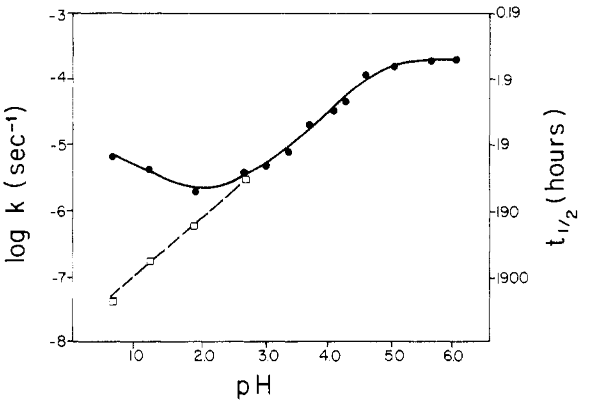


**Figure 7.** Rate of decomposition of $Ni^{III}L$ as a function of pH in a solution of 0.3 M phosphate at a pH controlled by NaOH, $H_3PO_4$, or $HClO_4$: (●) experimental points; (□) corrected values to a constant concentration of $H_2PO_4^- = 0.3$ M for solutions where the pH was controlled by the addition of $HClO_4$, with the assumption of $k_{obsd} \approx [H_2PO_4^-]^{-1.5}$ (see text).

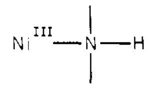
that the increase in concentration of $[Ni^{III}LOH]^{2+}$, $pK_4 = 3.7$, and/or $[Ni^{III}L(HPO_4)_2]^-$, $pK_5 = 3.8$, increases the rate of decomposition of $Ni^{III}L$. As $[Ni^{III}L(H_2PO_4)]^-$ is expected to have properties similar to those of $[Ni^{III}L(SO_4)_2]^-$, the major factor seems to be the increase in $[Ni^{III}LOH]^{2+}$. Above pH 4.2 the concentrations remain nearly constant as this is about 0.5 pH unit above $pK_4$ and $pK_5$ and far below the second $pK$ of phosphoric acid.

## Concluding Remarks

The results reported in this study indicate that simple anions stabilize $NiL^{3+}$ by axial coordination. The order of the stability constants for axial coordination found ($C_8H_4O_4^{2-} > SO_4^{2-} \geq HPO_4^{2-} > H_2PO_4^- > Cl^- >> ClO_4^-$) is in agreement with the basicity of these ligands.

The absorption spectra of all the complexes studied are similar with the exception of $Ni^{III}LOH^{2+}$, which has a relatively strong absorption band at 550 nm. The latter band was attributed to a distortion of the complex resulting in a pentacoordinated nickel.[7,9] (Further evidence for the pentacoordinated nature of $Ni^{III}LOH^{2+}$ is given in ref 29.) Thus we believe that all the complexes reported in this study are octahedrally coordinated, i.e., $Ni^{III}L(H_2O)_2^{3+}$, $Ni^{III}LX_2$, and $Ni^{III}LXH_2O$.

The results indicate that the mechanism of decomposition of $Ni^{III}LX_2$ is mainly via $NiL^{3+}$ and to some degree via $Ni^{III}LXH_2O$. For X = $Cl^-$ the latter route clearly contributes to the mechanism of decomposition. As the decomposition of the tervalent nickel complexes results in the oxidation of the ligand via introduction of imine groups it was suggested that the first step in the decomposition involves the proton in the


$Ni^{III}—N—H$

group.[7] Clearly the ligation of anions to the nickel decreases the inductive effect of the nickel on the N-H bond, thus decreasing the acidity of these protons. It is believed that this change in the acidity of the hydrogens bound to the nitrogens is of major importance in the stabilization of the tervalent nickel complex. It should however be noted that axial ligation of sulfate to $Ni^{III}$ cyclam has a considerably smaller stabilizing effect,[30] though the stability constant for ligation is similar to that observed here,[14] an observation indicating that other factors, probably steric ones, affect the rate of decomposition of tervalent nickel complexes with macrocyclic ligands. Studies to clarify this point are in progress.[29]

**Acknowledgment.** We are indebted to Ms. L. Carmel for technical assistance. A fellowship to E.Z. from the A. K. Casali Foundation is appreciated.

**Registry No.** $[NiL(H_2PO_4)_2]ClO_4$, 79329-56-9; $[NiL(SO_4)(H_2O)]ClO_4$, 79329-58-1; $NiL(H_2O)_2^{3+}$, 79329-59-2; $NiLCl_2^+$, 79329-60-5; $NiL(SO_4)_2^-$, 79329-61-6; $NiL(C_8H_4O_4)_2^-$, 79329-62-7; $NiL(ClO_4)_2$, 79389-94-9.

