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ABSTRACT

Tri-2-propyl phosphate (T2PP) reacts with lanthanide nitrates to form two series of solid complexes, $Ln(NO_3)_3 \cdot 3T2PP$ and $Ln'(NO_3)_3 \cdot 2T2PP \cdot H_2O$, where Ln includes all lanthanides and Ln' only Tb through Lu. These complexes were characterized by elemental analyses. X-ray diffraction patterns showed a single structure for each series, and infrared spectra showed that both nitrate and T2PP ligands were coordinated with lanthanide ions.

Absorption, proton magnetic resonance (PMR), and infrared spectra demonstrated the dissociation of $Yb(NO_3)_3 \cdot 3T2PP$ in CH_2Cl solution to $Yb(NO_3)_3 \cdot 2T2PP$ and T2PP; complexes of other small lanthanide ions (Tb-Lu) were shown by infrared spectra to dissociate in the same fashion. Dissolution of $Ln'(NO_3)_3 \cdot 2T2PP \cdot H_2O$ in CH_2Cl_2 solution yielded a mixture of $Ln'(NO_3)_3 \cdot 3T2PP$ and $Ln'(NO_3)_3 \cdot 2T2PP$ in solution and a precipitate of $Ln'(NO_3)_3 \cdot 6H_2O$.

The relative stabilities of the different species are discussed in terms of a model where ligand-ligand repulsive forces increase with decreasing Ln^{3+} size (or increasing Z) more rapidly than ion-ligand attractive forces. The increase in frequency of vibrational bands due to coordinated P-O and N-O is shown to be consistent with this model.

INTRODUCTION

Organic phosphates [$(RO)_3PO$] coordinate strongly with polyvalent metal ions, and are widely used in solvent extraction separation processes for lanthanide and actinide nitrates.[3,4] The nature of the coordination complexes formed between organic phosphates and nitrates of the lanthanides and actinides is not well known, although the tri-n-butyl phosphate (TBP) complexes with lanthanide nitrates have been investigated by infrared, Raman, NMR, and visible absorption spectra.[5-10] The $Ln(NO_3)_3 \cdot 3TBP$ complexes, like most metal nitrate-organic phosphate complexes, are oily liquids that can only be approximately characterized in composition; the role of the small amount of water[9] in $Ln(NO_3)_3 \cdot 3TBP$ complexes is still undefined. Complexes of the lanthanide nitrates with tri-2-propyl phosphate (T2PP) are crystalline solids of definite composition, and are thus more attractive compounds for detailed coordination and structural studies. This paper reports their preparation and characterization, and some studies of their association and dissociation in organic solutions.

EXPERIMENTAL SECTION

Materials

Lanthanide nitrates of 99.9% metal purity were obtained from commercial suppliers. Tri-2-propyl phosphate (T2PP) was synthesized by the reaction of 2-propanol with $POCl_3$ in the presence of pyridine (as an HCl scavenger) and purified by vacuum distillation.[11]

The reagent grade solvents [methylene chloride, hexane, petroleum ethers (bp 20-40°, 40-60°C) and acetone] were used without further purification. For spectral studies, solvents were dried by passage through a column of Linde* 4Å "Molecular Sieve".

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* Tradename of Linde Air Products

Preparation of $Ln(NO_3)_3$-T2PP Complexes

$Ln(NO_3)_3 \cdot 3T2PP$ Complexes (Ln = all lanthanides)

Tris-T2PP complexes were prepared at room temperature by stirring a slight excess of the finely powdered lanthanide nitrate hydrate with T2PP for 20-30 min; the complexes were recovered from the mixture by leaching with methylene chloride. The crude product was recovered in good (70-90%) yield by evaporating the methylene chloride. A pure product was recrystallized from hexane or petroleum ether, and dried in vacuum. Tm, Yb, and Lu complexes were prepared with a slight excess of T2PP present; without excess T2PP, a mixture of bis-T2PP and tris-T2PP complexes was formed. Analytical data for the $Ln(NO_3)_3 \cdot 3T2PP$ complexes are given in Table I.

$Ln'(NO_3)_3 \cdot 2T2PP \cdot H_2O$ Complexes (Ln' = Tb, Dy, Ho, Er, Tm, Yb, and Lu)

A methylene chloride solution of T2PP was added dropwise to a threefold excess of the lanthanide nitrate hydrate dissolved in acetone. This solution was evaporated to dryness, and the T2PP complexes were extracted with hot hexane from the mixed solids. Bis-T2PP-hydrate complexes were isolated from the hexane solution by fractional crystallization. Analytical data for the $Ln'(NO_3)_3 \cdot 2T2PP \cdot H_2O$ complexes are given in Table II.

Properties

$Ln(NO_3)_3 \cdot 3T2PP$ Complexes

Tris-T2PP complexes crystallize from hexane as elongated flat plates that are very soluble in CCl_4, $CHCl_3$, and CH_2Cl_2. Their density is roughly 1.30, as measured by displacement in saturated n-hexadecane. The complexes dissolve slowly in water, probably by displacement of T2PP with water because they cannot be recovered from aqueous solution by evaporation or extraction with methylene chloride. Exposed to air, the crystals slowly absorb water and dissolve.

Ln'$(NO_3)_3 \cdot 2T2PP \cdot H_2O$ Complexes

The bis-T2PP monohydrate complexes crystallized as fine needles that contain 1.1 to 1.4 molecules of water per lanthanide ion. Prolonged vacuum drying at room temperature yields the monohydrate, but the solid rapidly reabsorbs water from the air. An anhydrous bis-T2PP complex could not be prepared by heating bis-T2PP-monohydrate complexes to 100°C in a vacuum of 10^{-5} torr. Some of the T2PP evaporated, but little, if any, water. The residue from these experiments was a viscous liquid that did not solidify at room temperature.

Bis-T2PP-monohydrate complexes could not be completely dissolved by CCl_4, $CHCl_3$, or CH_2Cl_2. The residue from dissolution of the complex of $Er(NO_3)_3$ was 35 wt % erbium, in agreement with the erbium content of $Er(NO_3)_3 \cdot 6H_2O$ (calcd Er, 36.2 wt %). The residue was 8.8% of the total weight; a residue of 9.0% is calculated for the reaction:

$$\begin{aligned} 6\ \mathrm{Er(NO_3)_3\cdot 2T2PP\cdot H_2O_{(s)}} \xrightarrow{\mathrm{CH_2Cl_2}}\ & \mathrm{Er(NO_3)_3\cdot 6H_2O_{(s)}} \\ & + 2\ \mathrm{Er(NO_3)_3\cdot 3T2PP_{(\ell)}} \\ & + 3\ \mathrm{Er(NO_3)_3\cdot 2T2PP_{(\ell)}} \end{aligned}$$

Further evidence for this reaction will be presented with the PMR and infrared spectra.

Analyses

Lanthanide ion content was determined by titration of a weighed sample with EDTA, using arsenazo indicator.[12] Carbon, hydrogen, and nitrogen were analyzed with an F&M Model 185 CHN analyzer. Melting points were determined with a block melting point apparatus. Molecular weight measurements were attempted by osmometry, but no credible results could be obtained.

The water content of $Ln'(NO_3)_3 \cdot 2T2PP \cdot H_2O$ complexes was determined by an adaptation of the Karl Fischer method. The samples were titrated in a dry nitrogen atmosphere, and the endpoint was determined from the conductivity of the solution with an Aquametry Meter Electrode (Labindustries, Inc.).

Spectral Measurements

Infrared absorption spectra were measured with a Perkin-Elmer Model 521 infrared spectrometer for CCl_4 solutions and solid samples mulled with paraffin oil or hexachlorobutadiene. Mulls were supported on CsBr plates; solutions were contained in 0.02 mm cells with NaCl windows, and the absorbance of the solvent was balanced with a reference cell.

Polarized Raman spectra were measured with a Spex Ramalog Raman spectrophotometer on saturated CH_2Cl_2 solutions of the complexes sealed in glass capillaries. This spectrophotometer uses He-Ne 6328 Å laser excitation, and the scattered beam is measured at 90° to the incident exciting beam.

Absorption spectra in the visible and near-infrared regions (3500-25000 cm^{-1}) were measured with a Cary Model 14 spectrophotometer. Absorption intensities, presented as oscillator strengths, were determined as in previous studies.[13] Where applicable, the independence of oscillator strength from concentration was verified.

