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Effects of Inorganic Countercations on the Fluorescence Spectra of the Tetrakis(1-phenyl-1,3-butanedionato)europium(III) Anion

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The fluorescence and excitation spectra, for selected regions, of the sodium, potassium, rubidium, and cesium salts of tetrakis(1-phenyl-1,3-butanedionato)europium(III) are presented under high resolution and at low temperature (77 K). The alterations, in the spectral patterns, line widths, and relative intensities as produced by changing cations are examined and discussed. The ligand field splittings in the europium spectra suggest the following point symmetries for the compounds: sodium, D_4; potassium, C_4 or C_{4v}; rubidium, D_{2d}; cesium, D_2.

Introduction

Among the most interesting aspects of the fluorescence spectra of many rare-earth compounds are their characteristically narrow features. These features are the result of intra-4f electronic transitions. Although the spectra of many purely inorganic rare earth compounds have been routinely investigated at high resolution (0.5 Å) and low temperatures (10–77 K),[1] most investigations of rare-earth chelate compounds have been carried out with less resolution (on the order of a nanometer) at ambient temperature.[2] The few low-temperature spectra that have been previously obtained on rare-earth chelates have generally not allowed the determination of all the detail present in many of the features. Also, the excitation spectra of these compounds, when presented, were performed with relatively large band-pass sources. In the low-temperature spectra, which are the subject of this investigation, several manifolds of Eu^{3+} compounds are explored in detail, with emphasis on the splittings of the $^7F_1$ and $^7F_2$ levels.

In the past, studies of the effects of differing counterions on the spectra of rare-earth chelate compounds have centered on large organic moieties. Variations in the spectra of these compounds were generally ascribed to the steric effects caused by the differing sizes of the cations, with little contribution being attributed to changing charge densities.[3] Although rare-earth chelate compounds possessing inorganic counterions have been examined in the past,[4] there are few instances in which more than one or two different counterions have been used in homologous compounds. The following account presents the fluorescence and excitation spectra of a series of homologous europium chelate compounds with four different inorganic cations.

Experimental Section

The group of compounds prepared for this investigation was a series of tetrakis chelates employing the β-diketone benzoylacetone (1-phenyl-1,3-butanedione). This ligand was chosen because it should produce a highly symmetric, singly negatively charged rare earth ion complex. The synthesis method for this series of compounds was adapted from a method for sodium tetrakis(1-phenyl-1,3-butanedionato)europium(III) described by Melby and associates.[2] First, a 0.284 M stock solution of EuCl$_3$ was produced for use in this and subsequent syntheses. This was accomplished by dissolution of 25.000 g of the oxide in 35.2 mL of concentrated HCl, followed by dilution with deionized water to a final volume of 500.0 mL. A solution of 10 mmol of benzoylacetone in 50 mL of acetone was prepared. To this solution was added 10 mL of an aqueous solution of 1.0 N alkali-metal hydroxide. The mixture was heated to reflux, and a diluted stock solution of 2 mmol of EuCl$_3$ in 10 mL of water was added. The final mixture was then maintained at reflux for at least 30 min. The resultant solution was cooled in an ice bath, and the precipitated solid was removed by filtration. The filtrate was a collection of pale yellow microcrystals. These crystals were dried in a 60° C oven for 1 h. The procedure proved successful for the synthesis of the sodium, potassium, rubidium, and cesium salts. However, this method and several other variations failed to produce a lithium salt that exhibited a narrowly featured spectrum. Of the other compounds, both the potassium compound and the cesium compound were found to produce a more narrowly featured spectrum after being annealed. The annealing process was performed by heating the salt in a 80 °C oven for 24 h and then allowing the compound to cool slowly. In repeated experiments it was observed, however, that all of these compounds seemed to anneal to some extent, as evidenced by cleaner spectra, when left for a long time, up to 1 year, at ambient conditions. The infrared spectra of the above compounds were found to be very similar and in each case peaks from 1600 to 1400 cm^{-1} indicated coordinated benzoylactone. An example of the infrared spectrum of the potassium salt is given in Figure 1. Results of elemental analyses performed on these compounds are given in Table I.

Table I. Results of Elemental Analyses

compd	calcd (found) % C	calcd (found) % H
Na[Eu(Bzac)$_4$]	58.61 (57.56)	4.44 (4.38)
K[Eu(Bzac)$_4$]	57.18 (56.76)	4.33 (4.24)
Rb[Eu(bzac)$_4$]	54.19 (53.47)	4.11 (4.09)
Cs[Eu(Bzac)$_4$]	51.66 (50.71)	3.91 (3.86)

Chemicals used in the above syntheses included the following: 1-benzoylacetone 98%, purchased from Aldrich Chemical Co., 940 West Saint Paul Ave., Milwaukee, WI 53233; europium oxide, 99.9%, purchased from Alfa Products, 152 Andover St., Danvers, MA 01923. Two laser dyes were employed in this investigation: Rhodamine 590 tetrafluoroborate was obtained from Exciton, P.O. Box 31126, Overlook Station, Dayton, OH 45431, and Rhodamine 19 perchlorate was obtained from Eastman Kodak Co., Rochester, NY 14650.