**Supplementary Material Available:** Listings of thermal parameters and observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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Contribution from the Chemistry Department,
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# Mixed-Ligand Complexes of Trivalent Lanthanide Ions with β-Diketones and Heterocyclic Amines

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*Received November 11, 1980*

The diaquo bipyridyl adducts of tris(heptafluorooctanedionato)lanthanide(III), $[Ln(fod)_3bpy\cdot 2H_2O]$, and $[M(fod)_3phen]$ where M = Y, La, or Lu have been synthesized and characterized. The Ln(III) in $[Ln(fod)_3bpy\cdot 2H_2O]$ are 10-coordinate and retain this higher coordination number even in solution for several days without any trace of dissociation. These seem to have achieved their coordinative saturation and therefore $[Pr(fod)_3bpy\cdot 2H_2O]$ does not act as a lanthanide-induced shift reagent. The values of interelectronic and spectral parameters $\beta$, $b^{1/2}$, and $\delta$ have been computed, and the higher values of $\delta$ for the Pr, Nd, and Er complexes indicate higher covalency. Some ligand field parameters ($b^{1/2}$ and $T_\lambda$) and oscillator strengths ($P$) have been calculated, and evidence has been presented to evince the partaking of f orbitals in bonding. The higher values of magnetic moments are also a manifestation of higher coordination number.

## Introduction

The paramagnetic tris lanthanide(III) chelates[1] of heptafluoro-7,7-dimethyl-4,6-octanedione (Hfod), $Ln(fod)_3$, have been increasingly used as NMR shift reagents. The chemical property that permits this application is the Lewis acidity that the chelate possesses as a consequence of its coordinative unsaturation. The neutral tris chelates dissolve in organic solvents and form labile adducts with a large variety of nucleophilic substrates. The Lewis acidity of these chelates also causes two side interactions, which may interfere with their usage as NMR shift reagents. Sources of interference are

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**Table I.** Characterizing Data for [$Ln(fod)_3bpy\cdot 2H_2O$] and [$Ln(fod)_3phen$] Complexes

| complexes | mp, °C | % metal[a] | % C[a] | % H[a] | % N[a] | $\mu_{eff}$, $\mu_B$ | Λ, $\Omega^{-1}$ $cm^2$ $mol^{-1}$ | color |
|---|---|---|---|---|---|---|---|---|
| $La(fod)_3bpy\cdot 2H_2O$ | 101 | 11.67<br>(11.43) | 40.04<br>(39.47) | 3.00<br>(3.29) | 2.23<br>(2.30) | diamag | 33.93 | white |
| $Pr(fod)_3bpy\cdot 2H_2O$ | 83 | 11.84<br>(11.58) | 39.27<br>(39.40) | 3.23<br>(3.28) | 2.19<br>(2.29) | 4.44 | | green |
| $Nd(fod)_3bpy\cdot 2H_2O$ | 80 | 11.62<br>(11.79) | 40.00<br>(39.31) | 3.63<br>(3.28) | 2.40<br>(2.29) | 4.67 | | violet |
| $Sm(fod)_3bpy\cdot 2H_2O$ | 76 | 12.63<br>(12.25) | 39.51<br>(39.12) | 3.12<br>(3.26) | 2.19<br>(2.28) | 3.10<br>(1.93)[b] | | white |
| $Eu(fod)_3bpy\cdot 2H_2O$ | 78 | 12.76<br>(12.37) | 40.57<br>(39.06) | 3.70<br>(3.25) | 2.30<br>(2.28) | 3.90<br>(4.20)[b] | 19.70 | white |
| $Gd(fod)_3bpy\cdot 2H_2O$ | 84 | 12.89<br>(12.72) | 39.60<br>(38.90) | 3.50<br>(3.24) | 2.03<br>(2.27) | 9.13 | 5.3 | white |
| $Tb(fod)_3bpy\cdot 2H_2O$ | 74 | 13.35<br>(12.86) | 40.10<br>(38.83) | 3.49<br>(3.24) | 2.43<br>(2.27) | 10.00<br>(9.88)[b] | 10.6 | dirty white |
| $Dy(fod)_3bpy\cdot 2H_2O$ | 85 | 13.46<br>(13.11) | 39.10<br>(38.73) | 3.42<br>(3.23) | 2.21<br>(2.26) | 13.31<br>(13.56)[b] | 9.50 | white |
| $Ho(fod)_3bpy\cdot 2H_2O$ | 88 | 13.86<br>(13.29) | 38.60<br>(38.65) | 3.24<br>(3.22) | 2.30<br>(2.25) | 11.23<br>(10.80)[b] | 10.70 | light yellow |
| $Er(fod)_3bpy\cdot 2H_2O$ | 95 | 13.03<br>(13.42) | 38.20<br>(38.59) | 3.30<br>(3.22) | 2.46<br>(2.25) | 10.36 | 9.50 | pink |
| $Tm(fod)_3bpy\cdot 2H_2O$ | 86 | 13.85<br>(13.56) | 39.52<br>(38.52) | 3.51<br>(3.21) | 2.40<br>(2.24) | 7.95 | | white |
| $Yb(fod)_3bpy\cdot 2H_2O$ | 93 | 14.19<br>(13.84) | 39.63<br>(38.48) | 3.03<br>(3.20) | 2.40<br>(2.24) | 4.79 | | white |
| $Lu(fod)_3bpy\cdot 2H_2O$ | 90 | 13.90<br>(13.98) | 39.37<br>(38.34) | 3.25<br>(3.19) | 2.23<br>(2.24) | diamag | 6.30 | white |
| $Y(fod)_3bpy\cdot 2H_2O$ | 83 | 7.68<br>(7.63) | 41.23<br>(41.17) | 3.38<br>(3.43) | 2.46<br>(2.40) | diamag | 5.0 | white |
| $Y(fod)_3phen$ | 105 | 8.36<br>(8.54) | 42.78<br>(43.67) | 3.31<br>(3.26) | 2.54<br>(2.43) | diamag | 4.70 | white |
| $La(fod)_3phen$ | 95 | 11.95<br>(11.54) | 42.34<br>(41.86) | 3.09<br>(3.16) | 2.35<br>(2.33) | diamag | 8.70 | white |
| $Lu(fod)_3phen$ | 115 | 14.06<br>(14.11) | 41.07<br>(40.65) | 3.26<br>(3.06) | 2.10<br>(2.26) | diamag | 5.00 | white |

