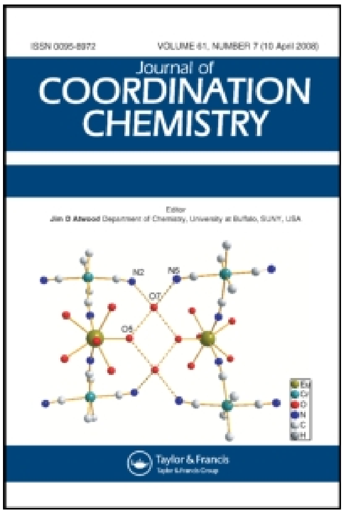

## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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**To cite this Article** De Carvalho, L. R. F. and Vicentini, G.(1981) '*N, N*-DIMETHYL-DIPHENYLPHOSPHINAMIDE (DDPA) LANTHANIDE SALT ADDUCTS. CONSIDERATIONS ABOUT Nd$^3$ AND Eu$^3$ SPECTRA', Journal of Coordination Chemistry, 11: 2, 67 — 72

**To link to this Article: DOI:** 10.1080/00958978108079049

**URL:** http://dx.doi.org/10.1080/00958978108079049

J. Coord. Chem., 1981, Vol. 11, pp. 67–72
0095-8972/81/1102-0067 $06.50/0

# *N,N*-DIMETHYL-DIPHENYLPHOSPHINAMIDE (DDPA) LANTHANIDE SALT ADDUCTS. CONSIDERATIONS ABOUT $Nd^{3+}$ AND $Eu^{3+}$ SPECTRA

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*(Received November 17, 1979; in final form August 14, 1980)*

A comparative study concerning absorption and emission spectra of the perchlorate, hexafluorophosphate, nitrate and isothiocyanate of neodymium and europium adducts with *N,N*-dimethyl-diphenylphosphinamide (DDPA) was realized. From the absorption spectra the parameters $\beta$, $b^{1/2}$ and $\delta$ and the oscillator strengths, $P$, were determined for the neodymium adducts, as were the emission spectra of the corresponding europium compounds. Suggestions concerning symmetry and geometry of the adducts are given.

## INTRODUCTION

Previous reports from this laboratory have described addition compounds containing lanthanide nitrates,[1] perchlorates,[2] isothiocyanates[3] and hexafluorophosphates[4] with DDPA.

In this paper we report absorption and emission spectra of several addition compounds with DDPA, with the following compositions: $Ln(ClO_4)_3 \cdot 4DDPA$, $Ln(PF_6)_3 \cdot xDDPA$, $Ln(NO_3)_3 \cdot 3DDPA$ and $Ln(NCS)_3 \cdot 4DDPA$ (Ln = Nd, Eu). The main purposes of the study were to obtain information concerning the bond character, the influence of temperature and symmetry on the intensities of neodymium hypersensitive bands, and with the aid of IR and conductance data, to infer types and numbers of ligands, apparent coordination numbers, symmetries and geometries around the central lanthanide ions.

## EXPERIMENTAL

### *Preparation of the Adducts*

The hydrated lanthanide perchlorates, nitrates and isothiocyanates were dissolved in absolute ethanol and treated with a sufficient amount of the ligand in ethanolic solution.[1–3] A concentrated aqueous solution of the neodymium hexafluorophosphate was treated with an ethanolic solution of DDPA.[4] The neodymium and europium nitrate adducts were prepared for the first time.

### *Analysis and Measurements*

The purity of the compounds was checked by EDTA titrations[5] and by microanalytical procedures. Absorption spectra of Kel-F mulls at room temperature and at 77K (Figure 1) of the neodymium compounds were recorded in a Cary 17 spectrophotometer with a different absolute range (A.R.) for each case. The electronic spectra of the adducts in nitromethane and acetonitrile solutions were obtained in a Zeiss DMR-10 spectrophotometer (Figure 2). The emission spectra of the solid europium adducts, at 77K, were recorded in a Perkin–Elmer MPF-4 spectrofluorimeter, with 394 nm excitation radiation (Figure 3). The refractive indexes of the solutions were determined at 20°C, with an Abbe, Model G, refractometer.

