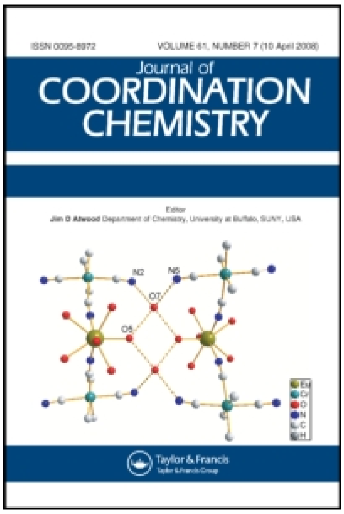

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Lanthanide Coordination Chemistry: Spectroscopic Properties of Terbium and Europium Poly(Pyrazol-1-YL)- and Poly(Imidazol-1-Yl)Borate Complexes

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LANTHANIDE COORDINATION CHEMISTRY: SPECTROSCOPIC PROPERTIES OF TERBIUM AND EUROPIUM POLY(PYRAZOL-1-YL)- AND POLY(IMIDAZOL-1-YL)BORATE COMPLEXES

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omplexes formed between poly(pyrazol-1-yl)- or poly(imidazol-1-yl)borate anions and tripositive cations terbium or europium were examined by infrared, UV absorption, and emission spectroscopy. Tris- and trakis(heterocycle)borates yielded isostructural compounds with both lanthanides, but having a different olecular geometry than the bis(heterocycle)borate complexes. Electronic spectra indicate that the oly(pyrazol-1-yl)borate complexes emit from a ligand-to-metal (LMCT) charge transfer state. The free gands are UV transparent however, suggesting that the sensitizing chromophore responsible for emission created only upon complex formation. The poly(imidazol-1-yl)borate compounds exhibit a more omplicated excited state profile, with emission apparently originating from both LMCT and intraligand ates.

Keywords: Lanthanides, organic borates, complexes, spectra, luminescence.

NTRODUCTION

ransition metal complexes containing poly(pyrazol-1-yl)borates and related ligands ave been under study for two decades following the seminal work of Trofimenko.[1,2] lthough recently reported research describes main group element-poly(pyrazol-1-yl)borate complex formation,[3,4] there has been little information in the literature n lanthanide chemistry involving these versatile ligands. Thus far, a note on the reparation of several compounds in this series with various lanthanide cations,[5] and apers describing the crystal structure of tris[hydridotris(pyrazol-1-yl)borate]ytterium(III),[6] and the solution structure of the same complex and its lutetium analogue ave appeared.[7] Uncharacterized terbium compounds ligated simultaneously with ydridotris(pyrazol-1-yl)borate and β-diketonate groups have been briefly discussed s phosphors in organic resin matrices.[8]

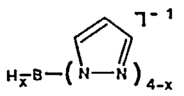
In the course of a study of lanthanide–nitrogen ligand complexes, we synthesized ompounds *via* the interaction of terbium and europium salts with poly(pyrazol-1-)- and poly(imidazol-1-yl)borates. The chemical nature of these products has been haracterized as far as possible, and their UV absorption and emission behaviour has een investigated. Presented here are structural comparisons among the title compounds as determined by infrared spectroscopy, and electronic spectral data supporte of the unusual excited state properties observed in complexes of Tb^{+3} or Eu^{+3} nd the two ligand families.

Author for correspondence.

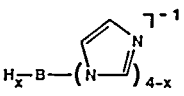
RESULTS

Structural Considerations

Ligand families **I** and **II** react with Tb^{+3} or Eu^{+3} salts in aqueous solution, yielding insoluble white precipitates.