[a] Calculated values are in parentheses. [b] Magnetic moments in parentheses are of complexes in the solid state and were found with the Faraday balance.

formation of hydrates[2,3] and formation of self-associated oligomers.[4-7] McConnell and Robertson[8] derived the relationship for the dipolar shift as

$$\Delta H/H = -K_p[f(\theta,r)][f(g_\parallel,g_\perp)]$$

where all the notations have their usual connotations. The dipolar shift depends upon the geometry and magnetic anisotropy of the complex. Thermogravimetric analysis is a useful tool in comparing the relative volatilities and thermal stabilities of the different metal 1,3-diketo–enol chelates. Some chelates of acetylacetone are unstable and not volatile, while those of hexafluoroacetylacetone sublime, albeit in some instances with considerable decomposition.[9]

The absorption spectra of several of the trivalent lanthanide chelates are good tools to check the hypersensitive bands that vary with environment about lanthanide ions. The intensity of the band in the spectra of lanthanide(III) has been studied both theoretically and experimentally. The theory proposed independently by Judd[10] and Ofelt[11] has been reasonably successful in accounting for the intensity of most of the transitions on the basis of the crystal field induced electric dipole transitions between individual Stark components. The intensity of the normally weak quadrupole transition increases as a result of inhomogeneous field.

Our interest in these newly synthesized adducts of $Ln(fod)_3$ with 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bpy) is to check their ability as potential shift reagents, to investigate the possibility of the involvement of f electrons in bonding to conclusively prove that these β-diketonates and their adducts do not dissociate in solution to release the heterocyclic amine or one end of the coordinated β-diketone. Hinckley[1] reported dissociation of $Ln(dpm)_3\cdot 2py$ to give $Ln(dpm)_3\cdot py$ + py and it was followed by later workers.

## Experimental Section

Rare earth oxides (Leico Chemicals USA) converted to chlorides, Hfod (Pierce Chemicals USA), bpy (BDH England), and phen (E. Merck) were used in this study.

**Synthesis.** The $Ln(fod)_3$ chelates were prepared by the method of Sievers et al.[2] with a slight modification. The adducts of all the lanthanide (except Ce and Pm) chelates with bpy were prepared by mixing $Ln(fod)_3$ and bpy in the molar ratio of 1:1 in absolute ethanol. The products thus formed were crystallized from hexane by keeping the solution in the refrigerator for 30 days. Good crystals were formed by repeated crystallization. These were dried in vacuo over phosphorus pentoxide. The adducts of $Ln(fod)_3$ (where Ln is Y, La, or Lu) with phen were prepared by mixing $Ln(fod)_3$ chelates and phen in the molar ratio of 1:1 in absolute ethanol. The pure product was obtained by repeated crystallization from ethanol.