## RESULTS AND DISCUSSION

The absorption spectra of the neodymium compounds in the solid state are presented in Figure 1, showing the transitions: $^4I_{9/2} \rightarrow {}^2P_{1/2}$ and the hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$, which are commonly used to calculate the nephelauxetic parameters, $\beta$.[6,7] This parameter can be related to the covalent factor, $b^{1/2}$,[8] which measures the amount of mixing of the 4*f*-ligand orbitals or to Sinha's parameter, $\delta$,[9] which also gives the relative covalent character of the bond. The values obtained (Table I) suggest a small precipitation in bonding of 4*f* orbitals, that is, an

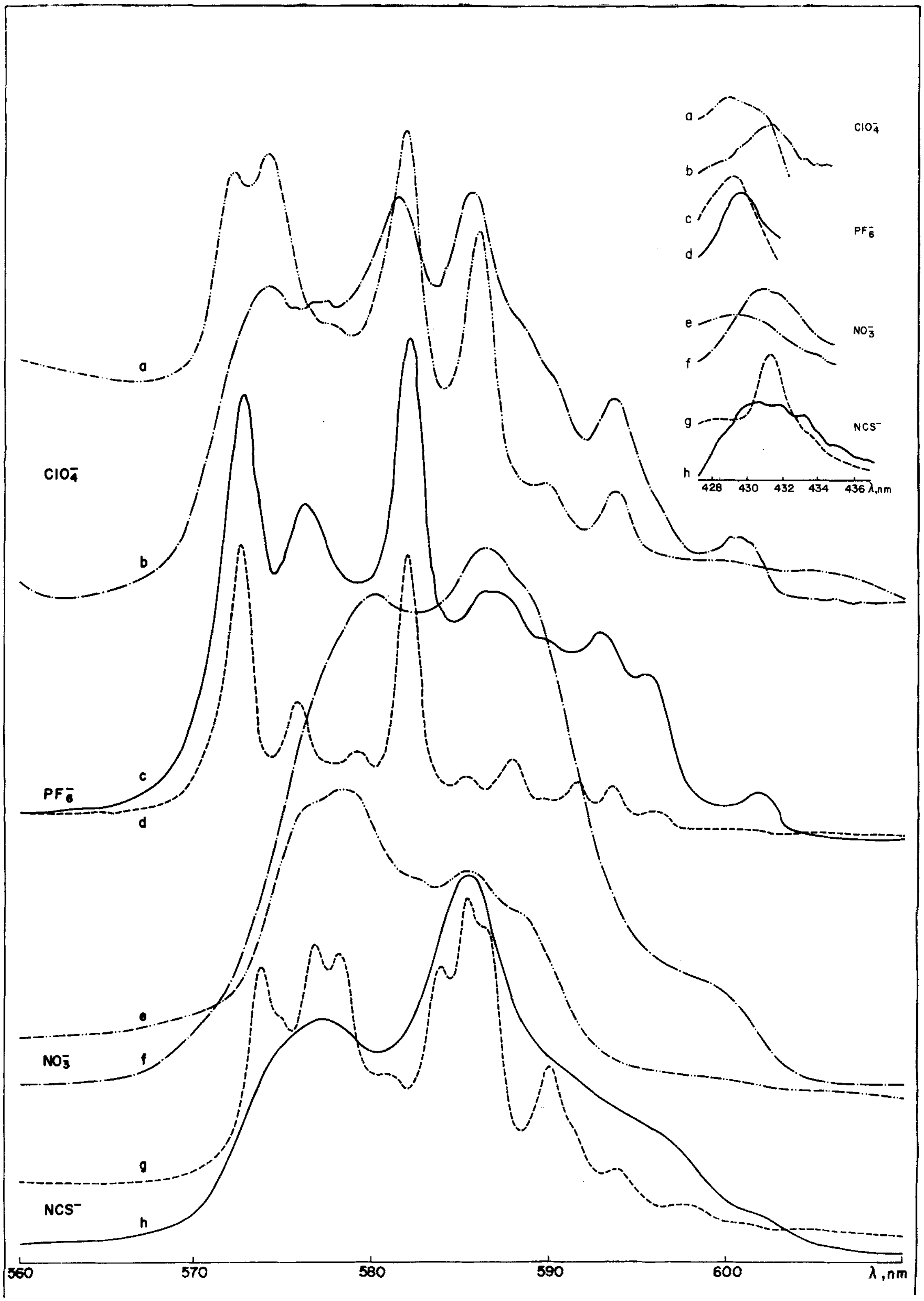

FIGURE 1 Absorption spectra of the neodymium adducts in the solid state: a) perchlorate, room temperature, A.R. = 0.2; b) perchlorate 77K, A.R. = 0.5; c) hexafluorophosphate, room temperature, A.R. = 0.2; d) hexafluorophosphate, 77K, A.R. = 1.0; e) nitrate, room temperature, A.R. = 0.5; f) nitrate, 77K, A.R. = 1.0; g) isothiocyanate, room temperature, A.R. = 0.5; h) isothiocyanate, 77K, A.R. = 0.5.

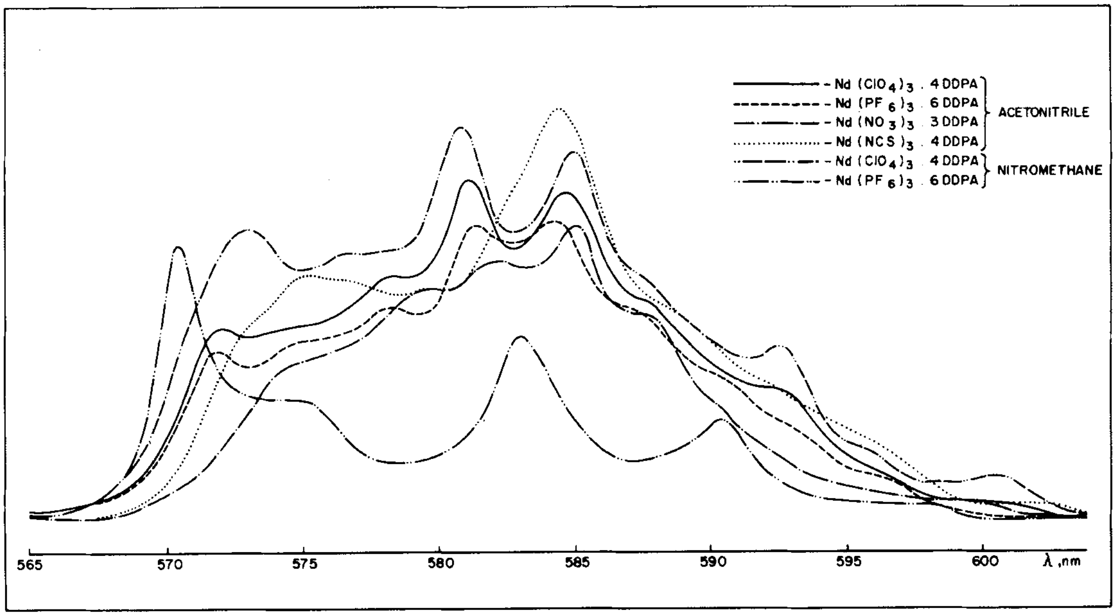

FIGURE 2 Absorption spectra of the neodymium adducts in solution, at room temperature.