Proton magnetic resonance (PMR) spectra were obtained with a Varian Model A-60 NMR spectrometer. Samples were dissolved in $CDCl_3$ for measurements.

X-Ray Diffraction

X-ray powder diffraction photographs were taken with a 57.3 mm Debye-Sherrer camera, Ilford G film, and nickel-filtered copper radiation. For measurement, samples were loaded in glass capillaries and sealed in wax. The d-spacings measured are estimated to be accurate to ±2%.

Association Studies

The association and dissociation of $Ln(NO_3)_3$-T2PP complexes in organic solutions were investigated by observing changes in the appearance and oscillator strengths of the hypersensitive absorption bands[13-15] in the visible absorption spectra of Ln^{3+} ions when measured quantities of the coordinating ligands (H_2O and T2PP) were added. The oscillator strengths were determined as a function of ligand-to-metal ion ratio.

RESULTS

Analyses and X-Ray Data

Elemental analyses for $Ln(NO_3)_3 \cdot 3T2PP$ complexes (Table I) agree well with the calculated compositions; analyses for $Ln'(NO_3)_3 \cdot 2T2PP \cdot H_2O$ complexes agree well with calculated composition except for some variation in water content. This variation is attributed to interstitial water, rather than analytical error. X-ray diffraction patterns for all $Ln(NO_3)_3 \cdot 3T2PP$ complexes were essentially the same, with a slight decrease in the d-spacings with increasing atomic number of the lanthanide ion. The d-spacings for the tris-T2PP complexes of La, Gd, and Lu nitrates are given in Table III. The X-ray powder patterns for bis-T2PP-hydrate complexes (Table III) were also identical; however they were different from the patterns of the tris-T2PP complexes, hydrated lanthanide nitrates, or a mixture of the two. The analytical and X-ray data characterized the $Ln(NO_3)_3 \cdot 3T2PP$ and $Ln'(NO_3)_3 \cdot 2T2PP \cdot H_2O$ complexes as two distinct series of compounds.

Infrared and Raman Spectra

The infrared and Raman spectral bands of T2PP, $Nd(NO_3)_3 \cdot 3T2PP$, $Yb(NO_3)_3 \cdot 3T2PP$, and $Lu(NO_3)_3 \cdot 2T2PP \cdot H_2O$ in CCl_4 (infrared) and CH_2Cl_2 (Raman) are listed in Table IV. Dissociation of the Yb^{3+} and Lu^{3+} complexes on dissolution yields solutions containing a mixture of species. Infrared spectra of $Ln(NO_3)_3 \cdot 3T2PP$ complexes were essentially the same for both solid samples and CCl_4 solutions; infrared spectra of solid $Ln'(NO_3)_3 \cdot 2T2PP \cdot H_2O$ complexes showed a strong OH stretching band ($\sim$3300 cm^{-1}) not present in the spectra of the CCl_4 solutions. Absorption bands at ca 1210, 1240, 1300, 1490, and 1510 cm^{-1} were identified with lanthanide ion-ligand vibrations by their increase in frequency with increasing Z of the lanthanide ion (Table V). Comparison of the vibration spectra with those of other complexes identifies the three higher frequency bands as resulting from lanthanide ion-nitrate complexing[7,10,16-19] and the two lower frequency bands as resulting from lanthanide ion-phosphate $[M \leftarrow O\text{-}P\equiv]$ complexing.[7,10,20]

Infrared spectra of CCl_4 solutions of mixed $Ln'(NO_3)_3 \cdot 3T2PP$ and $Ln'(NO_3)_3 \cdot 2T2PP$ complexes (prepared by dissolving $Ln'(NO_3)_3 \cdot 2T2PP \cdot H_2O$ and centrifuging) show strong bands at 1520, 1270 and 1190 cm^{-1} (Figure 1). These bands vary in strength among the spectra of solutions of $Ln(NO_3)_3 \cdot 3T2PP$ complexes. For the complexes of the light lanthanides, these absorption bands are quite weak, but increase in strength for the complexes of higher lanthanides and are strong for the complexes of the heaviest lanthanides. When T2PP is added to a solution of $Lu(NO_3)_3 \cdot 3T2PP\text{-}Lu(NO_3)_3 \cdot 2T2PP$, the infrared spectra changes to a spectrum closely resembling that of solutions of $Lu(NO_3)_3 \cdot 3T2PP$ (Figure 2); the addition of large amounts of T2PP ($\sim$20 T2PP/Ln^{3+}) to the solution almost eliminates the 1270, 1190, and 1525 cm^{-1} band from the spectra. This suggests that the infrared absorption at 1190, 1270, and 1525 cm^{-1} is due to the $Ln'(NO_3)_3 \cdot 2T2PP$ complex only, and the presence of these bands in the spectra of solutions of $Ln'(NO_3)_3 \cdot 3T2PP$ complexes is evidence of dissociation. The 1520 cm^{-1} band, although a major absorption band for $Ln'(NO_3)_3 \cdot 2T2PP$ complexes, may be present as a weak band in the infrared spectra of $Ln(NO_3)_3 \cdot 3T2PP$ complexes.

The Raman spectra of the vibrational bands associated with ligand-lanthanide ion coordination showed that the weak absorption in the 1510-1530 cm^{-1} region was polarized and possibly complex (Figure 3). The 1485-1500 cm^{-1} infrared-active band was too weak in Raman spectra to determine its polarization. The 1285-1300 cm^{-1} band found in infrared spectra could not be detected in the Raman. A 1230-1250 cm^{-1} absorption band (polarized) was present in the Raman spectra, but not in the infrared, and is presumed to be due to a symmetric stretching vibration of coordinated P-O. The NO_2 stretching vibration (1040 cm^{-1}, polarized) was the strongest band in the Raman spectra. This band is strong and polarized for both ionic and coordinated nitrates. A band at 1020 cm^{-1} occurs in the infrared, but not in Raman spectra, and is sufficiently different in energy that it is assigned as a different vibration, rather than infrared activity of the 1040 cm^{-1} NO_2 stretching mode. The 1020 cm^{-1} infrared band does not change in energy or intensity between complexes of different lanthanide ions.

PMR Spectra of Ytterbium Complexes

PMR spectra of $CDCl_3$ solutions of $Yb(NO_3)_3 \cdot 3T2PP$ and $Yb(NO_3)_3 \cdot 2T2PP \cdot H_2O$ provide substantial evidence of the dissociation of $Yb(NO_3)_3 \cdot 3T2PP$ to form

$Yb(NO_3)_3 \cdot 2T2PP$ and T2PP, and of the presence of $Yb(NO_3)_3 \cdot 3T2PP$ and $Yb(NO_3)_3 \cdot 2T2PP$ species in solutions prepared by dissolution of $Yb(NO_3)_3 \cdot 2T2PP \cdot H_2O$. A solution of $Yb(NO_3)_3 \cdot 3T2PP$ at -30°C showed a strong peak at +2.02 ppm (relative to TMS) and a weak peak at -2.73 ppm. Addition of 0.3 equivalent of free T2PP proportionately increased the signal at -2.73 ppm; the signal at -2.73 ppm was assigned to the methyl protons of free T2PP, and the signal at +2.02 ppm to methyl protons of the T2PP coordinated in $Yb(NO_3)_3 \cdot 3T2PP$. No signal was observed that could be assigned to a $Yb(NO_3)_3 \cdot 2T2PP$ species or to the methine protons. The concentration of $Yb(NO_3)_3 \cdot 2T2PP$ is presumed to be too low to allow its detection, and the broadening of the methine signals by the paramagnetic ion could prevent their detection. The detection of T2PP agrees with other evidence that $Yb(NO_3)_3 \cdot 3T2PP$ dissociates appreciably in solution.

PMR spectra at -34° of $CDCl_3$ solutions of $Yb(NO_3)_3 \cdot 3T2PP$-$Yb(NO_3)_3 \cdot 2T2PP$ (prepared by dissolution of $Yb(NO_3)_3 \cdot 2T2PP \cdot H_2O$ and centrifuging) showed strong broad signals at +2.13 ppm and +3.78 ppm and a weak signal at -2.52 ppm. Signals at +2.13 ppm and -2.52 ppm correspond to those identified as $Yb(NO_3)_3 \cdot 3T2PP$ and T2PP in the spectra of solutions of $Yb(NO_3)_3 \cdot 3T2PP$; the signal at +3.78 ppm is assigned to a $Yb(NO_3)_3 \cdot 2T2PP$ species. The integrated intensities of the signals at +2.13 ppm and +3.78 ppm were equal, and agreed with intensities predicted for the proposed reaction on dissolution of $Yb(NO_3)_3 \cdot 2T2PP \cdot H_2O$. An increase in temperature increased the rate of ligand exchange between the two T2PP complexes; the signals coalesce into a broad band at -13°C, and become a comparatively sharp single peak at 7°C.