**Methods.** A Beckman DU-2 spectrophotometer was used for obtaining optical spectra in hexane in the range of $10^{-2}$–$10^{-3}$ M at

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Table II. TGA Data for [Ln(fod)$_3$bpy·2H$_2$O] Complexes

| complexes | temp, °C | % wt loss for (H$_2$O)$_2$ theor | % wt loss for (H$_2$O)$_2$ exptl |
|---|---|---|---|
| Y(fod)$_3$bpy·2H$_2$O | 196 | 3.09 | 3.50 |
| Gd(fod)$_3$bpy·2H$_2$O | 160 | 2.90 | 2.58 |
| Ho(fod)$_3$bpy·2H$_2$O | 140 | 2.89 | 3.00 |
| Er(fod)$_3$bpy·2H$_2$O | 180 | 2.89 | 2.75 |
| Lu(fod)$_3$bpy·2H$_2$O | 190 | 2.87 | 3.00 |

room temperature. The magnetic susceptibility was measured in chloroform with use of Evans'[12] nuclear magnetic resonance method at the probe temperature. The magnetic susceptibility was also measured with use of a Faraday balance. The NMR spectra of the complexes were recorded on a Varian A-60 machine and the IR spectra on a Perkin-Elmer Model 137-B infrared spectrophotometer in Nujol mulls. The Gd(fod)$_3$bpy·2H$_2$O complex was subjected to mass spectral analysis at 225 °C in CHCl$_3$ on an HP 5985 GC/MS system at Louisiana State University.

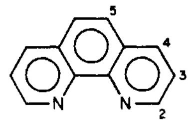
## Results and Discussion

The adducts on the basis of their elemental analyses for carbon, hydrogen, nitrogen, and metals and their molar conductances, IR, TGA, and mass spectra have been assigned the general formula [Ln(fod)$_3$bpy·2H$_2$O] and [Ln(fod)$_3$phen] (Table I). The adducts of bpy and phen are very well-defined crystalline solids. It is very interesting and striking that even in the presence of three bulky Hfod ligands the lanthanide ions show marvelous avidity for chelating bpy and two water molecules, increasing the coordination number of lanthanide ions from 6 to 10. The adducts are soluble in almost all common organic solvents and insoluble in water. The molar conductances of these adducts at $10^{-3}$ M concentration in methanol[13] showed their nonelectrolytic behavior. The phen adducts melt at higher[14] temperature than the bpy ones. Perhaps the rigidly planar phen ligand, which in its planarity is like the skeletal $\beta$-keto–enolate anion, permits a more stable crystal packing.

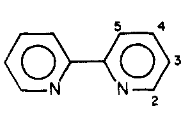
The thermogravimetric analyses of bpy adducts show that the two water molecules present are coordinated to metal ions. In Y, Gd, Ho, Er, and Lu complexes the weight loss is from 2.5 to 3.0% (theoretical weight loss is from 2.90 to 3.09%) in the temperature range of 140–196 °C. This strongly indicates that the water present is coordinated (Table II).

The IR spectra of the adducts show a change in the functional-group frequencies as compared to those of their respective chelates. These adducts show a strong band in the region 1560–1580 cm$^{-1}$ and a band between 1600 and 1630 cm$^{-1}$, which are assigned to C=O and C=C stretchings, respectively. The bands occurring in the region 370–400 cm$^{-1}$ are attributed to metal–oxygen frequencies. The metal–oxygen frequencies are lower than those reported in the literature.[15] This lowering in $\nu_{M-O}$ may be due to an increase in coordination number. The most diagnostic band suggested for cordinated water lies in the region 800–1000 cm$^{-1}$.[16] On this ground the bands appearing in the range of 932–924 cm$^{-1}$ in the adducts of bpy are an added proof that water is present in the inner coordination sphere, which raises the coordination number of Ln from 8 to 10 in bpy adducts. The band in phen at 415 cm$^{-1}$ has shifted to a higher frequency, i.e., 468 cm$^{-1}$, in the [La(fod)$_3$phen] spectrum. The IR shows that both the nitrogens are coordinated to lanthanide[17] ion.

Table III



A



B

| | compd | chemical shifts[a] H-2 | chemical shifts[a] H-4 | chemical shifts[a] H-5 | chemical shifts[a] H-3 |
|---|---|---|---|---|---|
| A | phen | 9.16 | 8.13 | 7.64 | 7.75 |
| B | bpy | 8.70 | 7.80 | 8.53 | 7.22 |
| 1 | La(fod)$_3$phen[b] | 9.60 | 8.29 | 7.73[e] | |
| 2 | Y(fod)$_3$phen[b] | 9.58 | 8.30 | 7.75[e] | |
| 3 | Lu(fod)$_3$phen[b] | 9.45 | 8.26 | 7.71[e] | |
| 4 | Pr(fod)$_3$phen[b,f] | *d* | 2.54 | 3.01 | −0.65[c] |
| 5 | Yb(fod)$_3$phen[b,f] | *d* | 8.95 | 14.50 | 13.60 |
| 6 | La(fod)$_3$bpy·2H$_2$O[b] | 8.81 | 7.96 | 8.10 | 7.33 |
| 7 | Y(fod)$_3$bpy·2H$_2$O[b] | 9.44 | 7.88 | 7.99 | 7.47 |
| 8 | Lu(fod)$_3$bpy·2H$_2$O[b] | 9.35 | 7.91 | 8.00 | 7.46 |
| 9 | Pr(fod)$_3$bpy·2H$_2$O[b] | | | | |
| 10 | Eu(fod)$_3$bpy·2H$_2$O[b] | | | | |

