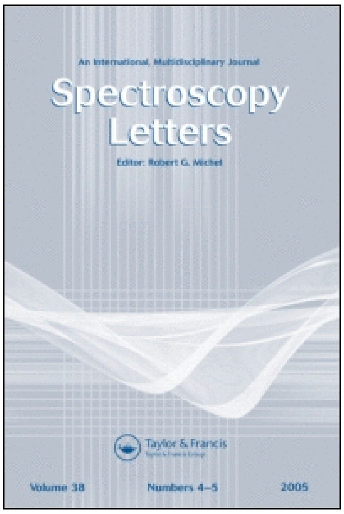

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Spectroscopic and Structural Studies of the Cobalt Clathrate Compound $[CO(NO_3)_2(4,4'\text{-Bipyridine})1.5]\infty$

Li Jianmin[a]; Xu Haitao[a]; Zhang Yugen[a]

[a] Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui, P.R.China

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SPECTROSCOPIC AND STRUCTURAL STUDIES OF THE COBALT CLATHRATE COMPOUND [$CO(NO_3)_2$(4,4'-BIPYRIDINE)1.5]$_\infty$

key words: electronic absorption spectrum, Cobalt compound,
ligand field theory and structural studies

Li Jianmin, Xu Haitao, Zhang Yugen

Email: jmli@ustc.edu.cn
Department of Chemical Physics
University of Science and Technology of China
Hefei, Anhui 230026, P.R.China

ABSTRACT

The electronic absorption spectrum of the crystals of [$Co(NO_3)_2$(4,4'-bpy)$_{1.5}$]$_\infty$ (4,4'-bpy = 4,4'-bipyridine) was recorded at room temperature. Eight absorption bands appeared at about 6808,7246,8312,125184,18302,20709,21594 and 24389

cm^{-1}. The experimental results agree with the value calculated with the ligand field theory (LFT) and the radial wave function of the non-free Cobalt(II) ion. As a result, the d-d transition spectrum of the title complex is explained satisfactorily.

INTRODUCTION

Crystal engineering of supramolecular architectures sustained by coordinate covalent bonds[1,2] or hydrogen bonding, represents a rapidly expanding field that offers potential for rational development of new classes of functional solids. Rational design of solid state architecture has become a particularly interesting topic, and an important subject[3,6]. Previously, research work focused mostly on the design and synthesis of new supramolecular structures. The studies of spectroscopic properties and the relation between their structures and spectroscopic responses are very limited. However, the electronic absorption spectra of complexes are the basis for studies of electronic structure, and the spectroscopic properties may act as a bridge to link the crystal structure and the electronic structure. Recently, we have been interested in the structure and spectroscopic properties of supramolecular architectures. Here, we report the spectroscopic properties of $[Co(NO_3)_2(4,4'\text{-bpy})_{1.5}]_\infty$, which is a noninterpentrated molecular ladder[7], and an open framework infinite ladder of the clathrate compound reported by Pierre Losier and Michale J. Zaworotko[8], which is well explained.

EXPERIMENTAL

The complex crystal of $[Co(NO_3)_2(4,4'\text{-bpy})_{1.5}]_\infty$ was prepared as follows: a solution of $[Co(NO_3)_2]\cdot 6H_2O$(0.290g, 1.0 mmol) in MeOH (20 ml) was added to a solution of 4,4'-bpy(0.23g, 1.5 mmol) in MeCN(20 ml). After the solution was left to stand at room temperature for 3 hours, red crystals were obtained.

Elemental analysis was carried out with a Perkin-Elmer 240 C and found: C: 42.75, H: 2.61, N: 16.91, Calc. for $C_{15}H_{12}N_5O_6Co$ C: 43.17, H: 2.88, N: 16.78%.

The electronic absorption spectrum(diffuse reflection spectrum) of $[Co(NO_3)_2(4,4'\text{-bpy})_{1.5}]_\infty$ crystals was measured at room temperature in the reign 200-2500 nm 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 Figure 1.