(x = 2, 3, 4)



I
Poly(pyrazol-1-yl)borate

II
Poly(imidazol-1-yl)borate

(Throughout the paper the following nomenclature convention will be used: **I-4** = tetrakis(pyrazol-1-yl)-borate anion, **II-2** = bis(imidazol-1-yl)borate anion, *etc*.). Infrared spectra indicate that the precipitates are ionic compounds incorporating the anion present in the lanthanide salt used as starting material. For example, diffuse reflectance Fourier transform infrared (FTIR) spectra of the products precipitated from Na(**I-3**) and either terbium(III) chloride or terbium(III) acetate in water are identical except for the carbonyl stretching region between 1450–1600 cm^{-1}. Subtraction of the chloride spectrum from the acetate spectrum leaves carbonyl bands coincident with those observed in sodium acetate. Similar data obtain on comparing products from Na(**I-3**) and terbium(III) nitrate or terbium(III) sulfate with the precipitate from Na(**I-3**) and terbium(III) chloride. Thus, the water-insoluble solids from these reactions contain the anion originally associated with terbium, and are therefore more structurally complex than the neutral tris chelates $Ln(\mathbf{I\text{-}3})_3$, (Ln = Yb,[6] Lu[7]).

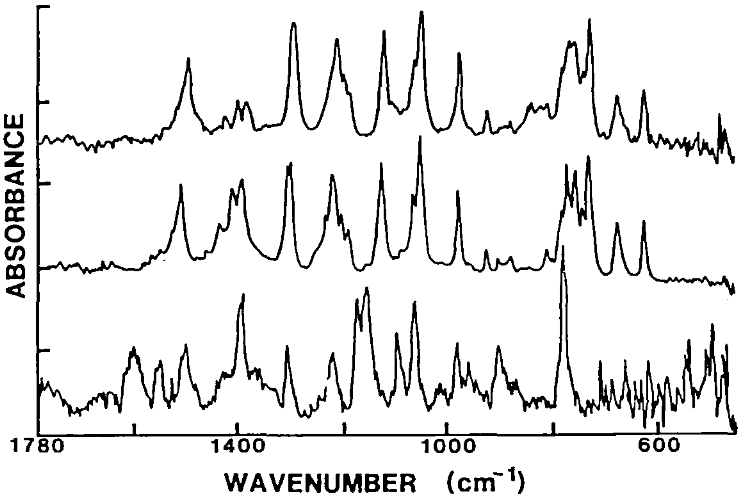


FIGURE 1 Diffuse reflectance infrared spectra of solids formed from terbium(III)nitrate and sodium bis-, tris-, or tetrakis(pyrazol-1-yl)borate; lower, middle, and upper traces respectively. Concentration = 0.10% in KBr.

Figure 1 combines diffuse reflectance FTIR traces for the precipitates obtained om sodium salts of (**I-2**), (**I-3**), and (**I-4**) added to terbium nitrate. The spectra are rtually identical for Tb(**I-3**)$_x$ and Tb(**I-4**)$_x$, but the Tb(**I-2**)$_y$ complex exhibits a rikingly different fingerprint between 500 and 1700 cm^{-1}. Spectra for Tb(**II-2**)$_y$, b(**II-3**)$_x$, and Tb(**II-4**)$_x$ show the same similarity in the tris- and tetrakis(imidazol--yl)borate complexes in contrast to the bis complex.

Diffuse reflectance FTIR spectra of complexes formed between Na(**I-3**) and either rbium(III) nitrate or europium(III) nitrate exhibit bands of similar position and tensity in the 600–1600 cm^{-1} region. The congruency of structure implied in the TIR measurements is supported by data in Table I, which compare elemental nalyses for the above complexes.

TABLE I
Analytical data for selected tris(pyrazol-1-yl) complexes.

alc (TbL$_3$)^a	Found	Empirical Formula	Calc (EuL$_3$)^a	Found	Empirical Formula
%C = 40.64	%C = 37.71	C = 22.33	%C = 41.00	%C = 33.97	C = 22.16
%H = 3.79	%H = 3.75	H = 26.46	%H = 3.82	%H = 3.42	H = 26.59
%N = 31.59	%N = 28.91	N = 14.68	%N = 31.87	%N = 26.46	N = 14.80
Tb = 19.91	%Tb = 22.35	Tb = 1.00	%Eu = 19.21	%Eu = 19.39	Eu = 1.00

xpected stoichiometry.