Absorption Spectra

The shape of absorption bands due to the hypersensitive transitions of lanthanide ions has been shown to reflect the environment of the ion[13,14,21-23]; the absorption bands due to the Er^{3+} $^4I_{15/2} \rightarrow {}^2H_{11/2}$ and $^4I_{15/2} \rightarrow {}^4G_{11/2}$ transitions for CH_2Cl_2 solutions of $Er(NO_3)_3 \cdot$T2PP and a 3:2 mixture of $Er(NO_3)_3 \cdot$2T2PP-$Er(NO_3)_3 \cdot$3T2PP (Figure 4) demonstrate a difference in environment for the Er^{3+} ion in the different complexes. Addition of T2PP or H_2O resulted in the band shapes of the mixed complexes changing to a band shape identical with the $Er(NO_3)_3 \cdot$3T2PP solution (Figure 4). From a measurement of the oscillator strength of the $^4I_{15/2} \rightarrow {}^2H_{11/2}$ bands as increments of T2PP were added, 1.1 moles of T2PP per mole of Er^{3+} were required before a constant oscillator strength was reached (Figure 5).

The absorption spectra of solutions of $Yb(NO_3)_3 \cdot$3T2PP and $Yb(NO_3)_3 \cdot$2T2PP complexes have almost identical shape; the spectra are changed but still identical after the addition of T2PP to both solutions (Figure 6). This change involves the absorption at 10600 cm^{-1} (9380 Å), assigned[24] to the transition between the Γ_7 sublevel of the $^2F_{7/2}$ ground state and the Γ_7' sublevel of the $^2F_{5/2}$ state. (The oscillator strength over 9000-10800 A is constant, because the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition is not hypersensitive.) Changes in the peak height at 9380 Å indicate complexing effects of T2PP on species in solution. A graph of the peak height at 9380 Å vs. the T2PP/$Yb(NO_3)_3 \cdot$complex mole ratio shows (Figure 7) that 1.8 ±0.1 moles of T2PP reduce the peak height of the $Yb(NO_3)_3 \cdot$2T2PP to a constant value and 0.8 ±0.1 moles of T2PP added to $Yb(NO_3)_3 \cdot$3T2PP also yield a constant value. These data indicate that an equilibrium exists between bis-T2PP complex, T2PP, and the tris-T2PP complex. Assuming that the peak height at 9380 Å is due entirely to $Yb(NO_3)_3 \cdot 2T2PP$, and that the constant peak height after addition of 1.8 moles of T2PP is due entirely to a $Yb(NO_3)_3 \cdot 3T2PP$ species, an equilibrium constant of ∿250 was calculated for:

$$Yb(NO_3)_3 \cdot 3T2PP \rightleftharpoons Yb(NO_3)_3 \cdot 2T2PP + T2PP.$$

A 4 x 10^{-3}*M* solution of $Yb(NO_3)_3 \cdot 3T2PP$ is calculated to be 50% dissociated into $Yb(NO_3)_3 \cdot 2T2PP$ and T2PP.

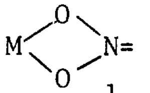
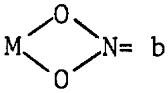
The shapes of bands due to hypersensitive transitions of $Nd(NO_3)_3 \cdot 3T2PP$, $Ho(NO_3)_3 \cdot 3T2PP$, and $Er(NO_3)_3 \cdot 3T2PP$ in halocarbon solutions were essentially identical with the band shapes found for the corresponding TBP, tri-n-pentyl phosphate, and tri-n-pentyl phosphine oxide complexes.[9] This is interpreted as indicating that the coordination spheres of the lanthanide ions in all four complexes are nearly identical as would be expected from the similarity of the phosphate ligands.

DISCUSSION

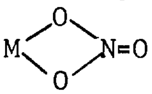
The relative stabilities of $Ln(NO_3)_3 \cdot 3T2PP$ and $Ln'(NO_3)_3 \cdot 2T2PP \cdot H_2O$ compounds can be explained qualitatively as a consequence of the decrease in size of lanthanide ions with increasing atomic number.[25] The major forces in the coordination sphere are the ion-ligand attractive forces and the ligand-ligand repulsive forces. The attractive forces are essentially electrostatic, proportional to R^{-2}; the repulsive forces depend on volume, and are assumed proportional to R^{-3}. As the size of the successive lanthanide ions decreases, the repulsive forces increase more rapidly than attractive forces; a coordination sphere that is stable for the larger lanthanide ions becomes increasingly less stable for the smaller ions. Ordinarily, some change in the coordination sphere occurs that decreases repulsive forces (decrease in number of ligands, substitution of a smaller ligand for a larger, etc.) for lanthanide compounds or complexes between the larger and smaller lanthanide ions.

$Ln'(NO_3)_3 \cdot 2T2PP \cdot H_2O$ compounds are derived from the $Ln(NO_3)_3 \cdot 3T2PP$ compounds by the substitution of one H_2O for the larger T2PP molecule, a substitution that decreases the repulsive forces. It is consistent with this model that the $Ln'(NO_3)_3 \cdot 2T2PP \cdot H_2O$ compounds could be isolated only for the smaller lanthanides. Infrared, NMR, and absorption spectra indicate that $Ln(NO_3)_3 \cdot 3T2PP$ compounds of the smaller lanthanides dissociate to $Ln(NO_3)_3 \cdot 2T2PP$ and T2PP, as might be expected from the formation of solid $Ln'(NO_3)_3 \cdot 2T2PP \cdot H_2O$ compounds.

The progressive increase in frequency with increasing lanthanide atomic number for vibrational bands resulting from lanthanide ion-ligand bonding is, in general, consistent with a balance of attractive and repulsive forces. The P-O asymmetric stretching mode is shifted from 1250 cm^{-1} to ca 1200 cm^{-1} as coordination with the positive lanthanide ion decreases the electron density of the P-O bond. As the size of the succeeding lanthanide ions shrink, the repulsive forces increase relative to attractive forces; the M-OP$\leq$ bond becomes weaker, and the MO-P$\leq$ bond stronger, as indicated by its increase in frequency. The MO-P$\leq$ asymmetric stretching mode occurs about 20 cm^{-1} lower for $Ln'(NO_3)_3 \cdot 2T2PP$ complexes than for $Ln(NO_3)_3 \cdot 3T2PP$ complexes, indicating a stronger M-OP$\leq$ bond. If the attractive forces are assumed equivalent, the energy change indicated by this frequency shift represents a decrease in the repulsive forces in the coordination sphere of the bis-T2PP complexes compared to the tris-T2PP complexes.

The same increase in frequency with increasing lanthanide atomic number is observed for the coordinated nitrate bands. The band at ca 1300 cm^{-1} is probably due to  $\mathrm{M}\begin{smallmatrix}\diagup\mathrm{O}\diagdown \\ \diagdown\mathrm{O}\diagup\end{smallmatrix}\mathrm{N}{=}$ asymmetric stretching vibration, and its increase in frequency from 1282 cm^{-1} for $La(NO_3)_3 \cdot 3T2PP$ to 1304 cm^{-1} for $Lu(NO_3)_3 \cdot 3T2PP$ can be accounted for by the same considerations applied to the MO-P$<$ asymmetric stretching vibration; this  band is ca 30 cm^{-1} lower for Ln'$(NO_3)_3\cdot$2T2PP complexes than for Ln$(NO_3)_3\cdot$3T2PP complexes.

Two vibrational bands due to coordinated nitrate are observed near 1500 cm^{-1} in solutions of the bis-T2PP and tris-T2PP complexes. The band at 1510-1525 cm^{-1} is strong in the infrared and weak, but polarized, in the Raman for bis-T2PP complexes; the band at 1483-1492 cm^{-1} is strong in the infrared spectra of tris-T2PP complexes, and not observed in the Raman. Solutions of Nd$(NO_3)_3\cdot$ 3T2PP in T2PP as a solvent showed the 1510-1525 cm^{-1} band (weak in both infrared and Raman), and this band is probably present in the spectra of the tris-T2PP complexes, although dissociation to the bis-T2PP complex in solution cannot be positively ruled out. Similarly, as solutions of the bis-T2PP complexes always have roughly equal amounts of the tris-T2PP complexes present, so the 1483-1492 cm^{-1} infrared band may be present, but weak, in the spectra of bis-T2PP complexes. As with other bands due to coordinated ligands, these bands all increase in frequency with increasing lanthanide atomic number.

