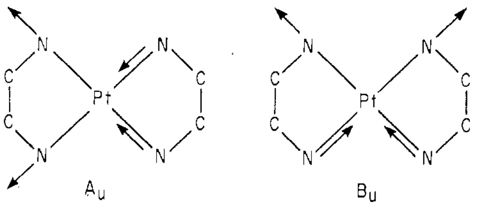

Figure 2.—Schematic drawings of infrared-active metal–nitrogen stretching vibrations.

infrared-active A_u and B_u metal–nitrogen stretching modes is depicted in Figure 2.

Undoubtedly, there is extensive coupling present in the metal–ligand vibrations. For instance, a deformation of N–C–C–N results in the simultaneous deformation of N–M–N. There would be coupling between the M–N stretch and the N–C–C–N deformation. Thus, the observed bands do have a significant degree of mixed character.

The series of six complexes each have two bands in the 500–600-cm^{-1} region that are assigned to the A_u and B_u M–N stretching modes (Figure 1). This assignment is supported by the calculations of Mizushima, *et al.*,[20] and the reported spectrum[21] of $[Pt(NH_3)_4]Cl_2$. Therefore the two infrared-active stretching vibrations are assigned at 571–589 and 508–546 cm^{-1}.

The next two absorption bands that appear in the spectra are assigned to the deformation of the N–C–C–N skeleton. In ethylenediamine[18] the two bending modes of the N–C–C–N skeleton occur at 510 and 468 cm^{-1}. These bands would be frequency dependent on the azimuthal angle between the two N–C–C planes, and hence their absorptions could be significantly shifted in the spectra of the complexes. Poulet, *et al.*,[21] have reported that the deformation of the N–M–N skeleton in $[Pt(NH_3)_4]Cl_2$ occurs below 300 cm^{-1}. Since under the C_{2h} point group two infrared-active N–C–C–N skeletal deformations are predicted ($A_u + B_u$), the two bands in the 355–479-cm^{-1} region are assigned to these vibrations.

The only other band present in the spectra is below 300 cm^{-1}. The broadness of the band suggests that two modes are superimposed and not resolved. The region below 300 cm^{-1} is most certainly the area of poorest resolution in that the instrument slits are at their maximum width. In view of reported data[21] for $[Pt(NH_3)_4]Cl_2$, the 250–300-cm^{-1} band is assigned to the in-plane deformations of the metal–nitrogen skeleton.

The study of Poulet, *et al.*,[21] supports the conclusion that the out-of-plane deformations of the metal–nitrogen skeleton occur below the CsI region.

The N–C–C–N skeleton possesses one infrared-active torsional mode (B_u). In ethylenediamine[11] this torsional motion is assigned at 186 cm^{-1}. Owing to the low frequency that the mode possesses in the uncombined ligand, it is assumed that the band lies below the CsI region in the present complexes.

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Some Spectral Anomalies in Neodymium and Erbium Aminopolycarboxylate Complexes[1]

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A new series of rare earth chelates with triethylenetetraminehexaacetate (TTHA) ligands has been prepared in solution and their electronic absorption spectra measured. The chelates of Nd^{3+} and Er^{3+} displayed particularly striking intensifications of certain absorption bands, and consequently the analogous chelates with ethylenediaminetetraacetate (EDTA) and *trans*-1,2-diaminocyclohexanetetraacetate (CDTA) ligands were also prepared and their absorption spectra studied, with the hope that some systematic correlation of the spectral enhancements could be made.

Experimental Section

Materials.—Aqueous Nd^{3+} and Er^{3+} solutions (0.1 *M*) were prepared from 99.99% pure chloride salts (Michigan Chemical Corp.). These were standardized by EDTA titration using a xylenol orange indicator. The 0.1 *M* solutions of EDTA and CDTA were prepared by dissolving an accurately weighed required amount of the appropriate acid in 100 ml of water. The 0.1 *M* TTHA (Geigy Chemical Corp.) solution was prepared by dissolving an accurately weighed required amount of the acid in 40 ml of water, to which was added with constant stirring 30 ml of 1.5 *M* NaOH. The solution was then heated to about 80° for 20 min to ensure complete dissolution and made up to 100 ml total volume subsequent to cooling to ambient temperature.

Chelates.—Appropriate volumes of 0.1 *M* rare earth chloride and 0.1 *M* chelon solutions were thoroughly mixed (pH ~8) and set aside for complete equilibration. Maximum spectral enhancements were observed to occur at a 1:1 molar ratio of rare earth ion to ligand in all cases.

Spectral Measurements.—Ultraviolet, visible, and near-infrared absorption spectra were obtained on a Beckman DK-1 recording spectrophotometer. Multiple scans were taken on several samples of each solution to confirm complete accuracy of the results.