The precipitates do not yield analytical data supportive of a tris chelate structure, r of any other simple metal–ligand combination. The similarity of calculated npirical formulae in columns 3 and 6, however, suggest that the terbium and uropium complexes exist in the same, but currently uncharacterized structure. pecific structural details for any of the complexes are currently lacking, as they are ll practically insoluble in water and common organic solvents, a fact which recludes complete spectroscopic analysis or molecular weight determination. The ompounds precipitate as amorphous solids under all conditions tried thus far. yntheses employing borates with organic functionality on the heterocyclic ring may ad to more tractable products by sterically limiting the coordination number round the relatively large Tb^{+3} or Eu^{+3} centres,[2] or imparting a high degree of rganic solubility. We are currently examining this possibility.

V Absorption and Emission Spectroscopy

igure 2 illustrates UV spectra of dilute Na(**II-4**) and saturated Tb(**II-4**)$_x$ in ethanol, lotted using the same absorbance units. Greater absorbance intensity in the 00 nm–320 nm region in the complex *vs* the sodium salt is evident, suggesting that nother chromophore is present in the Tb(**II-4**)$_x$ precipitate. Similar enhancement of ear-UV absorbance is observed for all of the terbium and europium complexes ported here in comparison to their sodium salt precursors. Since the solubility of ne lanthanide complexes is extremely low (*ca* 10^{-5}–10^{-6} *M*), the observed UV ands correspond to strongly allowed charge transfer transitions with extinction oefficients of 10^4 M^{-1} cm^{-1} or greater. Charge transfer assignments are further ubstantiated by the fact that the band maxima are solvent dependent; for example, a aturated solution of Tb(**II-4**)$_x$ in tetrahydrofuran exhibits a band maximum at 90 nm compared to the 300 nm maximum observed in ethanol as shown in Figure 2.

Ligand field f → f transitions for trivalent terbium and europium cations are also found in the near UV,[9] but their molar extinction coefficients are too small to contribute to the observed bands. For example, $Tb(NO_3)_{3(aq)}$ and $Eu(NO_3)_{3(aq)}$ at concentrations below 0.005 *M* give no detectable spectra, while at higher concentration the following data are obtainable; $Tb(NO_3)_{3(aq)}$: $\lambda = 300\,nm$, $\varepsilon = 22\,M^{-1}\,cm^{-1}$. $Eu(NO_3)_{3(aq)}$: $\lambda = 392\,nm$, $\varepsilon = 2.0\,M^{-1}\,cm^{-1}$; $\lambda = 296\,nm$, $\varepsilon = 22\,M^{-1}\,cm^{-1}$.

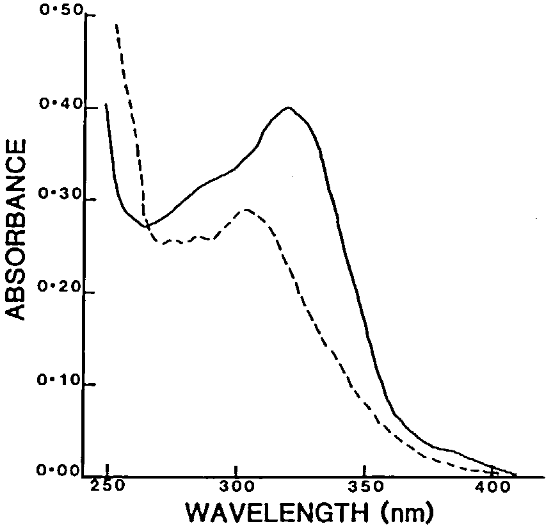
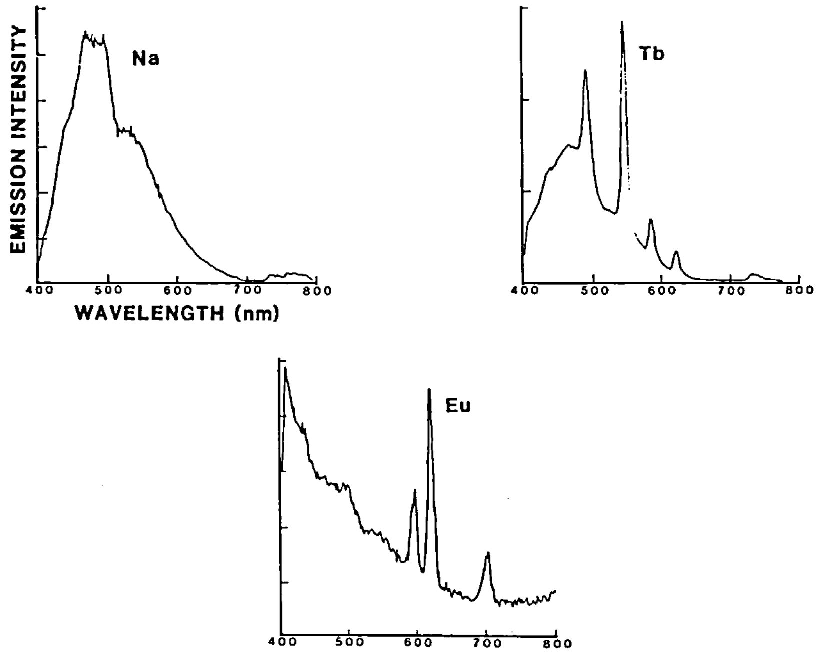