[a] In ppm downfield with respect to Me$_4$Si. [b] In CCl$_4$. [c] In ppm upfield with respect to Me$_4$Si. [d] Not observed. [e] Signals for H-3 and H-5 are in a quartet. [f] Syntheses of these compounds are reported in: M. Sayeed and N. Ahmad, *J. Inorg. Nucl. Chem.*, in press.

The mass spectra of Gd(fod)$_3$bpy·2H$_2$O recorded the four heaviest particles with masses 991.5 (0.7% of the most abundant particle, 57.2 amu, taken as 100), 992.6 (0.4%), 993.7 (0.4%), and 997.9 (0.4%). The calculated mass for Gd(fod)$_3$·2H$_2$O with use of the average atomic weight for Gd is 994.25. With the limitation of the machine to record only those particles that are capable of accepting a positive charge and having mass numbers 10–1000 amu, it was not possible to detect a particle representing H$_2$O or Gd(fod)$_3$bpy·2H$_2$O (mol wt = 1150.44). The percentage of the particle with amu 156.0 was 36.5, and the molecular weight for bpy is 156.18. Thus it is clear that the two water molecules are more tenaciously attached to Gd than the bpy itself and hence the two water molecules must be coordinated to Gd, confirming the coordination number as 10 for the trivalent lanthanides in the Ln(fod)$_3$bpy·2H$_2$O series.

NMR spectral data for several lanthanide adducts are summarized in Table III. NMR signals of (fod) moiety of adducts appear at 0.85–1.11 ppm for *tert*-butyl and at 5.6–5.82 ppm in the case of diamagnetic adducts for methine protons as a relatively sharp singlet. Other signals can be assigned to those of A or B coordinated to the complex.

The signals of coordinated A or B were found to shift remarkably to the lower fields as compared to free A or B. These protons, which are shifted to lower fields, are subjected to no perturbing influence other than deshielding expected from the electron-withdrawing inductive effect of coordination. H-2 atoms are reported to shift to high fields, in the case of transition metals, due to metal–nonbonded hydrogen interactions,[18] but in our case this interaction is not operative as the M–H distance is large. The H-5 atoms in **6**, **7**, and **8** (Table III) are shifted to high field. This can probably be related to the conversion of B from a preferred trans configuration when uncomplexed into a cis configuration when complexed, with attendant loss or reversal of the deshielding effect, specific to H-3, of the magnetic anisotropy of the heteroatom in the attached pyridine ring, the van der Waals repulsion of its lone pair, and the electronic dipole moment of the pyridine ring.[19] The *tert*-butyl and methine protons

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are shifted to high fields in the mixed-ligand adducts as compared to those of their respective chelates.[2] Perhaps it is after withdrawing electron density from A or B that the $Ln^{3+}$ ion becomes more polarized and transfers some charge via the $\pi$ system of the diketonate ring, and this can be very conveniently accommodated by fluorine (due to its high electronegativity).

The NMR spectra of **1** and **6** show no resonance for free A/B or free $\beta$-diketone; no change in signal line width or position is observed even on keeping this solution for 2 weeks. This clearly proves that both the ends of A as well as the diketone remain coordinated in solution and there is no dissociation even at one end of either of the two ligands. The spectra of paramagnetic praseodymium adducts of A or B showed broad proton signals, giving no high resolution signals due to A or B. This suggests that coordinated base does not dissociate from the praseodymium adduct in solution.

Information concerning electron delocalization in lanthanide complexes may be obtained from NMR studies of paramagnetic species, provided relaxation times are short enough to allow well-resolved spectra to be obtained. In the spectra of **4** and **5** the H-2 signal is not observed and the coupling interactions to this nucleus have disappeared, presumably due to paramagnetically enhanced relaxation of this nucleus. The paramagnetic adducts show a greater shift as compared to its diamagnetic analogue since the "g" tensor is anisotropic (i.e., $g_{\parallel} \neq g_{\perp}$) and pseudocontact interaction is dominant. If "g" is isotropic, this interaction goes to zero. The H-3 and H-5 signals, not resolved in diamagnetic adducts, separate in its paramagnetic analogue. The shifts in praseodymium are toward high fields as compared to those in ytterbium.