The nitrate vibrational bands in the 1400-1600 cm^{-1} region are normally due to either the N=O symmetric stretching vibration of bidentate nitrate or the MO-NO_2 asymmetric stretching mode of monodentate nitrate. For a nitrate ligand in C_{2V} symmetry, the N=O symmetric stretch is polarized, and the MO-NO_2 asymmetric stretch depolarized in Raman spectra. The polarization of the 1520 cm^{-1} band is indicative of one or more bidentate nitrate ligands.[26,27] The predicted effect of increasing M-O bond strength in the  system is an increase in frequency for the N=O symmetric stretching mode. The increase from ∿1490 cm^{-1} for a Ln$(NO_3)_3\cdot$3T2PP complex to ∿1520 cm^{-1} for a Ln'$(NO_3)_3\cdot$2T2PP species is consistent with this prediction, but the assignment of these bands to an N=O symmetric stretching mode is not consistent with the lack of Raman activity for the $\sim$1490 cm^{-1} band. The increase in frequency observed for both the $\sim$1520 cm^{-1} and $\sim$1490 cm^{-1} bands with increasing Z of the lanthanide ion is the reverse of the effect expected for the decreasing MO bond strength with increasing Z that was deduced from $\equiv$P-OM and MO-NO$_2$ vibrational bands.

The reverse also offers a contradiction: if the net M-O bond strength increases as required for a polarization effect to explain the increasing frequency of the bands at $\sim$1500 cm^{-1} with increasing lanthanide Z, then the frequency of MO-P$\leqq$ and MO-N$\leq$ asymmetric stretching bands should decrease, instead of the increase observed. A tentative explanation in accord with the experimental results is that these bands are not due to pure vibrations; the low symmetry of the complexes permits strong coupling between the N=O symmetric stretching mode, and some vibration that is influenced by the net decrease of M-O bond strength for increasing lanthanide atomic number. The domination of the former mode is responsible for the frequency difference between the tris-T2PP and bis-T2PP complexes; the domination of the latter mode determines the increase in band frequency with increasing lanthanide atomic number.

Bands due to coordinated nitrate and phosphoryl vibrations in $Ln(NO_3)_3$ - TBP complexes[7] and $Ln(NO_3)_3$ - Ph_3PO complexes[10] show the same increase in frequency with lanthanide atomic number observed for $Ln(NO_3)_3$ - T2PP complexes. Cousins and Hart[10] propose to explain this result by assuming an increasing M-O bond strength with the increasing lanthanide atomic number, and account for the increase in P-O bond strength by a progressive increase in the coupling of M-O and O-P$\leqq$ bonds with increasing lanthanide atomic number. Although this explanation may have some degree of validity, it requires a fortuitous combination of circumstances that is not easy to accept. The explanation proposed here, based on the relative influence of attractive and repulsive forces, appears more reasonable.

The absence of an abrupt change in infrared spectra through the lanthanide series for solutions of either $Ln(NO_3)_3 \cdot 3T2PP$ or $Ln(NO_3)_3 \cdot 2T2PP$ is considered to be evidence that the coordination of the lanthanide ion is constant through each series. The polarized Raman band at 1510 - 1525 cm^{-1} indicates one or more bidentate nitrate ligands. Although this band is assumed here to result from the coupling between the N=O symmetric stretching mode and another vibrational mode, the A_1 character of the symmetric stretch should be preserved. The infrared spactra does not, however, contradict the possibility of monodentate nitrate ligands. From vibrational spectra, coordination numbers of 7, 8, or 9 are possible for Ln^{3+} ions in $Ln(NO_3)_3 \cdot 3T2PP$, and 6, 7, or 8 for Ln^{3+} ions in $Ln(NO_3)_3 \cdot 2T2PP$ species.

Attempts to correlate the shape of absorption bands due to the hypersensitive transitions of Nd^{3+}, HO^{3+}, and Er^{3+} ions with the coordination number of these ions in solutions of the corresponding $Ln(NO_3)_3 \cdot 3T2PP$ complex yielded results that are inconsistent with the conclusions drawn from vibrational spectra. Using lanthanide β-diketonates of 6-, 7- and 8-coordination as standards for comparison, Nd^{3+} in $Nd(NO_3)_3 \cdot 3T2PP$ corresponded best to an 8-coordinate Nd^{3+}; Ho^{3+} in the $Ho(NO_3)_3 \cdot 3T2PP$ did not correspond to a complex of known coordination; and Er^{3+} in $Er(NO_3)_3 \cdot 3T2PP$ showed a band shape similar to 6-coordinate Er^{3+}. Besides the contradiction with deductions from vibrational spectra, the comparison of spectra between β-diketonates and nitrates does not appear sound. The distance between the two bonding oxygens in the chelate rings is about 2.8 Å[28] but only 1.8 Å between the oxygen atoms in a bidentate nitrate. The field on the lanthanide ion from a bidentate chelate ligand and a bidentate nitrate must differ to such a degree that a spectral comparison between β-diketonate and nitrate complexes of lanthanide ions is invalid.

In previous studies,[8,9] absorption and NMR spectra were used to deduce that a structural change occurs between the TBP-$Ln(NO_3)_3$ complexes of light and heavy lanthanide ions, and that this structural change is accompanied by a change in Ln^{3+} coordination. The band shapes for hypersensitive transitions of the tris-T2PP, TBP, and TAP complexes of Nd, Ho, and Er nitrates are nearly identical, and presumably are quite similar structures. Although the previous conclusions of the structure and coordination of $Ln(NO_3)_3 \cdot 3TBP$ complexes may be correct, the evidence of the absorption spectra must be regarded with suspicion, and differences in NMR spectra may be interpretable on some other basis.[29]

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PW:bch

TABLE I

ANALYTICAL DATA FOR $Ln(NO_3)_3 \cdot 3T2PP$ COMPLEXES

	Ln, %		C, %		H, %		H_2O, %		Melting Point,[a] °C
Ln	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
La	13.9	13.9	32.50	32.32	6.36	6.25	4.21	4.32	80-82
Ce	14.0	14.1	32.46	32.45	6.36	6.38	4.21	4.29	84-85
Pr	14.1	14.2	32.44	32.53	6.35	6.53	4.20	4.25	90-91
Nd	14.4	14.4	32.33	32.45	6.33	6.25	4.19	4.36	92-94
Sm	14.9	14.9	32.13	32.24	6.29	6.25	4.16	4.39	96-98
Eu	15.0	15.0	32.08	32.04	6.28	6.28	4.16	4.28	98-101
Gd	15.4	15.3	31.93	31.55	6.25	6.15	4.14	4.25	100-103
Tb	15.6	15.6	31.86	31.52	6.24	6.13	4.13	4.20	100-103
Dy	15.9	15.7	31.75	31.75	6.22	6.12	4.12	4.18	101-103
Ho	16.1	16.2	31.68	31.79	6.20	6.20	4.10	4.20	103
Er	16.3	16.3	31.61	31.37	6.19	6.12	4.10	4.22	104
Tm	16.4	16.4	31.54	32.20	6.18	6.22	4.09	4.19	105
Yb	16.8	16.9	31.43	31.02	6.15	6.04	4.07	4.21	107
Lu	16.9	16.9	31.37	31.80	6.14	6.06	4.06	4.17	108

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[a] Uncorrected

TABLE II

ANALYTICAL DATA FOR Ln'$(NO_3)_3 \cdot 2T2PP \cdot H_2O$ COMPLEXES

	Ln, %		C, %		H, %		N, %		H_2O, %		Melting Point,[a] °C
Ln'	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
Tb	19.6	19.9	26.64		5.41		5.17		2.21	2.86	85
Dy	20.0	19.7	26.52	26.89	5.40	5.44	5.16	5.19	2.21	2.28	83
Ho	20.2	20.3	26.07	25.85	5.39	5.31	5.14	5.05	2.20	2.61	84
Er	20.4	20.6	26.36	26.44	5.37	5.48	5.13	5.31	2.20	2.90	80
Tm	20.6	20.6	26.30	26.20	5.36	5.36	5.12	5.29	2.19	2.59	80
Yb	21.0	20.9	26.18	26.27	5.33	5.33	5.09	5.19	2.18	2.29	85
Lu	21.2	21.3	26.10	26.27	5.31	5.30	5.08	5.19	2.17	2.48	85