Two spectroscopic sources were employed. One source used was a Model UVS-11 UVP short-wave hand lamp purchased from Fisher Scientific Co., Fair Lawn, NJ 07410. Excitation spectra were obtained by using a Model CMX-4 tunable flashlamp-excited dye laser, from Chromatix, 560 Oak Mead Parkway, Sunnyvale, CA 94086. Refrigeration of the samples was provided by a Model CSW-204 Displex closed-cycle refrigeration system, from Air Products and Chemicals, Inc., ADP Cryogenics, 1919 Vultee St., Allentown, PA 18103. All spectra were obtained by use of a Model 1702 $^3/_4$-m Czerny-Turner scanning spectrometer, from Spex Industries, Inc., Box 798, Metuchen, NJ 08840. In order to provide maximum positional flexibility, fluorescence radiation was collected and fed to the monochromator through a Liquid Light Guide, Part No. 77556, from Oriel Corp., 250 Long Beach Blvd., P.O. Box 872, Stratford, CT 06497-0872. Light exiting the monochromator was detected by using an RCA Type No. C31034 photomultiplier tube, mounted in a Fact-50 MK III digital readout thermoelectric cooled housing, from EMI Gencom Inc., 80 Express St., Plainview, NY 11803. Detection electronics consisted of the following: a Model 9301 fast preamplifier, a Model 9302 amplifier discriminator, a Model 9315 photon counter, and a Model 9325 D-A converter, all manufactured by EG&G Ortec, 100 Midland Road, Oak Ridge, TN 37830. Spectra were then recorded by a Series 5000 Fisher Recordall strip chart recorder, from Fisher Scientific Co., 113 Hartwell Ave., Lexington, MA 32173-3190.

Results and Discussion

The details of the observed fluorescence spectra are given in Tables II–V. An example of the fluorescence spectrum of the sodium compound, from 575 to 660 nm, is given in Figure 2. Of primary interest are the transition manifolds, $^5D_0$ to $^7F_0$, $^5D_0$ to $^7F_1$, and $^5D_0$ to $^7F_2$, since these transitions are normally intense and may give vital clues as to the site symmetry around the Eu^{3+}

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(1) Hufner, S. *Optical Spectra of Transparent Rare Earth Compounds*; Academic Press: New York, 1978; pp 1-13.

(2) Whan, R. E.; Crosby, G. A. *J. Mol. Spectrosc.* **1962**, *8*, 315. Melby, L. R.; Rose, N. J.; Abramson, E.; Caris, J. C. *J. Am. Chem. Soc.* **1964**, *86*, 5117. Sinha, S. P. *J. Inorg. Nucl. Chem.* **1966**, *28*, 189.

(3) Filipescue, N.; Degnan, J. J.; McAvoy, N. *J. Chem. Soc. A* **1969**, 1594.

(4) Butter, E. *Z. Anorg. Allg. Chem.* **1968**, *356*, 294.

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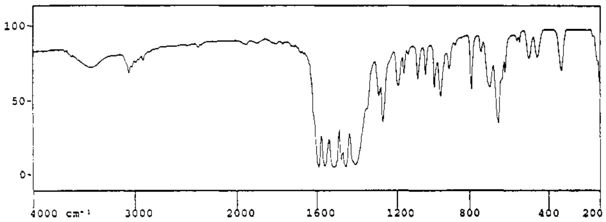

Figure 1. Infrared spectrum of K[Eu(Bzac)$_4$].

Table II. Fluorescence Transitions of Na[Eu(Bzac)$_4$]

wavelength, nm	wavenumber, cm^{-1}	fwhm, nm	rel intens	assgnt
537.66	18598	0.51	vw	$^5D_1$ to $^7F_1$
580.16	17237	0.10	vw	$^5D_0$ to $^7F_0$
591.54	16905	0.18	m	$^5D_0$ to $^7F_1$
593.15	16859	0.22	m	
593.44	16851	0.19	m	
610.55	16378	0.34	vw	$^5D_0$ to $^7F_2$
611.08	16365	0.08	vs	
614.51	16273	0.34	w	
615.04	16259	0.24	w	
651.29	15354	0.36	vw	$^5D_0$ to $^7F_3$
652.52	15325	0.25	m	
691.23	14467	0.39	w	$^5D_0$ to $^7F_4$
691.70	14457	0.44	w	