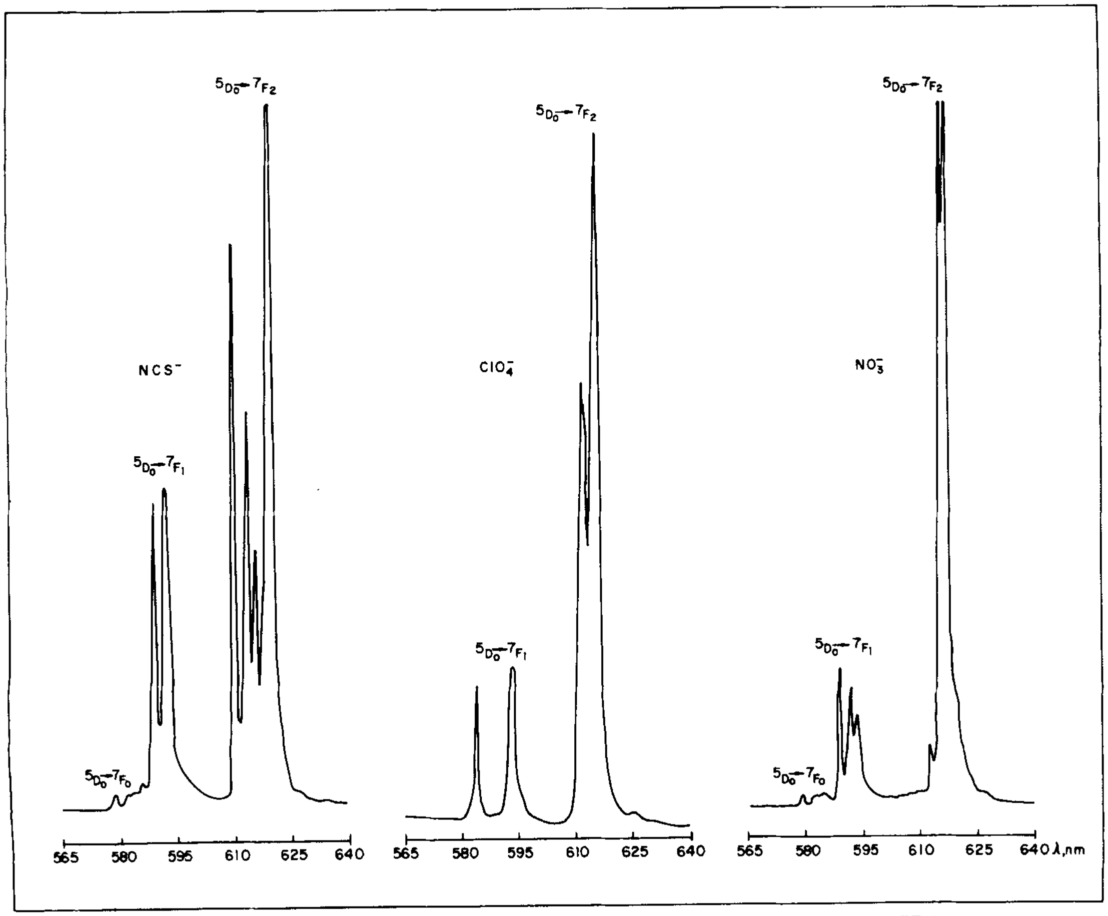

FIGURE 3 Emission spectra of the europium adducts in the solid state, at 77K.

TABLE I
Espectroscopic data for *N,N*-dimethyl-diphenylphosphinamide neodymiym salt adducts.

| Compound | Transition $^4I_{9/2} \rightarrow {}^2P_{1/2}$ |  |  | Transition $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | $\lambda$, nm | $\bar{\nu}$, cm$^{-1}$ | $\beta$ | $\lambda$, nm | $\bar{\nu}$, cm$^{-1}$ | $\beta$ | $\bar{\beta}$ | $b^{1/2}$ | $\delta$ |
| $Nd(ClO_4)_3 \cdot 4DDPA$ | 431.5 | 23174 | 0.9875 | 582.7 | 17161 | 0.9903 | 0.9890 | 0.074 | 1.12 |
| $Nd(PF_6)_3 \cdot 6DDPA$ | 429.4 | 23288 | 0.9923 | 582.3 | 17173 | 0.9910 | 0.9917 | 0.064 | 0.84 |
| $Nd(NO_3)_3 \cdot 3DDPA$ | 431.0 | 23201 | 0.9886 | 584.5 | 17108 | 0.9872 | 0.9879 | 0.078 | 1.22 |
| $Nd(NCS)_3 \cdot 4DDPA$ | 431.7 | 23164 | 0.9870 | 584.6 | 17104 | 0.9870 | 0.9870 | 0.080 | 1.31 |

almost complete electrostatic character of the $Ln^{3+}$-ligand interaction, in all cases.