In phen adducts of $Tb(fod)_3$, $Dy(fod)_3$, and $Ho(fod)_3$ no resonance is observed due to either phen or diketonate because of the high magnetic anisotropy of the central metal ion and the inadequacy of the range of the NMR apparatus.

One of the intents of this study was to examine **4** or **9** and the Eu analogue of **9** as potential shift reagents. [$Pr(fod)_3$phen] contains coordinated phen leading to a weak complexation with added substrate and a very small shift. In the $^1H$ NMR spectrum of 1-butanol two $CH_2$ groups appear as a single resonance. We found that [$Pr(fod)_3$phen] added to a $CCl_4$ solution of 1-butanol did not change the spectrum and very small shifts, which decrease rapidly with increasing distance of the proton from the hydroxyl group and $CH_2$ groups, remained as such. The small values of shifts show that it is unsuitable for general use as a shift reagent.

The addition of a small amount of ethanol to solutions of **9** or **10** in $CCl_4$, however, resulted in no change in resonances (even of the hydroxyl proton) of alcohol. The experiment was repeated using **10**, and it was found that no change occurs in the spectrum of butanol and in addition the signals of butanol resonate as broad singlets and coupling disappears. This is due to the bulky nature of the substrate (butanol). The same experiment was repeated using [$Pr(fod)_3bpy \cdot 2H_2O$], which resulted in a slight upfield shift of the entire butanol spectrum (due to a change in the bulk magnetic susceptibility of the solution) but essentially no alteration in the relative shifts. It is thus apparent from the above discussion that the entropic gain from the bidentate coordination to nitrogen atoms outweighs the higher intrinsic affinity of Ln for single oxygen atoms and that these adducts of bpy are totally inefficient as shift reagents.

Table IV. Covalency Parameters

| complexes | $b^{1/2}$ | $\delta$ | $\bar{\beta}$ |
|---|---|---|---|
| $Pr(fod)_3bpy \cdot 2H_2O$ | 0.0406 | 0.3312 | 0.9967 |
| $Nd(fod)_3bpy \cdot 2H_2O$ | 0.0771 | 1.2043 | 0.9881 |
| $Er(fod)_3bpy \cdot 2H_2O$ | 0.0652 | 0.8573 | 0.9915 |
| $Pr(fod)_3phen$ | 0.0442 | 0.3915 | 0.9961 |
| $Nd(fod)_3phen$ | 0.0692 | 0.9693 | 0.9904 |
| $Er(fod)_3phen$ | 0.0707 | 1.0101 | 0.9900 |

All the adducts exhibit a very strong spectral absorption at $34.48 \times 10^3$ cm$^{-1}$ with a shoulder at $43.48 \times 10^3$ cm$^{-1}$. These bands are attributed to intraligand, $\pi \rightarrow \pi^*$ transitions, and a band at $29.85 \times 10^3$ cm$^{-1}$ is attributed to a charge-transfer ($n \rightarrow \pi^*$) transition.[20] A general feature in the spectra of lanthanide ions is a shift of absorption bands toward lower energy on complex formation, i.e., the nephelauxetic effect, "$\bar{\beta}$". This is due to lowering of interelectronic parameters in the complex.[21] If the f orbitals are involved in covalent bond formation with the ligand, the metal wave function can be expressed[22] as

$$\langle \phi_{4f}| = (1 - b)^{1/2}\langle 4f| - b^{1/2}\langle \phi_{\text{ligand}}| \qquad (1)$$

$b^{1/2}$ measures[23] the amount of 4f orbital mixing, i.e., covalency. Sinha[24] has proposed a $\delta$ scale to express the covalency. Both the parameters $b^{1/2}$ and $\delta$ are related to the nephelauxetic effect, i.e., $\bar{\beta}$. We calculated the values of $\bar{\beta}$, $b^{1/2}$, and $\delta$ for the complexes of Pr, Nd, and Er (Table IV) as

$$\bar{\beta} = \frac{1}{n}\sum_{n=1}^{n}\frac{\nu_{\text{complex}}}{\nu_{\text{aquo}}} \qquad b^{1/2} = [\tfrac{1}{2}(1 - \bar{\beta})]^{1/2}$$

$$\%\ \delta = \frac{1 - \bar{\beta}}{\bar{\beta}} \times 100$$

The broadening in the spectral bands in the adducts of Pr, Nd and Er, as these are highly affected by the surroundings, and the higher values of $\delta$ and $b^{1/2}$ indicate greater covalency than that reported earlier.[25]