Table III. Fluorescence Transitions of K[Eu(Bzac)$_4$]

wavelength, nm	wavenumber, cm^{-1}	fwhm, nm	rel intens	assgnt
538.00	18587	0.51	vw	$^5D_1$ to $^7F_1$
580.04	17240	0.25	m	$^5D_0$ to $^7F_0$
589.70	16957	0.40	m	$^5D_0$ to $^7F_1$
590.25	16942	0.30	m	
592.17	16687	0.27	m	
611.55	16351	0.29	m	$^5D_0$ to $^7F_2$
611.82	16344	0.26	m	
612.69	16321	0.30	s	
654.39	15281	0.44	vw	$^5D_0$ to $^7F_3$
655.08	15265	0.79	w	
691.54	14460	0.59	vw	$^5D_0$ to $^7F_4$
692.77	14434	0.97	vw	

Table IV. Fluorescence Transitions of Rb[Eu(Bzac)$_4$]

wavelength, nm	wavenumber, cm^{-1}	fwhm, nm	rel intens	assgnt
579.95	17242	0.15	w	$^5D_0$ to $^7F_0$
589.30	16696	0.28	m	$^5D_0$ to $^7F_1$
592.23	16885	0.39	m	
596.62	16761	0.69	w	
611.56	16351	0.25	s	$^5D_0$ to $^7F_2$
612.82	16318	0.31	m	
654.42	15280	0.55	w	$^5D_0$ to $^7F_3$
691.43	14462	0.84	vw	$^5D_0$ to $^7F_4$

ion. The $^5D_0$ to $^7F_2$ transition is known as a hypersensitive transition due to a change in J value of 2 units. Hypersensitive transitions can be expected to be more sensitive to the ionic environment in terms of shifts in line position as well as more sensitive in terms of relative intensity. In the case of the four compounds under investigation, the intensities of the transitions in this manifold are greater than the others.

Table V. Fluorescence Transitions of Cs[Eu(Bzac)$_4$]

wavelength, nm	wavenumber, cm^{-1}	fwhm, nm	rel intens	assgnt
580.15	17236	0.31	vw	$^5D_0$ to $^7F_0$
589.97	16950	0.51	m	$^5D_0$ to $^7F_1$
592.40	16880	0.44	m	
594.98	16807	0.47	m	
611.19	16361	0.33	m	$^5D_0$ to $^7F_2$
611.80	16354	0.27	m	
612.42	16328	0.34	s	
652.69	15321	0.77	w	$^5D_0$ to $^7F_3$
654.04	15289	1.29	m	
696.69	14444	1.01	w	$^5D_0$ to $^7F_4$

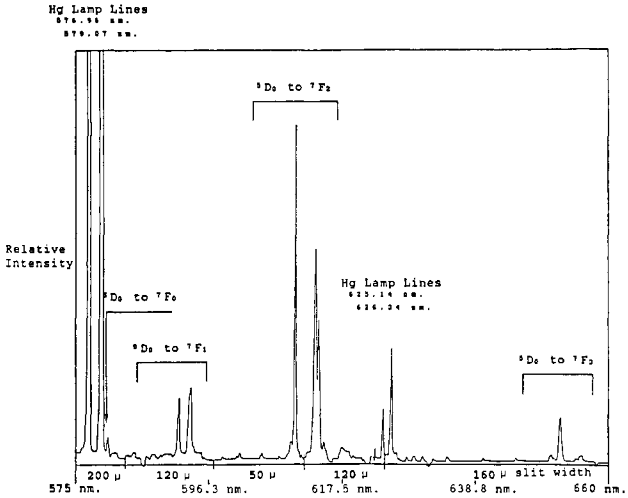

Figure 2. Extended-range fluorescence spectrum of Na[Eu(Bzac)$_4$], with the Hg-arc lamp as the excitation source. The monochromator slits used for each manifold are shown above.