The number of bands in all the spectra, at 77K, due to transitions $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$, indicates a non cubic site around tripositive neodymium ions. In practically all cases, as expected, the bands are well resolved at low temperature.

For the nitrate and isothiocyanate adducts the band intensities are not essentially altered with decreasing temperature; but the shape of the nitrate spectrum is modified, with some inversion in the relative intensities. For the perchlorate and hexafluorophosphate the band intensities rise appreciably at low temperature. One may fairly safely deduce from this experimental observation that the temperature effect upon intensity is related to the symmetry around the central ion. Electronic transitions may occur for complexes without inversion centre (i), but in centrosymmetric compounds transitions become partially allowed through vibronic interactions. When temperature is increased, *i* may be either removed or formed in a complex centrosymmetric or non centrosymmetric, respectively; therefore, the forbidden transitions become, in principle, allowed or vice-versa. The band intensity is related to the type of transition in question and this may on the other hand depend on temperature.

Figure 2 illustrates the spectra of the different compounds in acetonitrile and nitromethane solutions. The nitrate and isothiocyanate spectra were not recorded in nitromethane solution because they are not soluble enough. Table II contains the values of the oscillator strengths, *P*, in both solvents, calculated for the hypersensitive transition.[10] The area under the curve was determined by applying Simpson's rule.[11] The comparison of $Nd^{3+}$ hypersensitive band behaviour of the hexafluorophosphate, perchlorate, isothiocyanate and nitrate, in acetonitrile, indicates an increase of the oscillator strengths in the order $PF_6^- < ClO_4^- < NCS^- < NO_3^-$, following directly the influence of anion basicity, as also observed by Henrie *et al.*[12] and by Seminara *et al.*[13] Some observations concerning the spectra can be made:

a) the spectra of the solid perchlorate at room temperature and in acetonitrile and nitromethane solutions are practically identical; the isothiocyanate spectra in the solid state at room temperature and in acetonitrile solution are also equal;

b) the spectra of the solid nitrate and hexafluoro-

TABLE II
Oscillator strengths for $Nd^{3+}$ in acetonitrile and nitromethane solutions.

| Compound | Conc., M × $10^3$ | $\eta$ | $P \times 10^6$[a] $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ |
|---|---|---|---|
| $Nd(ClO_4)_3 \cdot 4DDPA$[b] | 25.4 | 1.3820 | 13.6 |
| [c] | 15.7 | 1.3504 | 17.7 |
| $Nd(PF_6)_3 \cdot 6DDPA$[b] | 26.5 | 1.3841 | 6.1 |
| [c] | 14.8 | 1.3510 | 16.8 |
| $Nd(NO_3)_3 \cdot 3DDPA$[c] | 3.42 | 1.3473 | 25.0 |
| $Nd(NCS)_3 \cdot 4DDPA$[c] | 11.5 | 1.3499 | 18.5 |

[a] cm$^2$ mole$^{-1}$ l.
[b] Nitromethane.
[c] Acetonitrile.

TABLE III
Proposed symmetries and geometries for $Eu^{3+}$ adducts.

| Compound | Apparent coordination number | Symmetry | Geometry |
|---|---|---|---|
| $Eu(ClO_4)_3 \cdot 4DDPA$ | 8 | $D_{2d}$ | dodecahedron |
| $Eu(PF_6)_3 \cdot 5DDPA$ | 6 | $C_{2v}$ | rectangular pyramide |
| $Eu(NO_3)_3 \cdot 3DDPA$ | 9 | $D_{3h}$ | tricapped trigonal prism |
| $Eu(NCS)_3 \cdot 4DDPA$ | 7 | $C_{3v}$ | monocapped trigonal prism<br>or octahedral monocapped |

phosphate adducts differ from those in acetonitrile solution, a fact which suggests an interaction with the solvent, probably due to the modification of the coordination number expected from the substantial donation capacity of this solvent;

c) the spectrum of the hexafluorophosphate in acetonitrile is close, but not identical, to that of the perchlorate with close oscillator strengths, whereas the hexafluorophosphate and perchlorate spectra and their values of the oscillator strengths in nitromethane are completely different.

