_{1gy}(te)$--${}^3A_{2g}(e^2)$, ${}^3T_{1gx}(t2)$--${}^3A_{2g}(e^2)$, ${}^3T_{1gz}(t2)$--${}^3A_{2g}(e^2)$, ${}^3T_{1gy}(t2)$--${}^3A_{2g}(e^2)$ respectively.

From Table 3, correlation between the compound and the guest is neglected, because of the length between the Ni(II) ion and the guest being long. The errors originate mainly from the central potential field approximation and non-centrosymmetric structure of the crystal. The results calculated closely agree with the experimental values.

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