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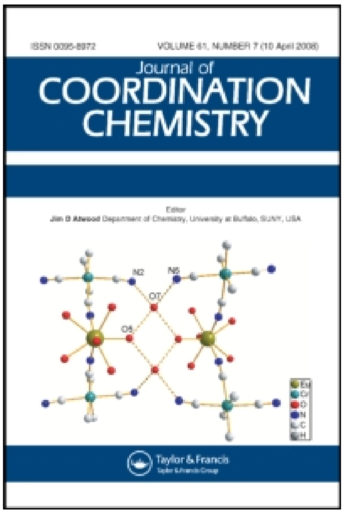

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# COORDINATION COMPOUNDS OF LANTHANIDE PERCHLORATES WITH PYRAZINEAMIDE

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# COORDINATION COMPOUNDS OF LANTHANIDE PERCHLORATES WITH PYRAZINEAMIDE†

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Lanthanide perchlorate complexes of the type $[Ln(pyaH)_4](ClO_4)_3$ where Ln = Pr, Nd, Sm, Eu, Tb and Lu, and pyaH is pyrazinamide have been isolated. The compounds were characterized by chemical analyses, molar conductance, vibrational spectra, and electronic absorption and emission spectra. The vibrational spectra and molar conductances indicate that the perchlorate groups are ionic and that pyaH acts a bidentate ligand. The oscillator strengths of the transitions of the Nd(III) complex were determined in terms of the Judd–Ofelt theory. It was possible to use the modified Judd–Ofelt parameters, $\tau\lambda$, for the evaluation of the spectral intensities. In addition, a group-theoretical analysis of the emission spectrum indicates an effective site symmetry $D_2$ for the Eu(III) complex between 77°K and 10°K.

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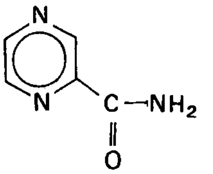
## INTRODUCTION

Complexes formed between transition metal ions and the ligand pyrazinamide (pyaH) have been extensively investigated [1–4]. However, the corresponding complexes with the lanthanide ions have not been reported in the literature.



(pyaH)

In this paper we describe the preparation and characterization of complexes of this ligand with perchlorates of praseodymium, neodymium, europium, terbium and lutecium.

This ligand was selected since it can potentially function as a bidentate ligand, with oxygen and nitrogen as donor sites, which would be expected to enhance the stability of any resulting complexes.

A significative part of this paper deals with the electronic spectroscopy of these complexes. The intensities of the solution spectra of the most lanthanide (III) have been interpreted by the Judd–Ofelt theory [5, 6]. This interpretation has been quite helpful in rationalizing certain transitions termed "hypersensitive" [7] and which are markedly affected by the chemical environment.

Carnall *et al.* [8] have correlated the experimentally determined band intensities in the absorption spectra of the trivalent lanthanides with the oscillator strength P, by the following theoretical expression, derived by Judd [5]:

$$P = \sum_{\lambda=2,4,6} \tau_\lambda \sigma (f^N \Psi_j \parallel U^{(\lambda)} \parallel f^N \Psi'_{J'})^2 (2J+1)^{-1} \quad \text{(I)}$$

where $\sigma$ is the energy of the transition $\psi'_{J'} \leftarrow \psi_{J'}$ i.e., the baricenter of the absorption band in $cm^{-1}$, and $U^{(\lambda)}$ is a tensor operator of rank $\lambda$. The $\tau_\lambda$ are parameters to be determined by fitting to the band observed intensities.

It is well known that complexes of this type with europium and terbium are generally liminescent when excited by near-ultraviolet radiation [9]. However, their emission spectra are remarkable, showing a very intense luminescence with characteristic sharp lines and allowing the symmetry of the chemical environment to be assigned.