These facts show that the hexafluorophosphate and perchlorate species are the same in acetonitrile solutions but not in nitromethane and indicate again the influence of the acetonitrile on the coordination number of the adducts. They seem not to be affected by nitromethane's presence.

Figure 3 contains the emission spectra of the europium at 77K. Table III presents the proposed symmetries and geometries. For the perchlorate, the conductance data in nitromethane (1 : 1 electrolyte) and the number and position of bands in the IR spectra may be interpreted in terms of the existence of two bidentate perchlorate ions,[2] suggesting an apparent coordination number eight to the complex species. The most frequent geometries for octacoordination in lanthanides are: square antiprism, $D_{4d}$, dodecahedron, $D_{2d}$, bicapped trigonal prism, $C_{2v}$, or bicapped octahedron, $D_{3d}$.[14] The $C_{2v}$ symmetry is excluded because the spectrum does not present a $^5D_0 \rightarrow {}^7F_0$ band (the band at 17152 $cm^{-1}$ is attributed to a $^5D_1 \rightarrow {}^7F_J$ transition). $D_{3d}$ was not considered because this site presents an inversion center and the spectrum shows medium $^5D_0 \rightarrow {}^7F_1$ as compared with the strong $^5D_0 \rightarrow {}^7F_2$ bands. For the $D_{4d}$ symmetry only one $E$ species is expected for the $^5D_0 \rightarrow {}^7F_2$ $(A_1 \rightarrow E_1)$ transition. The $D_{2d}$ symmetry, consistent with an $Eu(O)_8$ chromophore, is suggested because the $^5D_0 \rightarrow {}^7F_1$ transition presents one band and a shoulder and $^5D_0 \rightarrow {}^7F_2$ two bands, one of which shows a shoulder that may be due to an $E$ species.[15]

The hexafluorophosphate adduct's symmetry was interpreted as $C_{2v}$.[4] Admitting such symmetry and considering that the coordination number five very improbable for lanthanide ions, we suggest that one DDPA molecule is acting as a bridge between two europium ions; an apparent coordination number six may be attributed to the complex species. We propose rectangular pyramididal coordination geometry around one europium ion.

IR spectra and conductance data of the nitrate adducts in,[1] were interpreted as follows: three bidentate nitrated and three DDPA molecules give to the complex species an apparent coordination number nine. Two idealized polyedrons may be proposed: the monocapped square antiprism, $C_{4v}$, and the tricapped trigonal prism, $D_{3h}$.[14] This latter geometry is consistent with the emission spectrum (Figure 3). The band due to the $^5D_0 \rightarrow {}^7F_0$ transition is extremely weak and is attributed to a distortion of the polyhedron, as a consequence the $C_{4v}$ symmetry is excluded.[15] The spectrum contains three $^5D_0 \rightarrow {}^7F_1$ bands, two of which are attributed to an $E$ species, the spectrum also presents one weak and two strong peaks due to a $^5D_0 \rightarrow {}^7F_2$ transition.[15]

An apparent coordination number seven is indicated for the isothiocyanate adduct, since the conductance data show that all $NCS^-$ ions are coordinated. For the heptacoordination three types of structures may be considered: pentagonal bypyramid, $D_{5h}$, capped octahedron, $C_{3v}$, and facecapped trigonal prism, $C_{2v}$.[14] Among these structures, the first was excluded because of the number and type of ligands. Considering the weak band due to $^5D_0 \rightarrow {}^7F_0$ transition, the two peaks due to $^5D_0 \rightarrow {}^7F_1$, one sharp and the other broad, due to an unresolved $E$ species, and the four intense peaks due to $^5D_0 \rightarrow {}^7F_2$ transition, we suggest the $C_{3v}$ symmetry, consistent with a base-monocapped trigonal prism or a monocapped octahedral polyhedron.[15,16]

## ACKNOWLEDGEMENT

One of us (L.R.F.C.) is grateful to FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) for a Post-Doctoral fellowship.

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