RESULTS AND DISCUSSION

In the crystal structure of $[Co(NO_3)_2(4,4'\text{-bpy})_{1.5}]_\infty$, the coordination number of the Cobalt(II) ion is seven; three N atoms come from 4,4'-bpy, the bond length of Co-N is approximately 2.143Å. The other four O atoms are provided by NO_3. The length of two Co-O bonds is 2.1276Å, and the other two Co-O bonds are 2.436Å. The Cobalt(II) ion geometry is a slightly distorted five-angle bipyramid with 4,4'-bpy occupying two axial positions[8], this structure is clearly shown in Fig. 2. Two long Co-O bonds (2.436Å) were considered as one shorter bond(9). The data of the structure is listed in Table 1. N(1)-Co-N(3) is chosen as the Z axis. One N atom and three O atoms are in an approximate flattened plane, shown in Fig. 2. As a result, the approximate symmetry of the crystal structure of $[Co(NO_3)_2(4,4'\text{-bpy})_{1.5}]_\infty$ is C_{2h}.

In ligand field theory, we had suggested a non-free ions wave function radial scaling theory for which a program package(PLFT) had been developed. The radial wave function of Co(II) can be written in double ζ (10,12) as,

$$R(r, \Omega) = C^{-1/2}[0.509614STO(\zeta_1) + 0.65000STO(\zeta_2)]$$

$$= a_1STO(\zeta_1) + a_2STO(\zeta_2)$$

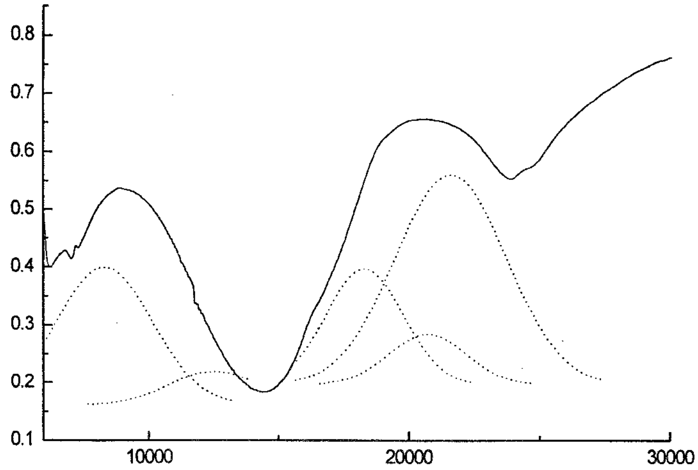

FIG.1. The electronic absorption spectra of the title complex.

$$\zeta_1 = 5.9068(1\text{-}0.23500\Omega\text{-}0.22160\Omega^2)$$

$$\zeta_2 = 2.3250(1\text{-}1.52803\Omega+0.396771\Omega^2)$$

$$C = 1\text{-}0.662498\{0.479689\text{-}[2(\zeta_1\zeta_2)^{1/2}/(\zeta_1+\zeta_2)]^7\}$$

where Ω is the so-called scale of non-freedom, which is the parameter variable to describe the deviation-free ion. It is given by the expression:

$$\Omega = N\mu/Ru^2 = KN\mu/[r^2(1\text{-}t/2)^2]$$

where N is the number of ligand ions, and R is the average bond length (Å). K = 0.393427, t is the ratio of dipole length and bond length, i.e. $t = 1/r$; μ is the dipole moment of the ligand ion (in debye).

U can be estimated by the atomic parameter method:

$$U = K_0 q\alpha/(\, r_c^+ + r_c^-)$$

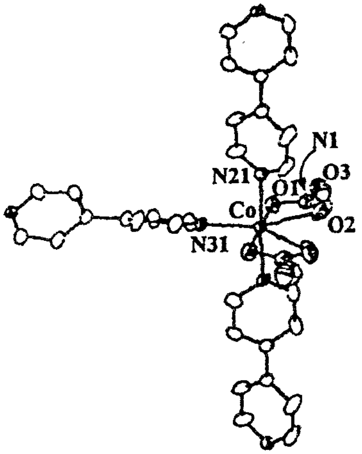

FIG. 2a. Molecular structure of the complex.

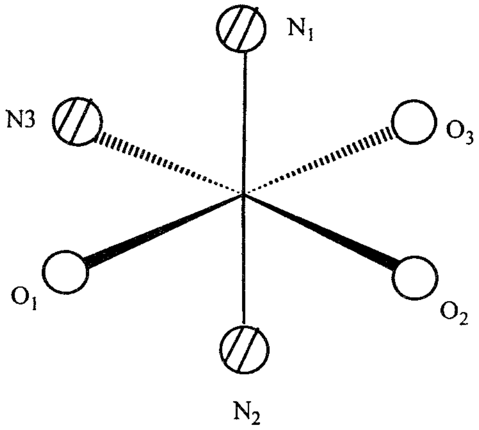

FIG. 2b. Coordinate structure of $[Co(NO_3)_2(4,4'\text{-bpy})_{1.5}]_\infty$.