## EXPERIMENTAL

### *Materials*

The rare earth oxides were 99.9% purity and were generously supplied by Molycorp. The pyrazineamide (Aldrich Chemical Co) was purified by recrystallization from ethanol–water solution. The

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ligand was characterized by microanalyses, melting point and IR spectrum. All the solutions containing acetonitrile were prepared and handled inside a glove bag containing $P_4O_{10}$ as a desiccant and filled with dry nitrogen. A solution of 4.3 mmole of ligand in 40 ml dioxan was added dropwise, under vigorous stirring, to a solution of 1 mmol of rare earth perchlorate in 3 ml of dry ethanol and 1 ml of triethylorthoformate. All operations were carried out in a dry, inert-atmosphere glove bag. The solution was then cooled to $-10°C$ for 40–48hr. The solid compounds that precipitated were filtered, washed with petroleum ether and purified by recrystallization from acetone.

The solid was then dried at 80°C over $P_4O_{10}$ at a pressure less than 1 mmHg in an Abderhalden drying apparatus.

### *Analysis*

The lanthanide content was determined by the standard EDTA compleximetric titration using xylenol orange as the indicator. Microanalyses were performed by PCR, Inc. (handled in dry box) and by the microanalytical laboratory of the University of São Paulo.

### *Instrumentation*

IR spectra were recorded with a Beckman IR–10 or a Perkin–Elmer model 180 spectrophotometer. Nujol and Flurolube mulls were prepared in a nitrogen-filled glove box using dry, degassed Nujol. Raman spectra were performed with a spex 1702 double nomochromator using an argon laser with excitation lines at 4880 and 5145Å. Conductance measurement were made in solutions of the complexes in acetonitrile with a metrohm E527 using a cell previously calibrated with aqueous potassium chloride. The emission spectra were measured with both a Beckman ACTA-CV equipped with the Model 569384 fluorescence attachment, and with the same apparatus for Raman, except that the excitation source was a 100-watt mercury lamp used in conjunction either with Corning CS–7–39 or CS–7–54 filters. The solids samples were placed in quartz tubes of 3 mm i.d. and inserted into a Dewar with a quartz tail.

Electronic absorption spectra were obtained and the absorption intensities, were integrated point by point making it possible to determine the experimental oscillator strengths ($P_{exp}$) described previously [10]. The $\tau_\lambda$ parameter (equation (I)) were calculated from the experimentally obtained oscillator strengths and the calculated reduced matrix elements of Carnall [8]. The $\tau_\lambda$ parameters were, in turn, used to obtain the "calculated oscillator strengths" and the root-mean-square deviation between the $P_{cal}$ and $P_{exp}$ were also obtained. All calculations were made with a 1130-IBM computer [11].

## RESULTS AND DISCUSSION

The reaction between the lanthanide perchlorates and pyrazineamide results in the formation of solid crystaline compounds. The analytical data for the metal, carbon, hydrogen, and nitrogen of the compounds all agree within 1% of the theoretical values. These results are in good agreement with the formulation as $[Ln(pyaH)_4](ClO_4)_3$, where Ln = Pr, Nd, Eu, Tb and Lu.

The analyses show that no water is present in the composition of these complexes. However, the compounds proved to be slightly hygroscopic on handling and special precautions (nitrogen atmosphere) were necessary to ensure that the complexes remained free of water throughout all subsequent measurements.

Molar conductivities ($\Omega\ cm^2\ mole^{-1}$) of, for example $[Nd(pyaH)_4](ClO_4)_3$, is 341.5 in acetonitrile. These results are typical of the whole series of compounds and indicate that all three perchlorate anions are uncoordinated [12, 13], as also suggested by the vibrational spectra.

The hardness of the lanthanide will favor the coordination to the oxygen and this will be indicated most clearly by the amide I band, which arises mainly from the CO stretching vibration. The Amide I band occurs at 1710 $cm^{-1}$ in pyaH [14] and at 1665 – 1670 $cm^{-1}$ in lanthanide complexes. This lowering is generally indicative of bonding through oxygen of the amide group [15, 16]. The Amide III band found in complexes at 1400–1405 $cm^{-1}$ in the free ligand, a shift normally associated with oxygen coordination [16].

