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Lanthanoid Methanesulfonate Complexes with 3-Picoline *N*-Oxide. Spectral Study of the Neodymium and Europium Complexes

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Abstract

Lanthanide methanesulfonate (MS) 3-picoline *N*-oxide (3-picNO) complexes, with general formula $[Ln(MS)_3(3\text{-}picNO)_2]$ (Ln = La–Yb, Y) present a non-electrolyte behavior in methanol, forming only one isomorphous series. The ligand is bonded through the oxygen, the MS^- ion being probably bidentate coordinated according to the IR data. From the electronic absorption spectra of the neodymium compound, the nephelauxetic and Sinha's parameters, covalent factor and the oscillator strength in solution were calculated and interpreted. The fluorescence spectrum of the europium complex was interpreted in terms of a C_{3v} symmetry, with the geometry of a bicapped trigonal prism. The crystal-field parameters (B_q^k) were also calculated.

Introduction

Several rare earth complexes containing aromatic amine oxides have long been under investigation in our group [1–8]. Our goal consists in determining the coordination of the ligands, the possible coordination of the MS^- ion and to study the spectral characteristics of the different complexes.

In this paper some spectral properties of the compounds of general formula $[Ln(MS)_3(3\text{-}picNO)_2]$ are studied, with emphasis on the absorption of the neodymium compound and emission spectra of the europium compound.

Experimental

The complexes were prepared from the hydrated lanthanoid methanesulfonate and 3-picNO in acetone, triethyl orthoformate or 2,2-dimethoxypropane as interaction medium [9]. The compounds present the same lanthanoid(III) colors. The hygroscopicity increases in the series. Conductance measurements in methanol indicate a non-electrolyte behavior (Λ_M = ~60 Ω^{-1} cm^2 mol^{-1}).

According to powder XRD data, only one isomorphous series was detected.

IR spectra were obtained on a Perkin-Elmer 180 spectrophotometer in Nujol mulls between KBr plates. The absorption spectra of the neodymium compound in silicone mulls at 77 and 298 K and in methanolic solution were recorded on a Cary 17 spectrophotometer. The fluorescence spectra of the europium compound at 77 K was measured on a Zeiss ZFM-4 spectrofluorometer, using 394 nm excitation radiation. The refractive index of the methanol solution was determined in an Abbe-type Bausch and Lomb refractometer.

Results and Discussion

From the IR spectra we could not distinguish the NO stretching band, ν(NO), from ν_{as}(SO) stretching, since they appear approximately in the same region, but it is certain that ν(NO) is shifted to lower frequencies. The negative shift is attributed to bond-order diminution due to the formation of the metal–oxygen bond [10, 11]. The δ(NO) (~815 cm^{-1}) vibration mode shows a slight shift to higher frequencies, while the out-of-plane CH deformation mode (~750 cm^{-1}) is shifted to higher frequencies. These shifts are due to a lowering of the electron density of the aromatic ring as a result of the coordination through the metal–oxygen bond of the NO group [10, 11].

The free MS^- ion, which has a C_{3v} point group symmetry, can give 9 to 11 experimental frequencies. Five of these belong to the symmetrical class A and six to the degenerate class E which are all Raman and IR active [12]. The MS^- group shows strong bands assigned to the antisymmetric and symmetric SO_3 stretching modes in the region between 1300 and 1040 cm^{-1}.

The coordination of the anion reduces the C_{3v} symmetry [13]. In our compounds, splittings of E