FIGURE 2 Ultraviolet absorption spectra in ethanol of sodium tetrakis(imidazol-1-yl)-borate, (solid line), (concentration = 1×10^{-3} *M*) and its products with terbium(III)nitrate, (dashed line), (concentration estimated to be 10^{-5}–10^{-6} *M*).

All of the solids formed from Tb^{+3} and Eu^{+3}, and ligand families **I** and **II** are emissive in the visible region (400 nm–800 nm) upon near-UV excitation (254 nm–366 nm). The sodium salts of (**II-2,3,4**) are themselves emissive as solids or in solution, in contrast to their (**I-2,3,4**) counterparts which exhibit no visible emission when exposed to near-UV radiation. Excitation spectra ($\lambda_{em} = 498\,nm$) of Na(**II-4**) and Tb(**II-4**)$_x$ in ethanol show broad bands between 300 nm–320 nm corresponding to the absorbance maxima in Figure 2. Excitation spectra of the remaining terbium and europium precipitates are also similar to their absorption spectra, indicating that observed emission originates in electronic states created upon complexation.

Solid state emission spectra for the terbium and europium complexes exhibit characteristically sharp lines coincident with known f → f transition energies for Tb^{+3} and Eu^{+3}, but the emission intensities are greatly enhanced compared to those observed in the corresponding nitrate or chloride salts.[10] Figure 3 illustrates emission spectra for Na(**II-4**), Tb(**II-4**), and Eu(**II-4**). Of interest is the fact that Tb(**II-4**) and Eu(**II-4**) yield spectra that include the sharp f → f lines typical of Tb^{+3} and Eu^{+3} and the broad signal due to Na(**II-4**), while the analogous spectra of lanthanide complexes synthesized from Na(**I-2,3,4**) shown only f → f transitions.



GURE 3 Solid state emission spectra of sodium tetrakis(imidazole-1-yl)borate and its oducts with terbium(III)nitrate or europium(III)nitrate.

ISCUSSION

ıe complexes reported here are significantly different from those described earlier r Na(I-3) and Ln^{+3}, (Ln = La, Ce, Pr, Sm, Gd, Er, Y).[5] There is no evidence to pport the existence of non-cluster, organic-soluble LnL_3 compounds with either :bium or europium and any of the ligands in families **I** and **II**. Higher coordination ımbers and enhanced ionic character are expected in complexes of the larger ıthanides, and it is likely that clustering and ionic bonding dominate the chemistry all Ln^{+3} ions larger than tripositive erbium.

Infrared spectra support the conclusion that (**I-3**), (**I-4**) and (**II-3**), (**II-4**) bind to e lanthanides in the same fashion, differing from (**I-2**) and (**II-2**). The structures of e new complexes remain unknown, and they may exhibit more than one type of ›nding between the lanthanides and the potentially multidentate borates.[2,6,11–17] ırther discussion must await the availability of crystallographic data.