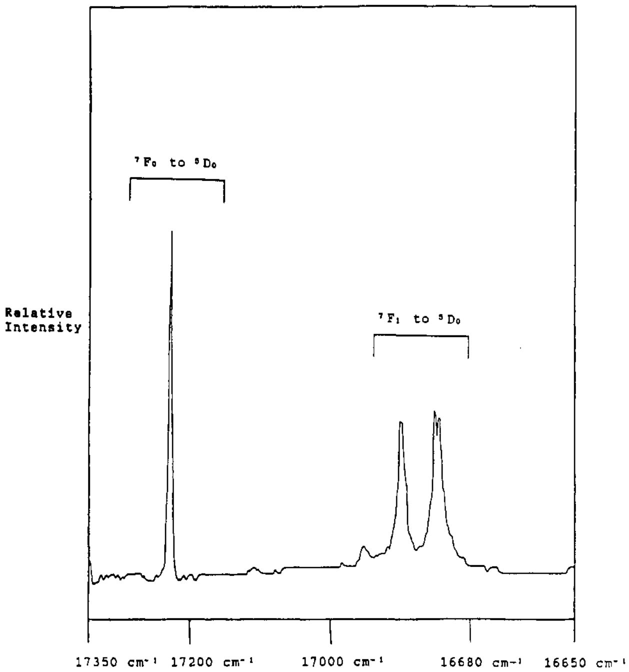

Figure 3. Excitation spectrum of Na[Eu(Bzac)$_4$] as seen at the 611.1-nm peak of the $^5D_0$ to $^7F_2$ fluorescence transition, with the tunable dye laser as the excitation source. A monochromator slit of 75 μm was employed for the first manifold, and a slit of 100 μm for the second. There has been no correction made in the spectrum for shifts in the laser intensities.

Band assignments were made by consideration of the calculated free-ion energy levels given by Dieke[5] and the calculations on similar compounds by Filipescue et al.[3] Point groups were assigned with the aid of the information and tables developed by Dieke,[5] Brecher et al.,[6] and Sinha and Butter.[7] The spectra that involve

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(5) Dieke, G. H. *Spectra and Energy Levels of Rare Earth Ions in Crystals*; Interscience Publishers: New York, 1968; pp 117–127.

(6) Brecher, C.; Samelson, H.; Lempicki, A. *J. Chem. Phys.* **1965**, 1081.

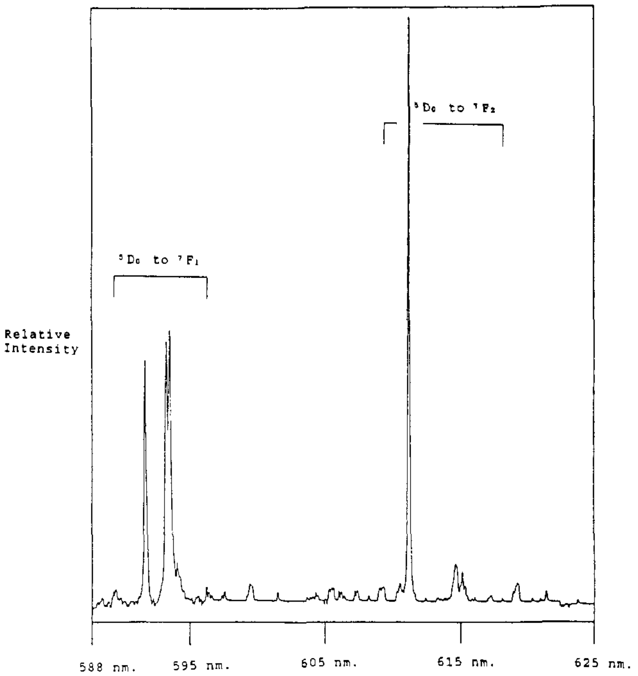

Figure 4. Fluorescence spectrum of Na[Eu(Bzac)$_4$], with the Hg-arc lamp as the excitation source. The monochromator slits were set at 60 μm for the first manifold and 20 μm for the second.

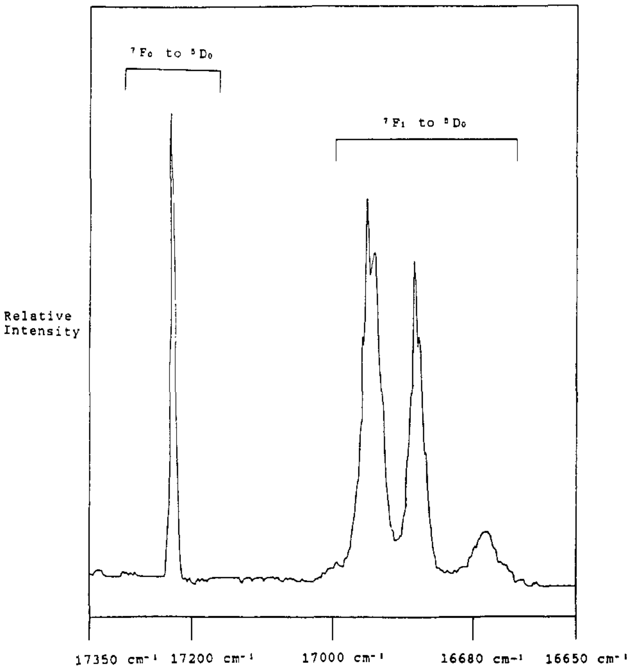

Figure 5. Excitation spectrum of K[Eu(Bzac)$_4$] as seen at the 612.4-nm peak of the $^5D_0$ to $^7F_2$ fluorescence transition, with the tunable dye laser as the excitation source. A monochromator slit of 100 μm was employed for the first manifold, and a slit of 200 μm for the second. There has been no correction made in the spectrum for shifts in the laser intensities.