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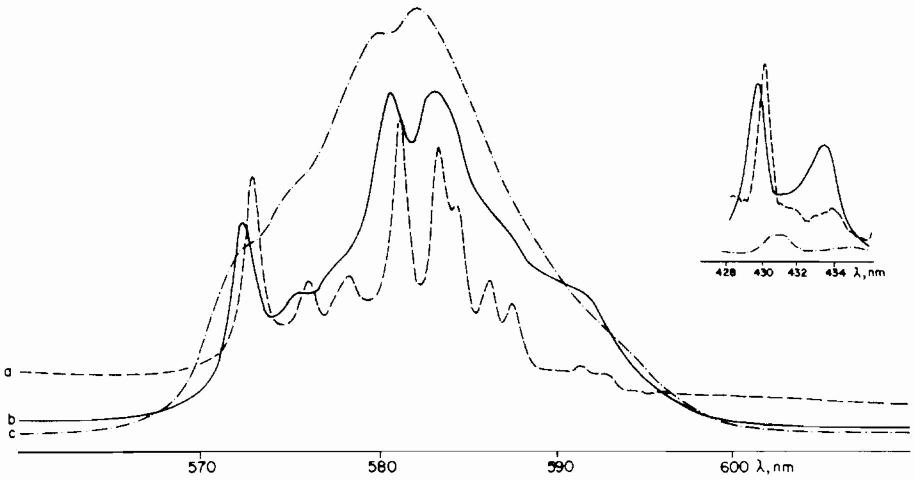

Fig. 1. Absorption spectra of $[Nd(MS)_3(3\text{-}picNO)_2]$: —— room temperature, – – – 77 K, –·– methanol solution.

species are observed, suggesting a lowering of the symmetry and that the MS^- anions are coordinated, behaving as bidentate ligands. Further evidence for anion coordination is the CS band, which appears at 780 cm^{-1} for the salt but is split in the addition compounds.

The absorption spectra of the neodymium compound in the solid state at room temperature and also at 77 K, and in methanol solution are presented in Fig. 1. From the spectrum at room temperature, using the $^2P_{1/2} \leftarrow {}^4I_{9/2}$, and $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ transitions, the wave numbers of the several peaks were determined. The nephelauxetic parameter β was calculated from the spectroscopic data by comparison with the corresponding values in the standard Nd^{3+}: LaF_3 [14] as follows:

$$G(Nd^{3+}:LaF_3)_{^4G_{5/2},\,^2G_{7/2}} = \frac{17\,089 + 17\,179}{2} + 195$$

$$= 17\,329\ cm^{-1}$$

(media of the centers of gravity of the two bands plus the crystal-field stabilization energy in cm^{-1}).

$$\beta_{^4G_{5/2},\,^2G_{7/2}} = \frac{G(\text{complex})}{G(Nd^{3+}:LaF_3)}$$

$$= \frac{17\,163\ cm^{-1}}{17\,329\ cm^{-1}} = 0.990$$

$$\beta_{^2P_{1/2}} = \frac{23\,276\ cm^{-1}}{23\,468\ cm^{-1}} = 0.992$$

(The value for $^2P_{1/2} \leftarrow {}^4I_{9/2}$ was determined from the higher energy of this transition).

From the above data we obtain $\bar{\beta} = 0.991$. The values of the covalency factor ($b^{1/2} = 0.067$) [15] and Sinha's parameter ($\delta = 0.91$) [16] were determined from $\bar{\beta}$. All the parameters suggest an essentially electrostatic metal–ligand bond. The number of bands at 77 K indicates that the Ln^{3+} ion is not involved in a cubic site.

The oscillator strength was calculated by applying Simpson's rule [17] to determine the area under the curve, employing the equation:

$$P = 4.31 \times 10^{-9} \frac{9\eta}{(\eta^2 + 2)^2} \int \epsilon(\nu)\, d\nu \qquad [18]$$

($\eta = 1.332$; concentration of the solution = 0.0205 mol l^{-1}; optical path = 2.00 cm; area = 183.44 and $P = 16.2 \times 10^{-6}$ $cm^2\ mol^{-1}\ l$).

The solution spectrum is different from that of the solid at room temperature but very similar to those of the hydrated [19] and anhydrous [20] MS^- salts and also to that of the $[Nd(MS)_3(2\text{-}picNO)_2]$ compound [7]. This fact is interpreted as being due to the solvolytic properties of the methanol, displacing the amine oxide groups.