Our interest in lanthanide complexes with ligand families **I** and **II** was stimulated their potential to be stable, high quantum yield emitters in the visible region. deed, every complex formed in this study exhibits solid state luminescence when cited in the near UV. The emission spectra of Tb^{+3} or Eu^{+3} with (**I-2**), (**I-3**) or 4) are similar in band position and intensity to those measured for the same ıthanides ligated with aromatic, electronically delocalized groups such as 2,6-picolinate[18] or other benzenoid compounds containing substituents with electron ›nding pairs that geometrically permit multidentate coordination.[19] Two unusual nclusions must be drawn from our data however: (1) a chromophore not present in the tripositive metal ions *or* in Na(I-Z) or Na(II-Z), (Z = 2, 3, 4) prior to coordination appears upon complex formation. This absorbing group apparently sensitizes energy transfer (LMCT) to lanthanide excited states that are emissive; (2) the excited states accessible by near-UV irradiation of complexes with **I** *vs* complexes with **II** are sufficiently different to yield altered emission characteristics.

Conclusion (1) is based on absorption and excitation spectra. The new complexes described here have resolved bands in the near UV with molar extinction coefficients estimated to be 10^4 or larger. Excitation spectra verify that the observed emission results from population of energy levels associated with these charge-transfer bands. The chromophores arise from extended delocalization of the ligand heterocyclic ring electrons upon coordination with Ln^{+3}. According to the Whan-Crosby model invoked to explain high quantum yield luminescence from lanthanide complexes, energy transfer *via* intersystem crossing from an excited ligand singlet to an excited metal triplet state must occur to account for observed luminescence intensity.[20] The low-lying ligand singlet in this case is created by complex formation. Existing literature includes numerous examples of emission enhancement in lanthanide complexes containing nucleic acid[21,22] or protein[23,24] ligands, and it is generally stated that proximal aromatic residues are responsible for sensitization. To our knowledge, there are no known systems analogous to those described here, where a sensitizing chromophore appears only upon complexation.

Conclusion (2) is drawn from Figures 2 and 3. Whereas imidazole is UV transparent to 240 nm, sodium salts of (II-Z), (Z = 2, 3, 4), have absorption bands at 310 nm–320 nm ($\varepsilon = 100\text{–}300\ M^{-1}\ cm^{-1}$). The salts are emissive as solids or in solution. Complexation with Tb^{+3} or Eu^{+3} leads to increased absorption intensity in the 300 nm–320nm region, but the solids thus obtained are qualitatively poorer emitters than their poly(pyrazol-1-yl)borate analogues upon near-UV excitation. Emission spectra have characteristics of the lanthanide-family I complexes *and* Na(II-Z), (Z = 2, 3, 4), as shown in Figure 3. We interpret the observed emission as originating from two independent excited states, one based on a $\pi \rightarrow \pi^*$ absorption in the ligand system, and the other arising from the ligand → metal electronically delocalized chromophore generated by nonbonding electrons on the imidazole rings interacting with the lanthanide centre as discussed under conclusion (1).

EXPERIMENTAL

Certain suppliers of chemicals and equipment are identified by name to specify experimental conditions. In no case does this imply endorsement or recommendation by the National Bureau of Standards, nor does it imply that the particular brands of chemicals and equipment are necessarily the best for the purposes.

Lanthanide salts were purchased from the indicated suppliers and used without further purification: $Tb(NO_3)_3 \cdot 5H_2O$ (99.999%–Aldrich Chemical Co.), $TbCl_3$ (99.9%–Morton-Thiokol, Inc., Alfa Products), $Tb(acetate)_3 \cdot xH_2O$ (99.9%–Alfa), $Tb_2(SO_4)_3$ (99.9%–Alfa), and $Eu(NO_3)_3 \cdot 5H_2O$ (99.9%–Aldrich). Starting materials for the synthesis of sodium poly(pyrazol-1-yl)- and poly(imidazol-1-yl)borates, including $NaBH_4$ (98%–Alfa), pyrazole (98%–Aldrich), and imidazole (99%–Aldrich) were also used as received. All reactions were carried out under ambient atmosphere with no special precautions to exclude oxygen or water. Organic solvents were undistilled reagent grade or better, and water was deionized to 10 megaΩ cm in a Millipore Milli-Q system.