Results and Discussion

The observed absorption maxima and ratios of molar extinction coefficients (ϵ_{max}) of complex to aqueous ion of the CDTA, EDTA, and TTHA Nd^{3+} and Er^{3+} chelates are given in Table I. It is observed that, while there is some enhancement in the various ϵ_{max} values for all of the chelates, the most significant effects are found with TTHA ligands, although the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ band in the Nd^{3+}–TTHA system is only about two-thirds as enhanced as that of the $^4I_{15/2} \rightarrow {}^4G_{11/2}$ band of the Er^{3+}–TTHA chelate. Furthermore, a red shift is apparent in this same band where CDTA and EDTA Nd^{3+} chelates are involved, while in the Er^{3+} chelates no shift is discernible except for perhaps a very slight red shift in Er^{3+}–EDTA. It is also interesting that those chelates having ϵ_{max} values significantly enhanced do not

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[1] Presented at the 5th Rare Earth Research Conference, Ames, Iowa, 1965.

TABLE I

COMPARATIVE SPECTRAL DATA FOR Nd^{3+} AND Er^{3+} AMINOPOLYCARBOXYLATE CHELATES

Chelate	$\epsilon_{max}/\epsilon^0_{max}$[a]	ν, cm^{-1}[b]
Nd^{III}(aq)	. . .	17,366
Nd^{III}(CDTA)	1.07	17,276
Nd^{III}(EDTA)	1.48	17,187
Nd^{III}(TTHA)	2.40	17,300
Er^{III}(aq)	. . .	26,533
Er^{III}(CDTA)	1.01	26,540
Er^{III}(EDTA)	1.33	26,463
Er^{III}(TTHA)	4.00	26,515

[a] Ratio of ϵ_{max} of chelate to that of aqueous ion, ϵ^0_{max}. [b] Observed values accurate to ±0.1%.

exhibit any shift in the position of their absorption maxima.

The results (Table I) for both Nd^{3+} and Er^{3+} chelates show that the intensity enhancements are in the order (relative to the ligands): TTHA > EDTA > CDTA. Any undisputable explanation of this observation will be rather tenuous, for the unique phenomenon of spectral hypersensitivity in rare earths has only recently received quantitative consideration.[2-4] Jørgensen and Judd[4] have given semiquantitative evidence supporting the suggestion that the hypersensitivity is most likely not pure electric dipole in origin, but rather electric quadrupole. These investigators have suggested that the electromagnetic field induces an asymmetrical distribution of dipoles in the medium surrounding the rare earth ion, thus inducing a large electric field gradient across the ion. The theoretical development leads to the quantum selection rule $\Delta J = \pm 2$ for such a pseudo-quadrupole transition, which is in complete accord with the data in Table I regarding the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ and $^4I_{15/2} \rightarrow {}^4G_{11/2}$ transitions for Nd^{3+} and Er^{3+}, respectively. Thus, it would appear that this mechanism may indeed provide a logical explanation for the data, wherein the aminopolycarboxylate ligand induces a more or less permanent asymmetry about the rare earth ion with this asymmetry increasing in the order CDTA < EDTA < TTHA.

In the absence of detailed information regarding coordination number, geometry, and other essential structural details in these aminopolycarboxylate chelates and additional spectral data of a more detailed nature, it is impossible to ascertain which parameters are most specifically associated with the hypersensitivity. However, if the pseudo-quadrupole mechanism[4] is accepted as plausible, then one thing of importance is the polarizability of the solvent environment. Although this effect is an indirect one, the intensity of the transition should increase with increasing solvent polarizability.[4] Unfortunately, the aminopolycarboxylate Nd^{3+} and Er^{3+} chelates are not amenable to a spectral study involving solvents of widely varying polarity, since they appear to be formed only in highly polar solvents such as water. However, spectra of the analogous Nd^{3+} and Er^{3+} acetylacetonates have been obtained in benzene, toluene, carbon tetrachloride, and chloroform,[5] thus allowing at least a qualitative evaluation to be made. These solvents have effective molar polarizabilities, $(\alpha_m)_{eff}$,[6] of 10.5, 13.3, 11.1, and 17.8 A^3, respectively. Attempts to correlate the ϵ_{max} values of $Nd(acac)_3$ and $Er(acac)_3$ with these data were of no avail, thus suggesting that spectral hypersensitivity as a consequence of quadrupolar enhancement *via* dielectric inhomogeneity should perhaps be viewed with caution. In fact, it has recently been pointed out that the symmetry of the local environment also plays a major role in the enhancement of pseudo-quadrupole transitions.[7] This would seem to be more in line with these reported observations.

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Preparation and Properties of Barium Pernitride, Ba_3N_4[1]

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The thermal decomposition of many inorganic azides, especially those of heavy metals, proceeds explosively and results in the formation of the corresponding metal and nitrogen.[2] However, the thermal decomposition reactions of certain of these azides, such as those of barium, calcium, and strontium are accompanied, although to a small extent, by the formation of the corresponding nitrides.[3-6] According to Andrew,[5] in the thermal decomposition of barium azide, nuclei of metallic barium are first formed which then react with undecomposed barium azide to form the nitride. Harvey[7] has reported that, if partially decomposed crystals are removed from the sample during the period of acceleration of the decomposition, the product is found to consist only of metallic barium.

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[1] Presented in part at the 141st National Meeting of the American Chemical Society, Washington, D. C., March 1, 1962.

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