The first of the two medium bands observed in the spectrum of the ligand at 1515 and 1570 $cm^{-1}$, which correspond to $\nu(C=C)$ and $\nu(C=N)$, is shifted to higher frequencies in the spectra of the complexes indicating that the double bond character of C = C and C = N increases as a consequence of the coordination by nitrogen [17]. The two ring deformations at 615 and 430 $cm^{-1}$ found in the ligand also shift to higher frequency, as a good indication of the coordination of the heterocyclic nitrogen [13, 17]. These same trends have been observed for pyaH with other metals [18, 19].

All IR spectra show a very strong broad band around 1100 cm$^{-1}$ ($\nu_3$) and another very strong band around 620 cm$^{-1}$ ($\nu_4$) neither of each has undergone any splitting, indicating the presence of ionic perchlorate with Td symmetry [20]. The weak band around 930 cm$^{-1}$ ($\nu_1$) is theoretically forbidden, but it also appears in the solid spectra of other lanthanide complexes containing tetrahedral perchlorate [21–23], due to activation by site symmetry [24].

The four possible bands of the perchlorate ion in Td symmetry are allowed in the Raman spectra. Although $\nu_3$ is obscured by rocking vibration of $NH_2$, the lack of splitting of $\nu_2$ and $\nu_4$ support the Td symmetry of the anion. The agreement between the vibrational data and the conductivity evidence suggest that the perchlorate ions are not coordinated in any of the complexes.

It is well established that all the absorption bands in the near-i.r., visible and near-ultraviolet spectra of tripositive rare earths exhibit a line-like character and are of low intensity [25]. We report here the oscillator strengths of the f ↔ f transitions of the solid compound $[Nd(pyaH)_4](ClO_4)_3$, dissolved in acetonitrile and briefly discuss the results in light of the concept of hypersensitivity [7]. The oscillator strengths ($P_{exp}$ and $P_{calc}$) obtained from the electronic absorption spectra are given in Table 1 together with the spectral assignments of the relevant transitions as taken from the work of Carnall *et al.* [8, 27]. The $\tau_\lambda$ parameters were calculated from these values of oscillator strengths as described in the introduction.

The $\tau_\lambda$ parameters $[\tau_\lambda = T_\lambda\ (2J + 1)]$ of $Nd^{3+}$ in $[Nd(pyaH)_4](ClO_4)_3$ are compared to previously obtained parameters of $Nd^{+3}$ in α-Picolinates and presented in Table III. The results are compared with the case of rare earth ions in aqueous solutions. The values of $\tau_4$ and $\tau_6$ are in good agreement with those of Carnall. On the other hand, $\tau_2$ differs significantly. These values of $\tau_2$ are higher than those reported for the α-Picolinates systems. This is probably due to a higher degree of covalency [26] and a lower symmetry of $Nd^{+3}$ site in the $[Nd(pyaH)_4](ClO_4)_3$ compound [29]. It is interesting to note that this result is also consistent with Judd's assumption that $\tau_2$ should be the most sensitive parameter to changes in environment.

TABLE I
Oscillator Strengths for Nd(III) in acetonitrile solution (P × 10$^6$).

| Transition (Assignment)$^b$ | Energy (cm$^{-1}$) | $[Nd(PyaH)_4](ClO_4)_3$ Exp | $[Nd(PyaH)_4](ClO_4)_3$ Calc | Aquo Ion$^a$ Exp |
|---|---|---|---|---|
| $^4F_{5/2}$<br>$^2H_{9/2}$ | 11.900 – 12.950 | 6.31 | 7.02 | 7.7 |
| $^4S_{3/2}$<br>$^4F_{7/2}$ | 12.950 – 14.100 | 7.62 | 7.27 | 7.6 |
| $^4G_{5/2}$<br>$^2G_{7/2}$ | 16.400 – 18.200 | 19.0 | 19.0 | 8.3 |
| $^2K_{13/2}$<br>$^4G_{7/2}$<br>$^4G_{9/2}$ | 18.400 – 20.200 | 6.04 | 5.47 | 5.8 |
| $^2K_{15/2}$<br>$^2G_{9/2}$<br>$(^2D, {}^2P)_{3/2}$ | 22.400 – 22.100 | 1.47 | 1.22 | 1.9 |
| $^2P_{1/2}$ | 22.880 – 23.530 | 0.33 | 0.56 | 0.30 |