The f–f transitions[26] are weakly allowed due to some mixing of the excited state of the opposite parity into the ground state (configuration interaction). This small mixing may be increased on complexation, if the energy of the excited state is lowered. Additional intensity may be gained by the mixing of ligand and metal wave functions due to orbital overlap, so the intensity of the hypersensitive transitions is significantly large. A covalent bond increases the mixing of states of opposite parity required to relax the selection rule for f–f transition, thus increasing their intensity. The intensity of hypersensitive transition changes very much on complex formation whereas that of nonhypersensitive does not, in these complexes. The higher values for hypersensitive transitions are due to eigen perturbation.[27]

The oscillator strength can be computed from an expression[10,11] derived from a theory in which the ligand field interaction with the central ion causes a mixing of higher configuration of opposite parity into the $4f^n$ configuration giving rise to induced electric dipole transitions:

$$P = \sum_{\lambda=2,4,6} T_\lambda \nu (f^N\Psi_J \| U^\lambda \| f^{N'}\Psi'_{J'})^2 (2J + 1)^{-1} \qquad (2)$$

where $\nu$ is the energy of transition, $\Psi_J \rightarrow \Psi'_{J'}$, $U^\lambda$ is a tensor operator of rank $\lambda$, and $T_\lambda$ are ligand field parameters. By

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Table V. Oscillator Strength

| complexes | $S'L'J'$ | $10^6 P_{\mathrm{exptl}}$ | $10^6 P_{\mathrm{calcd}}$ |
|---|---|---|---|
| $Pr(fod)_3bpy \cdot 2H_2O$ | $^3P_2$ | 11.8675 | 11.8675 |
| | $^3P_1$ | 7.0740 | 7.0794 |
| | $^1D_2$ | 3.7805 | 3.7805 |
| $Pr(fod)_3phen$ | $^3P_2$ | 8.0898 | 8.0897 |
| | $^3P_1$ | 6.3891 | 6.3890 |
| | $^1D_2$ | 4.5384 | 4.5384 |
| $Nd(fod)_3bpy \cdot 2H_2O$ | $^4G_{9/2}$ | 13.2364 | 13.3424 |
| | $^4G_{5/2}$ | 59.8545 | 61.2606 |
| | $^4G_{11/2}$ | 9.1650 | 9.1924 |
| $Nd(fod)_3phen$ | $^2D_{3/2}$ | 2.4024 | 2.4024 |
| | $^4G_{9/2}$ | 11.4478 | 11.4478 |
| | $^2G_{7/2}$ | 54.0085 | 54.0097 |
| $Er(fod)_3bpy \cdot 2H_2O$ | $^4F_{7/2}$ | 3.9745 | 4.0468 |
| | $^4F_{9/2}$ | 3.5250 | 3.5598 |
| | $^2H_{11/2}$ | 55.7494 | 57.5259 |
| $Er(fod)_3phen$ | $^4F_{3/2}$ | 1.1280 | 1.1279 |
| | $^4F_{7/2}$ | 2.5820 | 2.5820 |
| | $^2H_{11/2}$ | 22.8737 | 22.8729 |

Table VI. $T_\lambda$ Parameters for $[Ln(fod)_3phen]$ and $[Ln(fod)_3bpy \cdot 2H_2O]$ Complexes

| | $T_2$ | $T_4$ | $T_6$ |
|---|---|---|---|
| $Pr(fod)_3bpy \cdot 2H_2O$ | $35.8479 \times 10^{-9}$ | $5.8476 \times 10^{-9}$ | $17.9249 \times 10^{-9}$ |
| $Pr(fod)_3phen$ | $247.2788 \times 10^{-9}$ | $5.3053 \times 10^{-9}$ | $11.8666 \times 10^{-9}$ |
| $Nd(fod)_3bpy \cdot 2H_2O$ | $18.8317 \times 10^{-7}$ | $-8.1870 \times 10^{-7}$ | $11.8357 \times 10^{-7}$ |
| $Nd(fod)_3phen$ | $234.7719 \times 10^{-9}$ | $23.1079 \times 10^{-9}$ | $86.1192 \times 10^{-9}$ |
| $Er(fod)_3bpy \cdot 2H_2O$ | $47.80 \times 10^{-9}$ | $2.43 \times 10^{-9}$ | $1.9617 \times 10^{-9}$ |
| $Er(fod)_3phen$ | $19.9300 \times 10^{-9}$ | $0.151\,80 \times 10^{-9}$ | $1.5962 \times 10^{-9}$ |

the substitution of experimental[28] oscillator strengths, $P_{\mathrm{exptl}}$, and $U^\lambda$ values in eq 2 and with the use of the IBM-1130, a set of three parameters are obtained. These $T_\lambda$ values have been collected in Table VI. The values of oscillator strength, $P_{\mathrm{calcd}}$, calculated from these $T_\lambda$ values are also collected in Table V.