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[a] Uncorrected

TABLE III

REPRESENTATIVE X-RAY DATA FOR $Ln(NO_3)_3$ - T2PP COMPLEXES[a]

$La(NO_3)_3 \cdot 3T2PP$ d, Å	$Gd(NO_3)_3 \cdot 3T2PP$ d, Å	$Lu(NO_3)_3 \cdot 3T2PP$ d, Å	$Yb(NO_3)_3 \cdot 2T2PP \cdot H_2O$ d, Å	$Lu(NO_3)_3 \cdot 2T2PP \cdot H_2O$ d, Å
10.22	10.14	10.16	12.58	12.58
8.30	8.33	8.39	9.52	9.49
7.76	7.75	7.69	8.72	8.72
5.19	5.18	5.16	7.41	7.47
4.89	4.89	4.87	6.95	7.00
4.56	4.52	4.51	6.61	6.61
4.38	4.34	4.32	6.18	6.11
4.23	4.21	4.17	4.89	4.90
4.05	4.02	3.99	4.69	4.69
3.89	3.88	3.85	4.21	4.19
3.75	3.74	3.71	3.87	3.88
3.45	3.46	3.44	3.36	3.35
2.62	2.60	2.60	3.23	3.23
2.29	2.27	2.26	2.75	2.76
			2.09	2.09

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[a] Strong lines only

TABLE IV

INFRARED AND RAMAN SPECTRA FOR T2PP-$Ln(NO_3)_3$ COMPLEXES

T2PP		$Nd(NO_3)_3 \cdot 3T2PP$		$Yb(NO_3)_3 \cdot 3T2PP$		$Lu(NO_3)_3 \cdot 2.5T2PP$[c]		
Infrared	Raman	Infrared[a]	Raman[b]	Infrared[a]	Raman[b]	Infrared[a]	Raman[b]	Assignment
		1512 sh	1512 w p	1520 m	1522 w,p	1526 s	1531 w, p	N=O sym str;
1462 m		1488 s	1478 vw	1492 s		1494 sh	1498 vw	$M{<}^{O}_{O}{>}N{=}O$ asym str (?)
1450 sh	1455 s,dp	1456 sh	1458 s,dp		1456 s,dp	1450 sh	1459 s,dp	
	1425 sh	1430 sh	1428 w,dp		1427 w,dp		1431 w,dp	
1375 s	1395 w,dp	1388 m	1392 w,dp	1385 m	1390 w,dp	1388 m	1395 w,dp	
		1378 m		1375 m		1378 m	1362 m,dp	
	1360 m,dp		1362 m,dp	1355 sh	1358 m,dp	1359 sh	1352 sh,dp	
		1289 s		1302 s		1305 w		$MO-NO_2$ asym str
1255 s	1262 w	1258 sh				1262 s		
			1238 m,p		1250 m,p		1254 m,p	$MO-P(OR)_3$
		1202 s	1208 w,dp	1205 s	1210 w,dp	1212 sh	1222 vw,dp	$MO-P(OR)_3$ asym str
1172 m	1185 m,p	1180 m	1188 m,p	1179 sh	1185 m,p	1193 s 1174 sh	1188 w,p	
1138 m	1145 m,dp	1143 m	1148 m,dp	1139 w	1145 m,dp	1142 m	1150 m,dp	
1102 m	1115 m,p	1107 m	1108 m,dp	1101 w	1105 m,p	1103 m	1115 m,p	
	1032 m,p		1035 vs,p		1037 vs,p		1038 vs,p	NO_2-sym str
		1020 s		1020 s		1023 s		
985 s	1000 w	1010 sh						
933 sh	938 m,dp	935 w	938 m,dp	933 w	940 w,dp	934 w	945 w,dp	
	898 s,dp	900 w	904 sh,dp	898 w	905 sh,dp	900 w	905 m,dp	
895 m	885 s,p		888 m,p		890 m,p		890 m,p	
779 m	780 w,dp		788 sh,dp		785sh ,dp		792 sh,dp	
745 m	748 m,dp		748 m,dp		748 m,dp		748 m,dp	
720 w	714 vs,p		714 vs,p		712 vs,p		710 vs,p	
	550 vw		548 w,dp		555 w,dp		553 w,dp	
	505 vw		512 w,dp		512 w,dp		512 w,dp	
	443 m,p		450 m,p		458 m,p		452 m,p	

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[a] CCl_4 solution in 0.1 mm NaCl cell.

[b] CH_2Cl solution.

[c] Solution prepared by dissolving $Lu(NO_3)_3 \cdot 2T2PP \cdot H_2O$ and centrifuging to remove solids.
s, strong; m, medium; sh, shoulder; w, wide; v, very; dp, depolarized; p, polarized.

TABLE V

COORDINATED NITRATE AND PHOSPHORYL FREQUENCIES OF LANTHANIDE NITRATE-T2PP COMPLEXES

	$Ln(NO_3)_3 \cdot 3T2PP$ Complexes				
Ln	NO_3			P-O	
La	1509	1483	1282	1198	1231
Ce	1509	1482	1281	1198	
Pr	1512	1485	1284	1200	
Nd	1515	1488	1289	1202	1238
Sm	1512	1485	1291	1203	
Eu	1511	1487	1293	1205	
Gd	1516	1490	1297	1209	1242
Tb	1520	1491	1299	1210	
Dy	1519	1491	1300	1210	
Ho	1515	1490	1301	1211	
Er	1520	1488	1300	1211	1250
Tm	1520	1490	1302	1211	
Yb	1520	1492	1304	1212	
Lu	1525	1492	1304	1213	1250

	$Ln'(NO_3)_3 \cdot 2T2PP$ Complexes				
Ln	NO_3			P-O	
Dy	1521		1269	1197	
Ho	1522		1272	1190	
Er	1523		1271	1191	
Tm	1522		1271	1191	
Yb	1522		1271	1191	
Lu	1526		1272	1193	1254

Complexes dissolved in CCl_4 for infrared spectra (col. 1-4) and in CH_2Cl_2 for Raman spectra (col. 5).