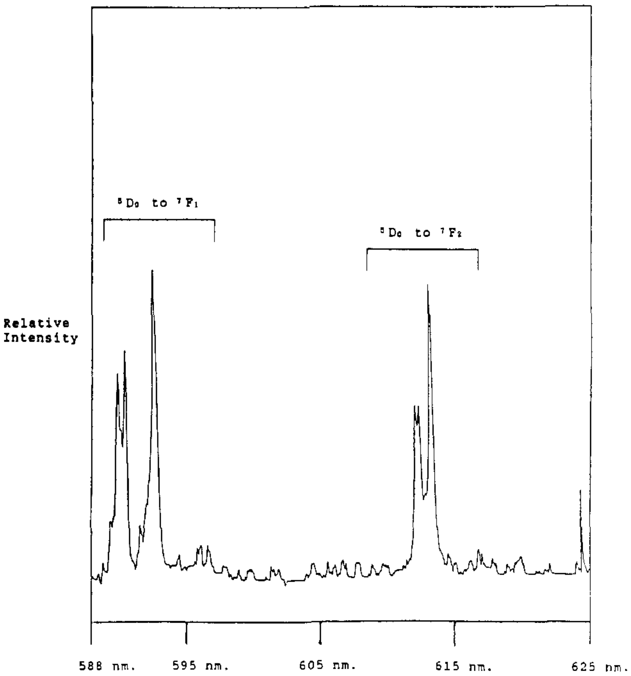

Figure 6. Fluorescence spectrum of K[Eu(Bzac)$_4$], with the Hg-arc lamp as the excitation source. The monochromator slits were set at 60 μm for the first manifold and 20 μm for the second.

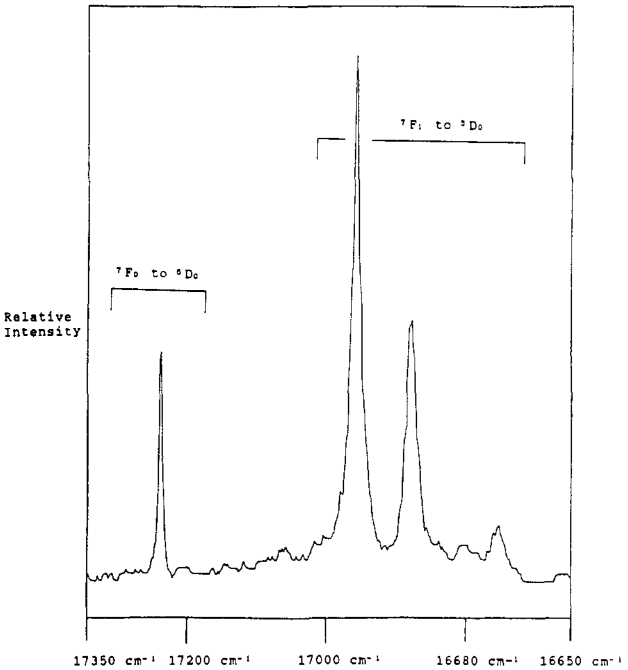

Figure 7. Excitation spectrum of Rb[Eu(Bzac)$_4$] as seen at the 611.6-nm peak of the $^5D_0$ to $^7F_2$ fluorescence transition, with the tunable dye laser as the excitation source. A monochromator slit of 100 μm was employed for the first manifold, and a slit of 150 μm for the second. There has been no correction made in the spectrum for shifts in the laser intensities.

the above mentioned manifolds are the emission and excitation spectra presented in Figures 3–10. The relative intensities assigned in the tables to the spectral data are qualitative, but the range from very weak to very strong encompasses roughly 2 orders of magnitude in peak area. In attempting to assign point symmetries, we have used only the transitions whose intensities are listed as moderate to very strong. Weak and very weak lines are assumed to result from a partial breakdown of the selection rules, from slight crystal distortions, and/or from vibrational contributions. In the cases of the $^5D_0$ to $^7F_1$ and the $^5D_0$ to $^7F_2$ manifolds, overlapping transitions can be expected from the $^5D_1$ to $^7F_3$ and the $^5D_1$ to $^7F_4$ manifolds, respectively.[7,8] Such overlapping manifolds should yield transitions of less intensity since the upper $^5D_1$ level can decay to the $^5D_0$ level by nonradiative means.

The determination of crystal field site symmetries by the examination of rare earth ion fluorescence band splittings is well understood. The method employed in this paper, for the determination of the band splittings that result from crystal field

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(7) Sinha, S. P.; Butter, E. *Mol. Phys.* **1969**, *16*, 285.