Fourier transform infrared spectra were obtained on an Analect AQS-20 spectro- eter by diffuse reflectance in a KBr matrix, by direct transmission through solid mples on a KCl plate on the stage of an Analect XAD infrared microscope tachment, or in aqueous solution by attenuated total reflectance in a Spectra-Tech ircle Cell equipped with a ZnSe crystal. Microscopic measurements employed a uid nitrogen-cooled narrow band mercury cadmium telluride detector, while the her two FTIR techniques used an ambient temperature triglycine sulfate detector. ectra were processed with standard Analect software through a MAP-67 Data stem.

Emission and uncorrected excitation spectra were run on a Carl Zeiss Epifluor- cence Universal Microscope system equipped with an Osram HBO 100 watt super essure mercury lamp, quartz objectives, and IBM PC-XT controlled emission and citation monochromators. Solid samples and solutions were held in a 2 mm depth pression slide on the microscope stage, employing a quartz cover slip when cessary. Data were processed using Zeiss λ-scan software, and plotted with the aid Grapher software (Golden Software, Inc.). Absorption spectra in the ultraviolet ere acquired on a Hitachi-Perkin Elmer 330 recording instrument in 10 mm quartz vettes. Saturated solutions of the lanthanide complexes with I and II in THF or hanol gave sufficient signal to qualitatively locate band maxima. Concentrations ere estimated to be 10^{-5}–10^{-6} *M*.

Uncorrected decomposition points were observed in a Mel-Temp apparatus in sealed pyrex capillary tubes. Elemental analyses were performed by Schwarzkopf icroanalytical Laboratory, Inc., Woodside, New York.

*nthesis of (I-2,3,4) and (***II-2,3,4***)*

e method of Trofimenko[11,25] was used to synthesize family **I**, and the same chniques were applicable to family **II** as well. The **II-4** salt was previously prepared a similar method.[26] Thus, when sodium borohydride and excess pyrazole or idazole were heated together in the absence of solvent in a silicone oil bath, the substituted product resulted at 100°C, the trisubstituted product formed at 170°C, d the tetrasubstituted product was obtained at 210°C. The melts were heated and irred until no more dihydrogen was evolved, and vacuum distillation of the maining solids at 100°C removed excess pyrazole or imidazole, leaving the latively non-volatile sodium salts behind. The borates (**II-3**) and (**II-4**) were ntaminated with brown decomposition products as isolated. All salts were recrys- llized from boiling water prior to further use. Yields were in the 40–80% range sed on 5.0 g (73.4 mmol) of $NaBH_4$ as the limiting reagent. Solid state infrared ectra of family **I** compared well with the results of Trofimenko.[11] Predictable fferences in vibrational band positions differentiated pyrazole from imidazole alogues; for example, the C–N–N ring vibration at 1390–1410 cm^{-1} in the former mily was absent in the latter, while the ring breathing vibration at 920–930 cm^{-1} in was absent in **I**.

nthesis of terbium and europium complexes

ll complexes were prepared as detailed below for Eu(**I-3**)$_x$. In deionized water, 500 *M* solutions of $Eu(NO_3)_3$ and Na(**I-3**) were prepared and filtered through hatman No. 1 paper. To a stirred 10 cm^3 aliquot of the europium solution, 30 cm^3 the borate solution was added dropwise, inducing the formation of a curdy, white precipitate. Reversing the order of reagent addition yielded a product that was identical to the first precipitate as evidenced by FTIR and emission spectroscopy. The solid was collected on a 5 μm porosity fritted glass disk, washed sequentially with 3 × 20 cm^3 of water, ethanol, THF, diethyl ether, and *n*-pentane, and dried in air. A yield of 3.65 g was realized, which corresponds to a calculated molecular weight of 730, assuming that the product precipitates quantitatively. This complex, as well as all of the other combinations of ligands with Tb^{+3} and Eu^{+3}, was virtually insoluble in water, aliphatic or aromatic hydrocarbons, chlorocarbons, ethers, and alcohols at room temperature. The latter two solvent classes dissolved minute quantities of the compounds, yielding solutions concentrated enough for UV absorption studies, but too dilute for other spectroscopic characterization. The complex decomposed without melting above 270°C, as did all other complexes synthesized in this study.

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