$^a$Reference [27]
$^b$Reference [28]

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TABLE II
$\tau_\lambda$ Parameters for $Nd^{+3}$ in Acetonitrile Solution.

| Compounds | $\tau_2$ | $\tau_4$ | $\tau_6$ | rms deviation $\times 10^6$ |
|---|---|---|---|---|
| | | (cm $\times 10^{-9}$) | | |
| $[Nd(PyaH)_4](ClO_4)_3$ | 6.86 | 6.55 | 7.70 | 0.59 |
| Aquo Ion[a] | 1.20 | 6.44 | 10.2 | – |
| α-Picolinates[b] | 4.05 | 13.3 | 13.2 | 1.56 |

[a] Reference [27]
[b] Reference [29]

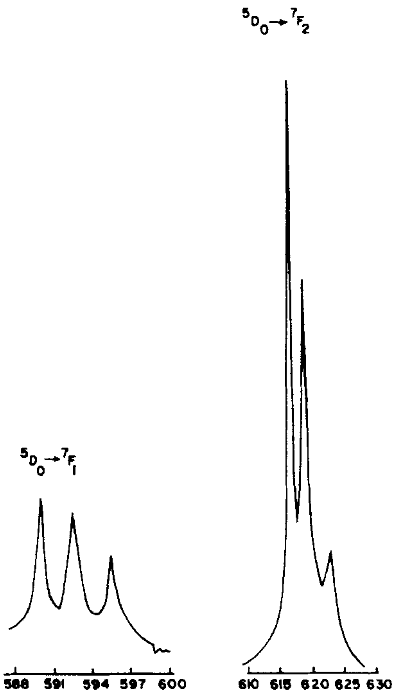

FIGURE 1 Emission spectrum of $Eu(PyaH)_4(ClO_4)_3$ from solid at 10° K.

The emission spectrum of the europium complex at 10° k is given in Figure 1 along with the suggested assignments for the transitions.

The dominant geometries for eight coordination complexes are those derived from the square antiprism ($D_{4d}$) or the tetragonal dodecahedron ($D_{2d}$) [30, 31]; Both of these can give rise to structures that possess $D_2$ symmetry. Distortion from the idealized square antiprism or from the dodecahedron may be attributed to the constraints imposed by the chelating ligands. A summary of the crystal-field splitting for the dominant angular momenta, J, in $D_{2d}$, $D_{4d}$ and $D_2$ symmetries together with the transitions allowed for magnetic dipolar selection rules ($^5D_0 \rightarrow {}^7F_1$) or electric dipolar selection rules ($^5D_0 \rightarrow {}^7F_0$, $^7F_2$) appears in Table III. The emission spectrum is in agreement with what would be expected of $Eu^{+3}$ in a $D_2$ environment but unfortunately it is not possible to choose between the structure which is derived from square antiprism and that which is derived from the dodecahedron.

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TABLE III
Allowed transitions between selected states in $D_{4d}$, $D_{2d}$ and $D_2$ symmetries.

| Transition | $D_{4d}$ | $D_{2d}$ | $D_2$ | Assignments (nm) | | |
|---|---|---|---|---|---|---|
| $^5D_0 \rightarrow {}^7F_0$ | none | none | none | – | | |
| $^5D_0 \rightarrow {}^7F_1$ | $A_1 \rightarrow A_2$ | $A_1 \rightarrow A_2$<br>$A_1 \rightarrow E$ | $A \rightarrow B_1$<br>$A \rightarrow B_2$<br>$A \rightarrow B_3$ | 590.1, | 592.8, | 595.7 |
| $^5D_0 \rightarrow {}^7F_2$ | $A_1 \rightarrow E_2$ | $A_1 \rightarrow B_2$<br>$A_1 \rightarrow E$ | $A \rightarrow B_1$<br>$A \rightarrow B_2$<br>$A \rightarrow B_3$ | 615.0, | 617.5, | 621.7 |

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