(8) Bjorkland, S.; Filipescue, N.; McAvoy, N.; Degman, J. *J. Phys. Chem.* **1968**, *72*, 970.

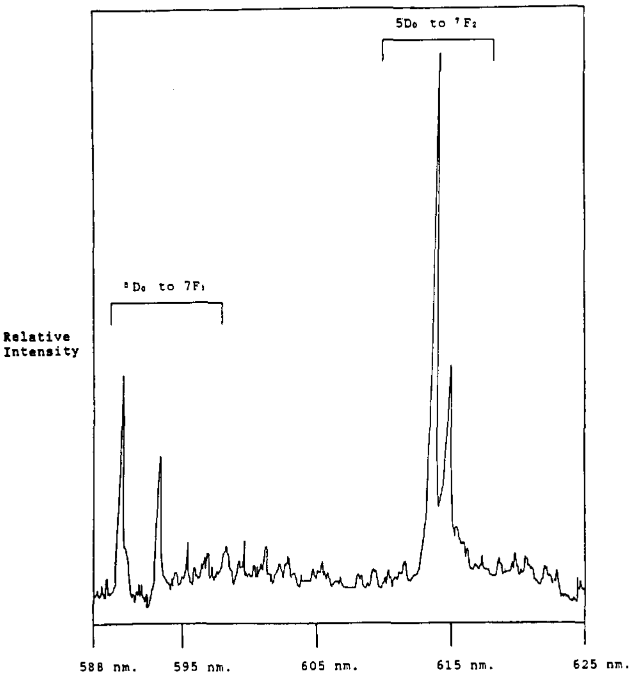

Figure 8. Fluorescence spectrum of Rb[Eu(Bzac)$_4$], with the Hg-arc lamp as the excitation source. The monochromator slits were set at 80 μm for the first manifold and 40 μm for the second.

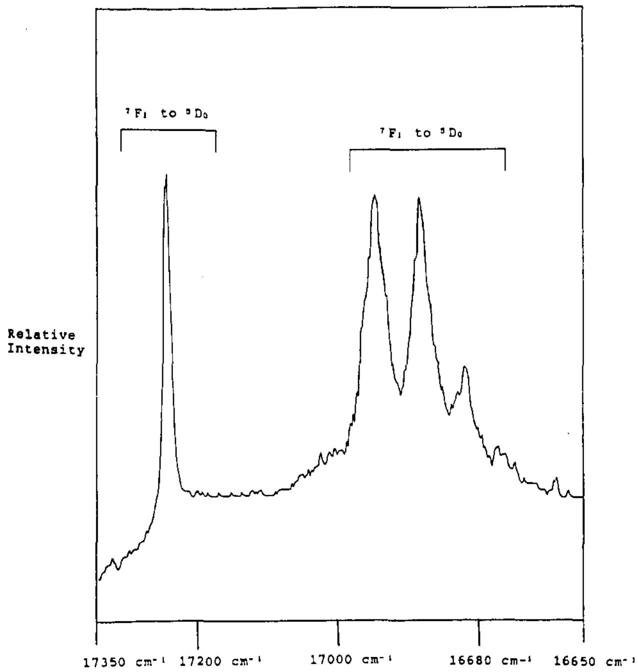

Figure 9. Excitation spectrum of Cs[Eu(Bzac)$_4$] as seen at the 612.3-μm peak of the $^5D_0$ to $^7F_2$ fluorescence transition, with the tunable dye laser as the excitation source. A monochromator slit of 150 μm was employed for the first manifold, and a slit of 200 μm for the second. There has been no correction made in the spectrum for shifts in the laser intensities.

splittings of the free ion energy levels, is the group-theoretical method described in detail by Wybourne.[9] As an example, the $^5D_0$ to $^7F_2$ fluorescence transition to the Eu^{3+} ion in a crystal symmetry of D_4 will be described. When a rare earth ion is placed in a crystal field, the free-ion levels will split into a number of sublevels that can be characterized by the irreducible representations of the appropriate point group. In D_4 symmetry, $J = 0$ yields an A_1 representation and $J = 2$ yields A_1, B_1, B_2, and E representations. A transition between a state of $J = 0$ and $J = 2$ is allowed by the electric dipole selection rule,[9] which possesses the same symmetry representations as translations along the three-dimensional coordinate axes, the A_2 and E representations. In order for the transition to occur, the multiplication of the ground state, the transition dipole, and the excited state must contain the completely symmetric representation, A_1. This results in one description for the $^5D_0$ to $^7F_2$ transition, A_1 to E. Slight distortions of this symmetry, due to steric effects from the bulky ring group of the ligand or crystal-packing considerations, may result in a very small splitting of degenerate transitions. Brecher et al. have compiled a table of the results of similar arguments for several point groups important in 8-fold coordination.[6]