The fluorescence spectrum of the europium compound at liquid nitrogen temperature is shown in Fig. 2. The spectral analysis and assignment were performed according to Forsberg [21]. A $^5D_0 \to {}^7F_0$ transition is observed at 578 nm, showing that the Eu^{3+} ion level lies in a C_n or C_{nv} symmetry site. Three well-defined peaks which appear in the 587–594 nm region are attributed to a $^5D_0 \to {}^7F_1$ transition. The two higher intensity peaks could be due to an E species or two other allowed (ED and MD) species. Another set of peaks of greater intensity appears at 610–620 nm, corresponding to a $^5D_0 \to {}^7F_2$ transition. The following assignments are suggested: (a) 2 peaks due to an E doubly allowed species; (b) 1 unfold doubly allowed E species; and (c) 1 for an A_1 species only allowed for ED. The most probable symmetry for the Eu^{3+} ion is C_{3v}.

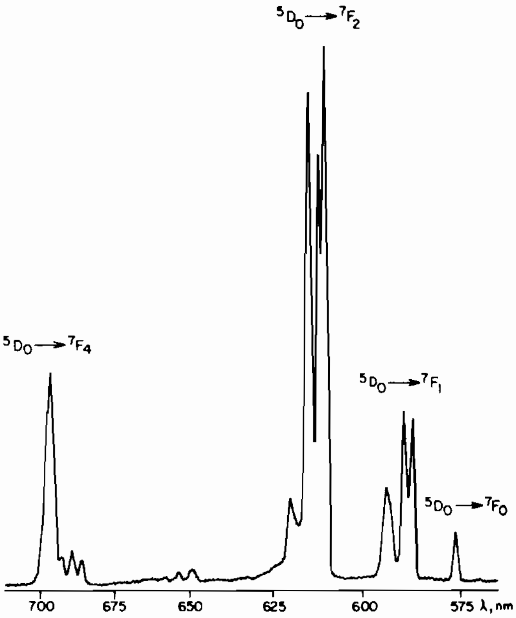

Fig. 2. Emission spectrum of $[Eu(MS)_3(3\text{-picNO})_2]$ at 77 K.

Since the IR data suggest a symmetry lowering of the MS ion acting as bidentate, we considered the apparent coordination number to be 8. The most probable geometry (for $CN = 8$) would be that of a bicapped trigonal prism with two oxygens (of the anion) occupying coordination sites at the vertex corresponding to the same prism edge, and the NO group (from 3-picNO) oxygens coordinating at the bases of the prism.

From the observed transitions for the europium compound it was possible to calculate the crystal-field parameters B_0^2, B_0^4 and B_3^4, considering a C_{3v} symmetry. The matricial elements were determined for the configuration $4f^6$ ($J = 1, 2$) by applying Racah's method [22]. The total Hamiltonian using Wybourne's notation [23] is given by:

$$\mathcal{H} = H_0 + H_1$$

$$H_1 = \sum_i \sum_{q=-k}^{q=+l} \sum_k B_q^k (C_q^k)_i$$

where H_0 corresponds to the Hamiltonian for the free ion, characterized by Racah's parameters E_1, E_2 and E_3, the spin–orbit coupling constant (ξ) and the configuration interaction parameters α, β, γ; H_1 is the crystal-field Hamiltonian, considered as a perturbation; C_q^k are operators associated to the spheric harmonic γ_q^k; B_q^k are crystal-field parameters associated to the symmetry of the compounds.

The matricial elements are calculated by the expression:

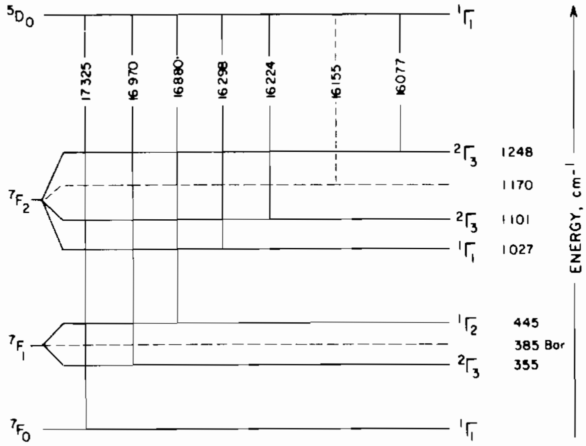

Fig. 3. Energy diagram for the compound with formula $[Eu(MS)_3(3\text{-picNO})_2]$.