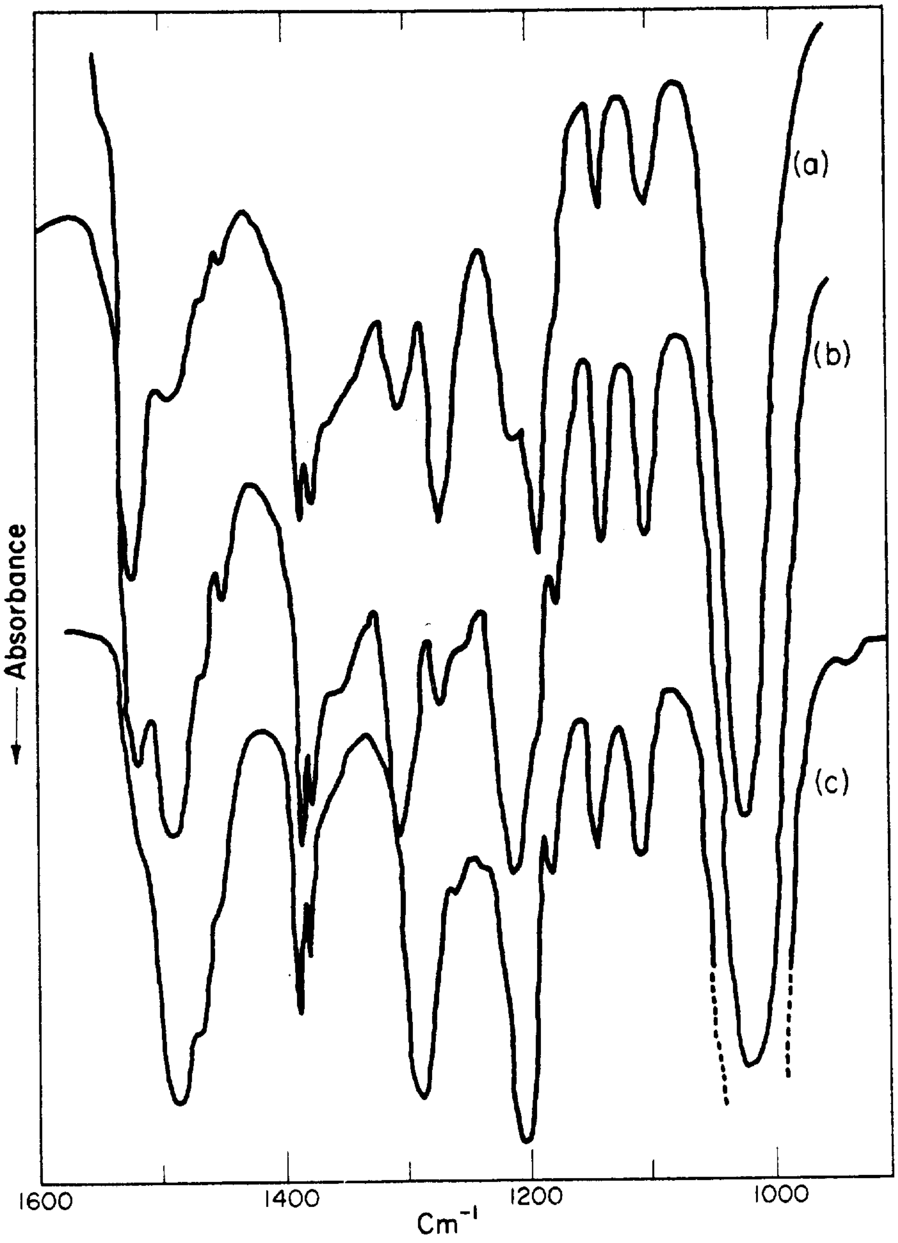

FIG. 1 INFRARED SPECTRA OF $Ce(NO_3)_3 \cdot 3T2PP$ AND $Yb(NO_3)_3$ - T2PP COMPLEXES IN CCl_4

(a) $Yb(NO_3)_3 \cdot 2T2PP - Yb(NO_3)_3 \cdot 3T2PP$
(b) $Yb(NO_3)_3 \cdot 3T2PP$
(c) $Ce(NO_3)_3 \cdot 3T2PP$