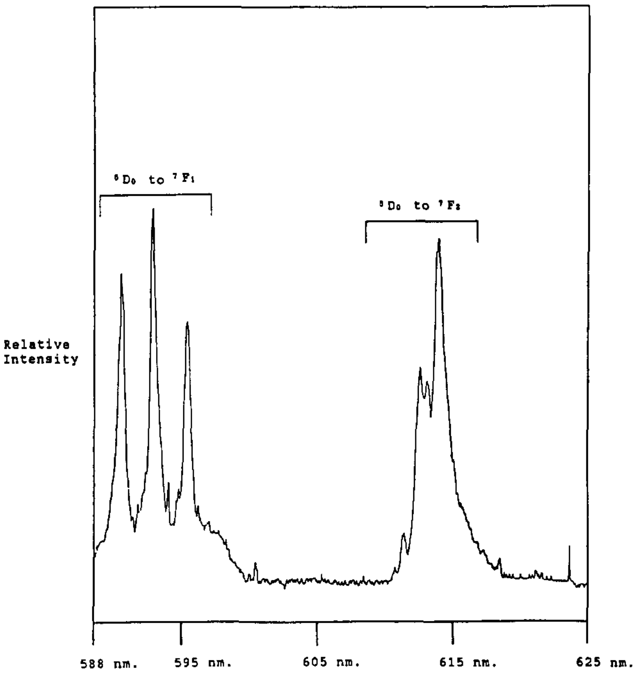

Figure 10. Fluorescence spectrum of Cs[Eu(Bzac)$_4$], with the Hg-arc lamp as the excitation source. The monochromator slits were set at 100 μm for the first manifold and 50 μm for the second.

The first compound to be considered is the sodium salt. Since the intensity of the feature in the 580-nm portion of the spectrum is very weak, it is considered to be a symmetry-forbidden transition, which would rule out C_n and C_{nv} point groups. The three features at ~590 nm have nearly the same intensity with the first two only narrowly split, indicating a doublet. In the region around 610 nm there exists one very strong transition, one very weak transition, and a weak doublet over 3 nm away. These features correspond with what would be expected from D_4 symmetry. In the case of the potassium compound, the feature at about 580 nm is of moderate intensity and hence is allowed. Again the 590-nm region shows a singlet and a doublet with similar intensities. The 610-nm region also shows the singlet–doublet pattern, with the doublet intensity roughly twice that of the singlet. Such an arrangement is consistent with either C_4 or C_{4v} symmetry. Assignment of the rubidium compound is slightly more difficult. The feature in the 580-nm region is weak and considered disallowed. There are only two well-resolved features in the 590-nm region with a diffuse feature at about 597 nm. The two features in the 610-nm region have intensity ratios of about 2:1. This situation corresponds best to D_{2d} symmetry. Finally, in the case of the cesium compound there is again a very weak feature in the 580-nm region. In both the 590- and the 610-nm regions there exist groups of three evenly spaced features of comparable intensity. This situation is indicative of D_2 symmetry. The result of these analyses is an apparent descent in symmetry with increasing size of the alkali metal cation.

Conclusions

It is readily apparent from the data displayed in the tables with the widths of the features exhibited by this set of rare-earth chelate compounds are extremely narrow. In fact, in the case of the sodium salt the width of the intense transition assigned to the $^5D_0$

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(9) Wybourne, B. G. *Spectroscopic Properties of the Rare Earths*; Interscience Publishers: New York, 1965; pp 163–219.

to $^7F_2$ manifold, 0.08 nm, is of the same order of magnitude as transitions often observed in transparent inorganic crystalline compounds.[1] This situation makes fluorescence spectroscopy an extremely useful tool for the elucidation of the structures and purities of appropriate rare-earth chelate compounds. Any irregularities in the synthesis method which may result in a crystallographically impure compound, undetectable by elemental analysis, are exposed by the appearance of the fluorescence spectrum in terms of broadened features and unrecognizable peaks.

The descent in symmetry with increasing size of the alkali metal counterion suggests that still larger cations should exhibit low symmetry. Previous investigations of this anion's solid compounds where large organic counterions have been employed have assigned point symmetries of C_{2v} or lower.[10] Also, when the assignment of point symmetry was performed on the piperidinium compound dissolved in a 3:1 mixture of ethanol and methanol, or a 4:1 mixture of the previous solvent and dimethylformamide, the resultant symmetry assignments were D_{2d} and C_{4v}, respectively.[6] All of the above observations seem to be consistent with the view of a highly symmetric anion being distorted to a varying extent due to the size of the counterion. A descent in symmetry with increasing cation size in the solid compounds could be expected as a result of the anion's response to crystal packing.