In the tris($\beta$-diketo-enolate) complex of $Pr^{3+}$ four transitions ($^3H_4 \rightarrow {}^1D_2$, $^3H_4 \rightarrow {}^3P_0$, $^3H_4 \rightarrow {}^3P_1$, and $^3H_4 \rightarrow {}^3P_2$) have been reported,[22] but in our adducts only three transitions ($^3H_4 \rightarrow {}^1D_2$, $^3H_4 \rightarrow {}^3P_1$, and $^3H_4 \rightarrow {}^3P_2$) are observed. This may be attributed to higher coordination numbers, i.e., 8 and 10. A good correlation between $P_{\mathrm{exptl}}$ and $P_{\mathrm{calcd}}$ for $Pr^{3+}$ adducts does not strengthen the conclusion of earlier workers[29,30] that the intensity theory of Judd[10] and Ofelt[11] is not applicable to $Pr^{3+}$ complexes. In $Nd^{3+}$ and $Er^{3+}$ adducts also only three transitions are observed, presumably due to the same effect (i.e., the bulky nature of $\beta$-diketones and heterocyclic amines and the increase in coordination number). A remarkable change in $P$ values is seen in the case of the hypersensitive transition for $Nd^{3+}$ ($^4I_{9/2} \rightarrow {}^2G_{7/2}, {}^4G_{5/2}$) and also for $Er^{3+}$ ($^4I_{15/2} \rightarrow {}^2H_{11/2}$). The lower value of $P$ ($^4I_{15/2} \rightarrow {}^2H_{11/2}$) in $[Er(fod)_3phen]$ is due to splitting of the one hypersensitive band into three. The higher values of $b^{1/2}$, $\delta$, $P$, and $T_\lambda$ parameters show that the $Ln^{3+}$ ions in solution are 8- and 10-coordinate in the case of phen and bpy adducts, respectively. Generally the $b^{1/2}$ value in phen adducts increases from $Pr^{3+}$ to $Er^{3+}$, which indicates that the covalency, i.e., the participation of 4f orbitals, increases as the atomic number increases, which cannot be easily explained.

Among the complexes studied, the variation in $P$ and $T_\lambda$ parameters[31,32] with their sensitivities to their environment and $T_\lambda$ being in order $T_2 > T_4 > T_6$ is reported.[33] This order is not strictly followed in our case as all these $T_\lambda$ parameters are highly sensitive to their environment and there is no remarkable trend.

The magnetic moments, $\mu_{\mathrm{eff}}$, of the bpy adducts are higher than those reported[14] for other complexes. This also indicates that 4f orbitals are playing a significant role in bonding. Unfortunately the band calculations are not yet able to describe the $4f^n$ states and their hybridization.[34] Qualitatively speaking, the hybridization should become important because of the closeness of d and f states in energy. The hybridization should become stronger for the light rare earths because of the large spatial extension[35] of the $4f^n$ shell, a fact that is manifested by the strong K–f scattering.

Square-prismatic coordination may be assigned to the 8-coordinate phen adducts of lanthanide chelates where the stereochemistry may be indicative of bonding using f orbitals.[36] For the case of cubical coordination, the $A_{2u}$ irreducible representation of the M–L $\sigma$ bond is spanned by the metal $f_{xyz}$ orbital but not by metal s, p, or d orbitals. So in the covalent description of the present adducts the ligand may be bonded to the metal by means of hybrid metal orbitals between $fd^3sp^3$ and $f^4d^3s$, both of which provide eight equivalent orbitals directed to the cube vertices.

**Acknowledgment.** K.I. and M.S. thank the CSIR and UGC, New Delhi, India, respectively, for the award of research fellowships to them.

**Registry No.** **1**, 79483-65-1; **2**, 79483-66-2; **3**, 79483-67-3; **4**, 79466-56-1; **5**, 79466-57-2; **6**, 79499-28-8; **7**, 79466-58-3; **8**, 79466-59-4; **9**, 79482-60-3; **10**, 79466-60-7; $Nd(fod)_3bpy \cdot 2H_2O$, 79466-61-8; $Sm(fod)_3bpy \cdot 2H_2O$, 79466-62-9; $Gd(fod)_3bpy \cdot 2H_2O$, 79466-63-0; $Tb(fod)_3bpy \cdot 2H_2O$, 79482-61-4; $Dy(fod)_3bpy \cdot 2H_2O$, 79482-62-5; $Ho(fod)_3bpy \cdot 2H_2O$, 79182-63-6; $Er(fod)_3bpy \cdot 2H_2O$, 79482-64-7; $Tm(fod)_3bpy \cdot 2H_2O$, 79482-65-8; $Yb(fod)_3bpy \cdot 2H_2O$, 79466-64-1; $Nd(fod)_3phen$, 79482-66-9; $Er(fod)_3phen$, 79482-67-0; phen, 66-71-7; bpy, 366-18-7.

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