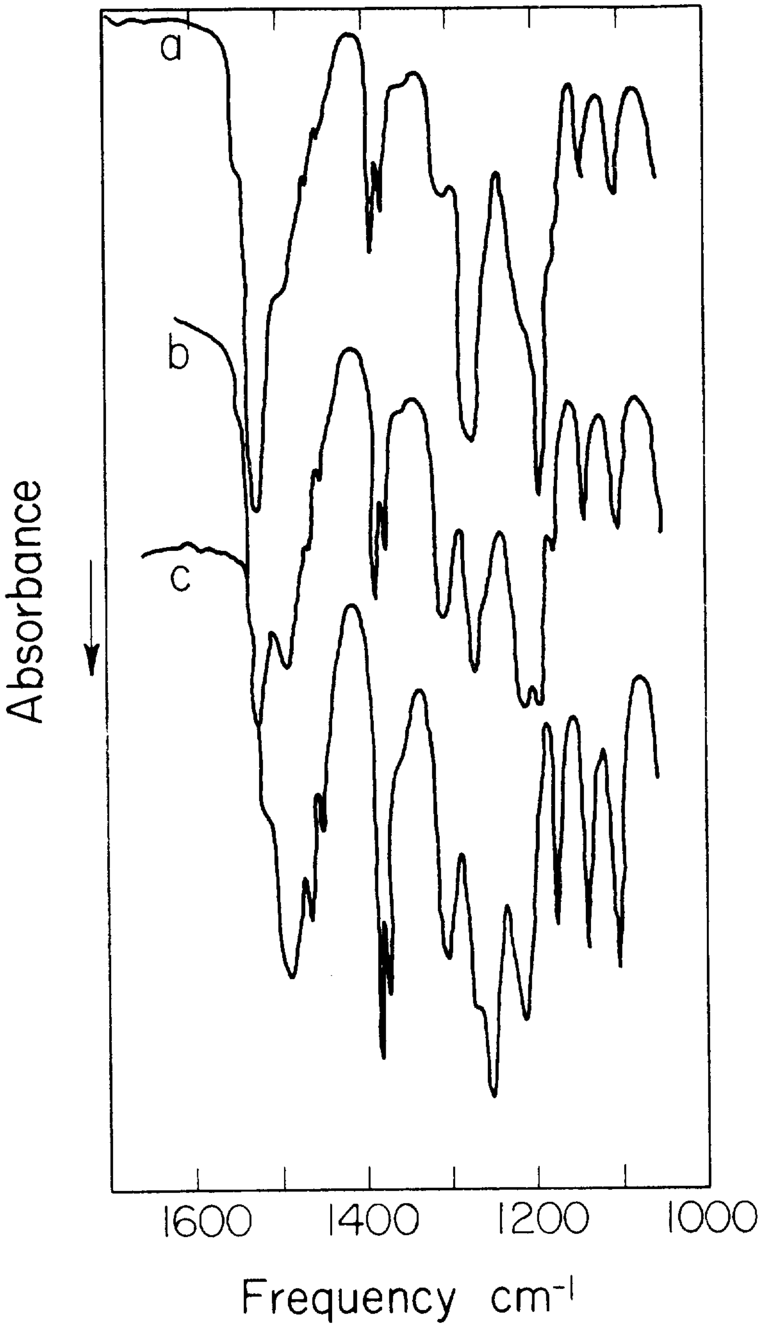

FIG. 2 INFRARED SPECTRA OF $Lu(NO_3)_3 \cdot 3T2PP$ SOLUTIONS

(a) $Lu(NO_3)_3 \cdot 3T2PP$-$Lu(NO_3)_3 \cdot T2PP$ In CCl_4

(b) a + T2PP

(c) b + EXCESS T2PP

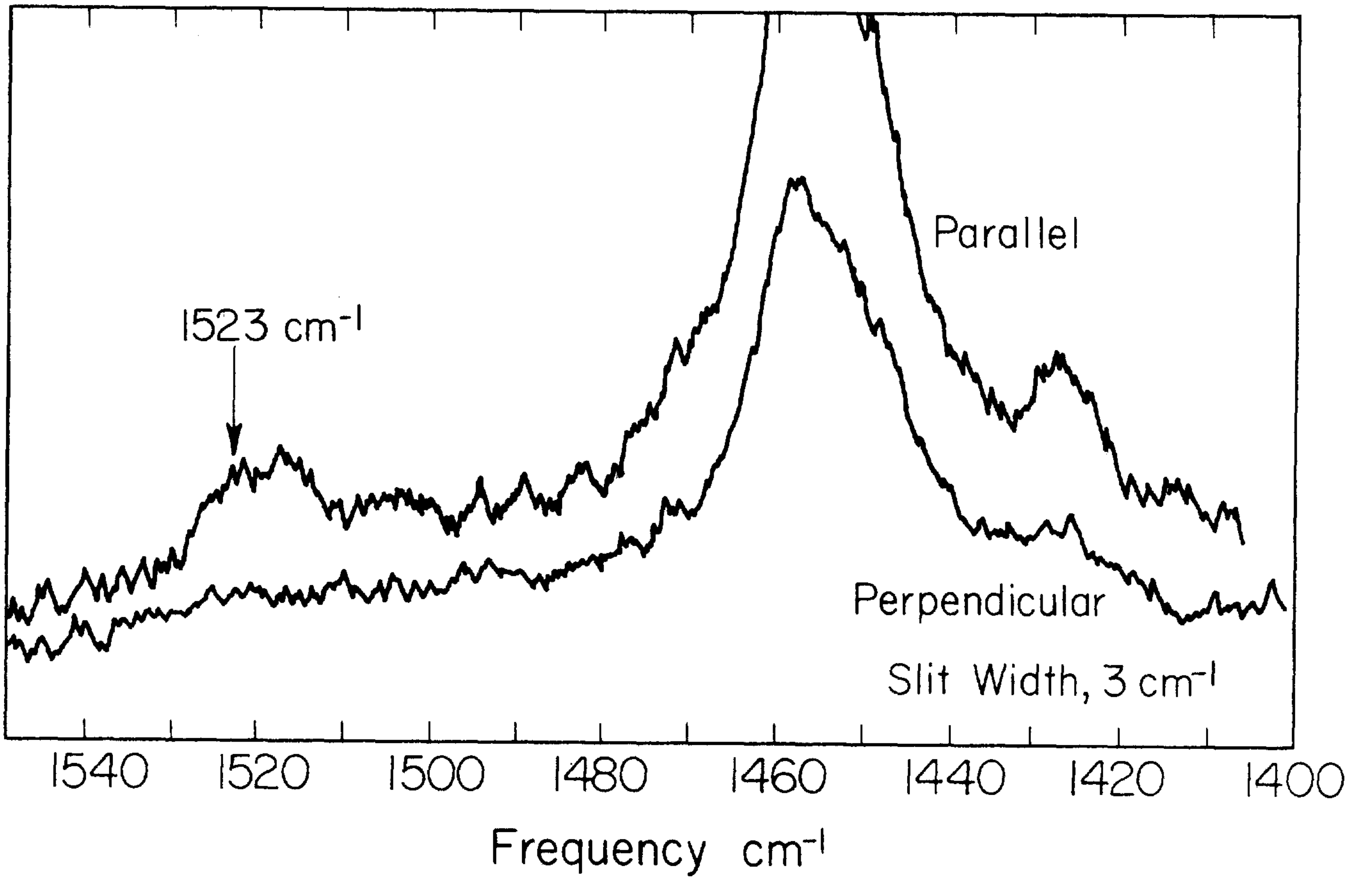

FIG. 3 RAMAN SPECTRUM IN 1500 cm^{-1} REGION FOR $Er(NO_3)_3 \cdot 3T2PP-Er(NO_3)_3 \cdot 2T2PP$ IN CH_2Cl_2

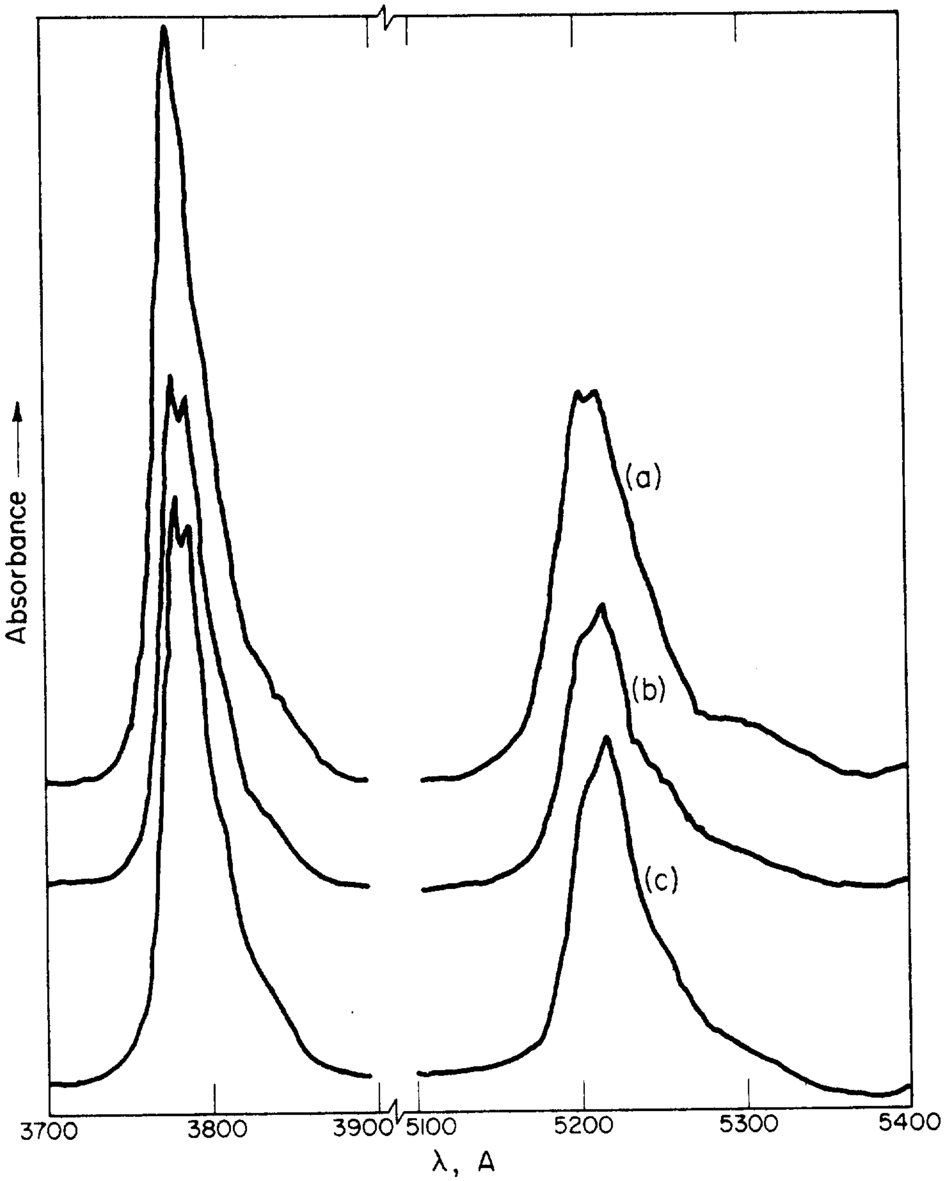

FIG. 4 SPECTRA OF $Er(NO_3)_3$ - T2PP COMPLEXES

(a) $Er(NO_3)_3 \cdot 2T2PP \cdot H_2O$ in CH_2Cl_2
(b) (a) + 1 Equivalent T2PP
(c) $Er(NO_3)_3 \cdot 3T2PP$ in CH_2Cl_2

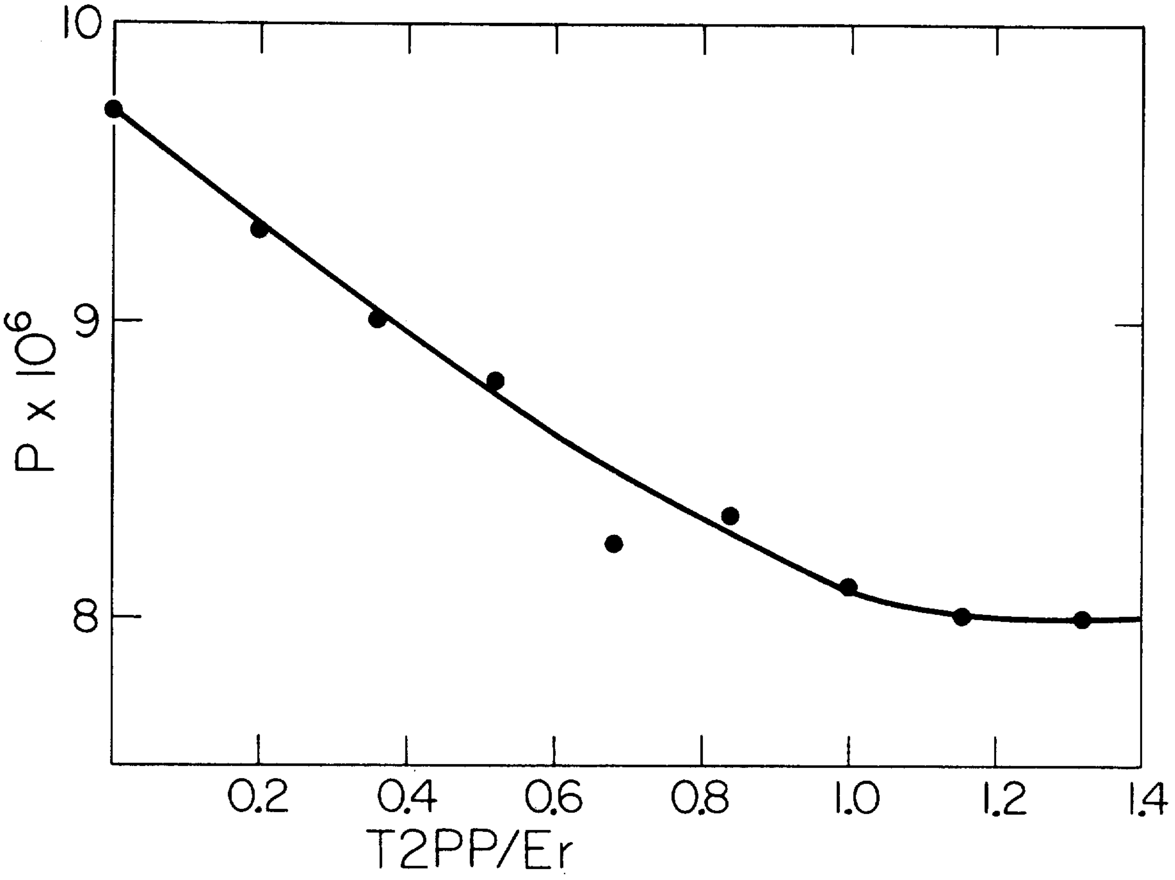

FIG. 5 OSCILLATOR STRENGTHS FOR Er^{3+} $^4I_{15/2} \rightarrow {}^2H_{11/2}$ TRANSITION FOR $Er(NO_3)_3 \cdot 3T2PP$-$Er(NO_3)_3 \cdot 2T2PP$ IN CH_2Cl_2 SOLUTION