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(10) Nugent, L. J.; Bhaumik, M. L.; George, S.; Lee, S. M. *J. Chem. Phys.* **1964**, *41*, 1305.

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Synthesis and Reaction Chemistry of the Coordinatively Unsaturated Heterobimetallic Complexes (CO)$_3$(PPh$_3$)Fe(μ-PCy$_2$)Rh(PPh$_3$)(CO) and (CO)$_4$Fe(μ-PCy$_2$)Rh(1,5-COD). Crystal and Molecular Structure of (CO)$_3$(PPh$_3$)Fe(μ-PCy$_2$)Rh(PPh$_3$)(CO)

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Reactions of Li[Fe(CO)$_4$(PCy$_2$)] with *trans*-RhCl(CO)(PPh$_3$)$_2$ and [RhCl(1,5-COD)]$_2$ result in the formation of the μ-PCy$_2$ complexes (CO)$_3$(PPh$_3$)Fe(μ-PCy$_2$)Rh(PPh$_3$)(CO) (**2**) and (CO)$_4$Fe(μ-PCy$_2$)Rh(1,5-COD) (**3**), respectively. These complexes are identified by ^{31}P{^{1}H} NMR and infrared spectroscopy, and **2** has been further characterized by a single-crystal X-ray diffraction study. It crystallizes in the space group $P2_1/c$ with $a = 23.746$ (3) Å, $b = 10.414$ (2) Å, $c = 19.823$ (3) Å, $\beta = 100.91$ (1)°, $V = 4813$ (1) Å^3, and $Z = 4$. The structure was refined to final $R = 6.85\%$ and $R_w = 7.74\%$ for 5041 reflections with $F_o^2 > 3\sigma(F_o^2)$. The Fe atom has trigonal-bipyramidal geometry, coordinating to the bridging PCy$_2$ group, one PPh$_3$ ligand, and three CO groups. The Rh atom has a distorted-square-planar geometry coordinating to the bridging PCy$_2$ group, one molecule of PPh$_3$, one CO group, and the Fe atom. The Fe–Rh distance is 2.660 (1) Å, implying a metal–metal interaction, and one of the CO groups on the Fe atom is semibridging to the Rh atom. **2** reacts with CO to give the products (CO)$_3$(PPh$_3$)Fe(μ-PCy$_2$)Rh(PPh$_3$)(CO$_2$) (**4**) and (CO)$_4$Fe(μ-PCy$_2$)Rh(PPh$_3$)(CO)$_2$ (**5**) and with PEt$_3$ to yield (CO)$_4$Fe(μ-PCy$_2$)Rh(PPh$_3$)(CO) (**6**), (CO)$_4$Fe(μ-PCy$_2$)Rh(PEt$_3$)(CO) (**7**), (CO)$_4$Fe(μ-PCy$_2$)Rh(PPh$_3$)(PEt$_3$) (**8**), and (CO)$_3$(PPh$_3$)Fe(μ-PCy$_2$)Rh(PEt$_3$)(CO) (**9**). **3** easily loses 1,5-COD under an atmosphere of CO(g) to yield (CO)$_4$Fe(μ-PCy$_2$)Rh(CO)$_x$ (x = 1–3). These reaction products (**4**–**9**) were identified in solution only, by ^{31}P{^{1}H} NMR.

Introduction

The diorganophosphide group (PR$_2$) has shown great versatility as a bridging ligand, and it is particularly suited for the synthesis of heterobimetallic complexes.[1] Although numerous studies have produced a variety of interesting metal combinations,[2-12] there are only a limited number of heterobimetallic complexes that contain easily displaced ligands[13-16] or coordinatively unsaturated metal centers[2,15,16] of the type usually found in reactive mononuclear species.

Our approach has been to employ sterically demanding dicyclohexylphosphido groups in an attempt to create heterobimetallic complexes containing one or both metals with a low coordination number. This is analogous to the use of bulky trialkylphosphines to create sites of coordinative unsaturation in mononuclear complexes.[17] Initially, we focused on complexes employing two dicyclohexylphosphido bridging ligands in order to maximize the steric effects of these groups. The resulting complexes, which linked Mo and W to Ni, Pd, or Pt, exhibited steric crowding at the metal sites, but this did not translate into increased chemical reactivity.[10] In fact, our conclusion was that the bulky phosphide ligands simply acted to shield the metal centers, resulting in relatively unreactive complexes. In this paper, we have taken the approach that a single bridging unit should lessen this steric shielding and the presence of more exposed metal centers may lead to increased chemical reactivity. The complexes described in this paper contain an Fe center and a coordinatively unsaturated Rh center linked by a *single* dicyclohexylphosphido bridge. Some simple reaction chemistry is described as well as

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