$$H_{ij} = \sum_{q,k} B_q^k \left[(-1)^{J-M_j} \begin{pmatrix} J & k & J' \\ -M_j & q & M_j' \end{pmatrix} \cdot D_j^k \right]$$

in which:

$$D_q^k = (-1)^{S+L'+J+k}(2J+1)(2J'+1) \begin{Bmatrix} J & J' & k \\ L' & L & S \end{Bmatrix}$$

$$(WUL \| U^k \| W'U'L') \times \langle l \| C^k \| l' \rangle$$

Figure 3 contains the energy diagram with data of the emission spectrum. The extremely weak $^5D_0 \rightarrow {}^7F_3$ transition was not considered.

The centers of gravity of the transitions were determined by applying Simpson's rule [17].

The Hamiltonian of the crystal field for the C_{3v} symmetry is given by [23]:

$$H_{cf} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_0^6 C_0^6 + B_3^4 (C_{-3}^4 - C_3^4) + B_3^6 (C_{-3}^6 - C_3^6) + B_6^6 (C_6^6 - C_{-6}^6)$$

Triangular conditions impose $k = 2$ and $q = 0$ for the $^7F_1$ level. The matrix for this level is indicated in Fig. 4.

Calculations for the energy levels give:

$$E(\pm 1) = H_{11} = -0.100000 B_0^2$$

$$E(0) = H_{00} = 0.200000 B_0^2$$

$$\begin{array}{c|ccc} M_j' \backslash M_j & 1 & -1 & 0 \\ \hline 1 & H_{11} - E & 0 & \\ -1 & 0 & H_{11} - E & \\ 0 & & & H_{00} - E \end{array} = 0$$

Fig. 4. Secular determinant for the $^7F_1$ level in the C_{3v} symmetry.

$$\begin{array}{c|ccccc} M_j' \backslash M_j & 2 & -1 & -2 & 0 & 1 \\ \hline 2 & a-E & -d & & & \\ -1 & -d & b-E & & & \\ -2 & & & a-E & 0 & d \\ 0 & & & 0 & c-E & 0 \\ 1 & & & d & 0 & b-E \end{array} = 0$$

Fig. 5. Secular determinant for the $^7F_2$ in the C_{3v} symmetry.

With these energy values and the data of Fig. 3, the $B_0^2 = 300\ \text{cm}^{-1}$ is calculated.

For the $^7F_2$ level the triangular conditions impose $0 \leqslant k \leqslant 4$ (k is even) and the parameters B_0^2, B_0^4 and B_3^4 are calculated by three 5 × 5 matrices (Fig. 5).

The matricial elements for the interaction $M_j \rightleftharpoons M_j'$ are given by

$$a = -0.104761 B_0^2 - 0.015873 B_0^4$$

$$b = -0.052380 B_0^2 + 0.063491 B_0^4$$

$$c = -0.104761 B_0^2 - 0.095237 B_0^4$$

$$d = -0.0939048 B_3^4$$

From the energy equation, in the Fig. 5 determinant, it is possible to calculate:

$$E(2,-1):\ E^2 - (a+b)E + ab - d^2 = 0$$

$$E(-2,0,1):\ E^3 + \underbrace{[-(a+b+c)]E^2}_{p}$$

$$+ \underbrace{(ab+bc+ac-d^2)}_{q}E + \underbrace{d^2c - abc}_{r} = 0$$

or

$$E^3 + pE^2 + qE + r = 0$$

After the appropriate substitutions, the values of B_0^4 and B_3^4 are obtained:

$$B_0^4 = 1179\ \text{cm}^{-1}$$

$$B_3^4 = -523\ \text{cm}^{-1}$$

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