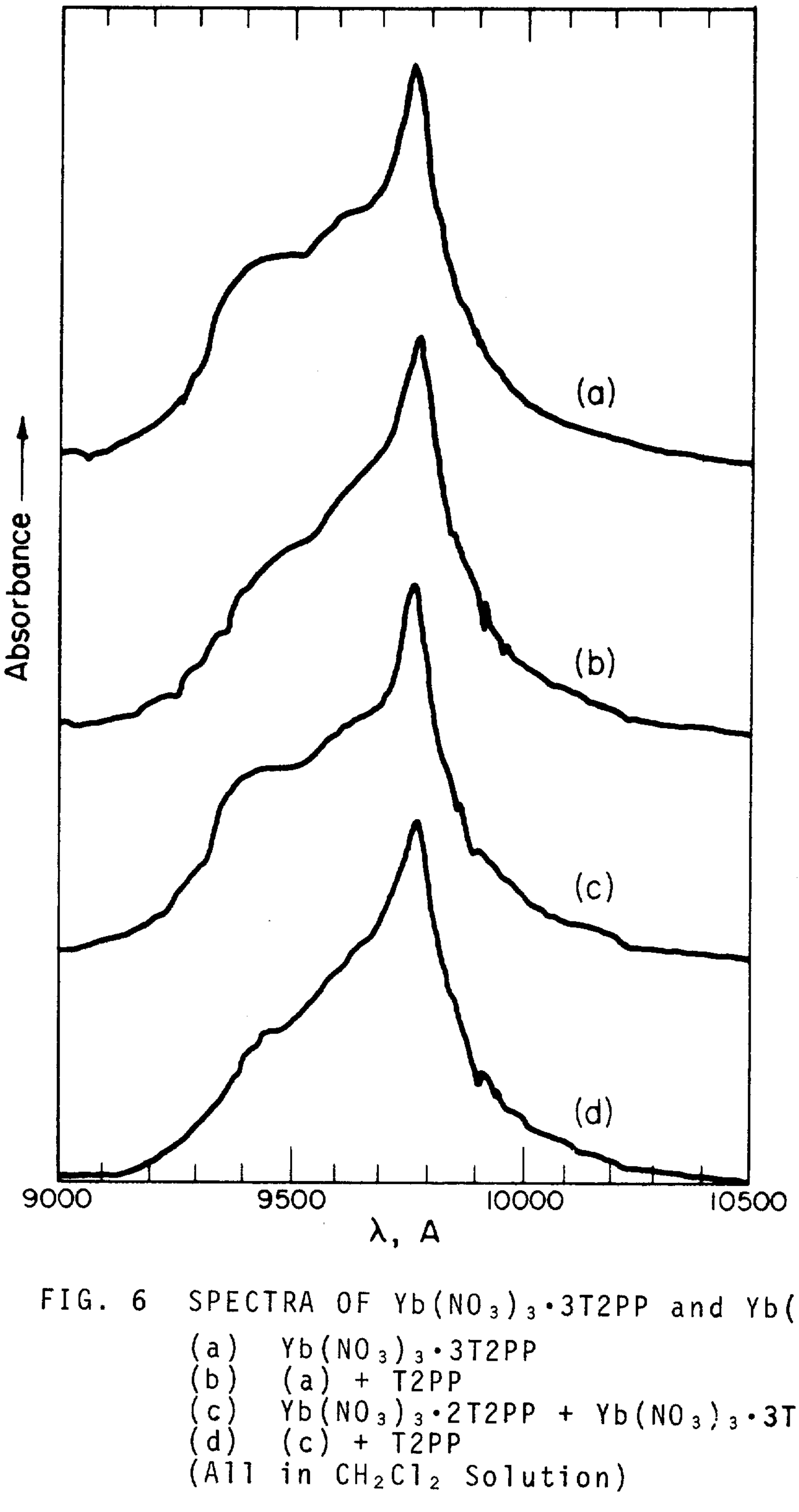

FIG. 6 SPECTRA OF $Yb(NO_3)_3 \cdot 3T2PP$ and $Yb(NO_3)_3 \cdot 2T2PP$

(a) $Yb(NO_3)_3 \cdot 3T2PP$
(b) (a) + T2PP
(c) $Yb(NO_3)_3 \cdot 2T2PP + Yb(NO_3)_3 \cdot 3T2PP$
(d) (c) + T2PP
(All in CH_2Cl_2 Solution)

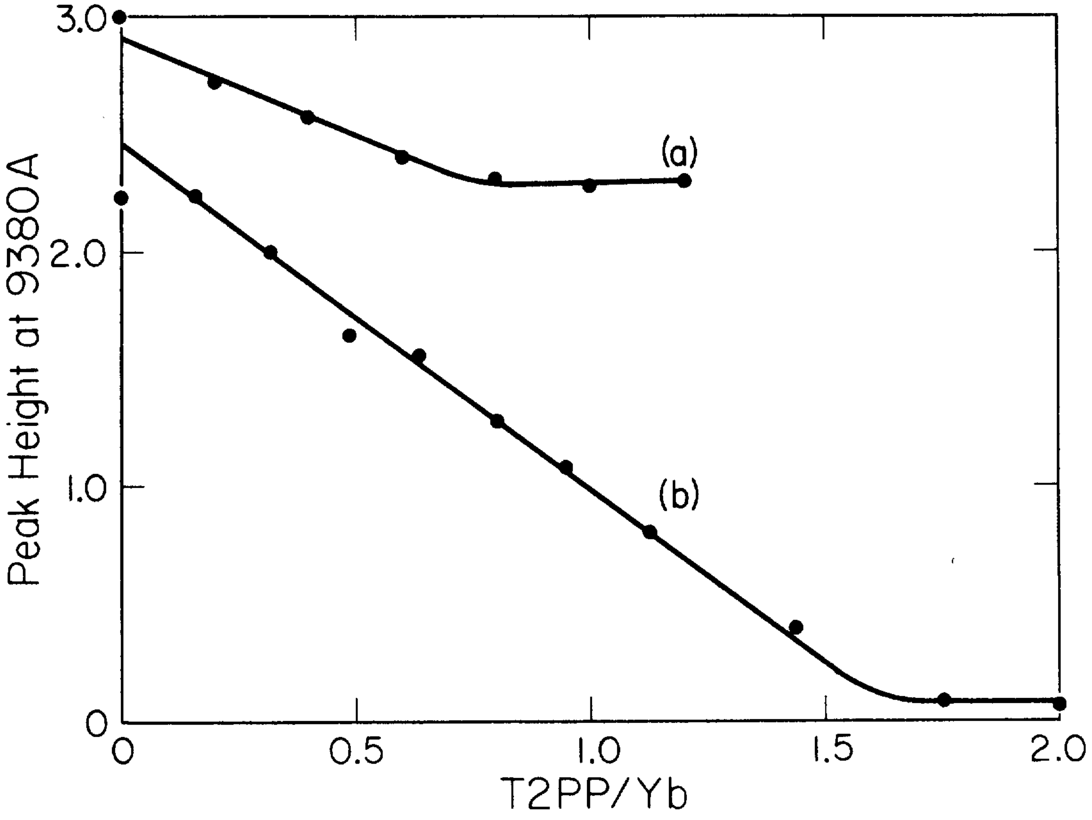

FIG. 7 CHANGES IN THE PEAK HEIGHT AT 9380 Å FOR T2PP/Yb COMPLEXES
(a) $Yb(NO_3)_3 \cdot 3T2PP$ + T2PP; (b) $Yb(NO_3)_3 \cdot 2T2PP$-$Yb(NO_3)_3 \cdot 3T2PP$
CH_2Cl_2 SOLUTIONS