TABLE 1.

The structural data of the crystal.

Atom	N(1)	N(2)	N(3)	O(1)	O(2)*	O(3)
R(Å)	2.1422	2.1435	2.1441	2.1276	2.1700	2.1276
θ(deg.)	0.0	180	90.5	89.3	90.7	89.3
φ(deg.)	0.0	0.0	270.07	0.0	117.35	180.4

* Two weak Co-O bonds were modified as one bond to fit our theory model by consideration of the same bond strengths.[12]

TABLE 2.

The crystal field parameters of the crystal.

$\bar{\mu}$ (Debye)	1.05450	a1	0.53653
Ω (Hartree)	0.15804	a2	0.68433
$\tilde{N}$	0.85	$<r^{2}>$(a.u.)	2.42674
$P^{(2)}$	1.48915	$<r^{4}>$(a.u.)	14.96945
$P^{(4)}$	1.83746	$<r^{-3}>$(a.u.)	4.48531
ζ_1	5.65473	B (cm^{-1})	895
ζ_2	1.78657	C (cm^{-1})	3100
$\bar{t}$	0.03956	ζ_{3d} (cm^{-1})	414

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.

where $K_0 = 1.442$, q is the ratio of the charge and the radius of the center ion, α is the electronic polarization rate of the ligand ion., and r_c^+ and r_c^- represent the radii of the positive and negative ion, respectively.

According to Table 1, the environment of Co(II), the coordinate system we have taken, and the original data file can then be set up. The parameters of the

TABLE 3.

Data of the electronic absorption spectrum

	Cal	Obs
${}^4A({}^4T_{1gx}, te2({}^3A_2))$	0.	0.
${}^4A({}^4T_{2ga}, t2({}^3T_1)e)$	6882	6808
${}^4A({}^4T_{2gb}, t2({}^3T_1)e)$	7335	7246
${}^4A({}^4T_{2gc}, t2({}^3T_1)e)$	8230	8312
${}^4A({}^4A_{2g}, t_3)$	12619	12518
${}^4A({}^4T_{1gx,} t2({}^3T_1)e)$	18475	18302
${}^4A({}^4T_{1gz}, t2({}^3T_1)e)$	20486	20709
${}^4A({}^4T_{1gy}, t2({}^3T_1)e)$	21378	21594
${}^4A({}^2T_{1g,} t2({}^1T_2)e)$	23742	24389

crystal field and the electronic energy of the crystal can be calculated by using the PLFT. The calculated values are listed in Table 2 and Table 3. The observed values in Table 3 represent the resolved absorption.

From the observed d-d transitional spectrum (Fig. 1.), five strong absorption peaks lying at 8312 ,12518 , 18302 , 20709 , 21594 cm^{-1} are observed. They are assigned as transitions of ^{4}A(4T2gc , t2(3T1)e) → ^{4}A(4T1gx, te2(3A2)), ^{4}A(4A2g , t3) →^{4}A(4T1gx, te2(3A2)), ^{4}A(4T1gx ,t2(3T1)e) →^{4}A(4T1gx, te2(3A2)), ^{4}A(4T1gz, t2(3T1)e) →^{4}A(4T1gx, te2(3A2)),^{4} A(4T1gy ,t2(3T1)e) → ^{4}A(4T1gx, te2(3A2)) respectively. In addition , one much weaker absorption peak is observed at 24389 cm^{-1} , which is assigned as transition ^{4}A(2T1g ,t2(1T2)e) →^{4}A(4T1gx, te2(3A2)). The transition from the ground state ^{4}A(4T1gx) to state (2T1g) has a much weaker absorption strength, about one hundredth of that of the normal d-d transition band, due to the forbidden spin rule.

From Table 3, the results calculated agree well with the experimental values. At first, it means that the guest molecule has nearly no effect on the crystal field, because the distance between it and the central metal ion is too long. For this reason, a satisfactory result was obtained under the central potential field approximation, and the ideal model structure of the crystal that we have taken. Agreement with the electronic structure and the crystal structure is embodied.

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