Inorg. Chem. **1980**, *19*, 640-643

Contribution from the Department of Chemistry,
Seton Hall University, South Orange, New Jersey 07079

Solution Chemistry of Lanthanide Complexes. 2. Emission Titration Studies of the Adduct Formation between Europium(III) β-Diketonate Complexes and Phosphate Esters

HARRY G. BRITTAIN

Received September 14, 1979

A series of luminescence titrations have been used to study the adduct formation between six europium(III) β-diketonate complexes and four phosphate esters. The formation constants of the adducts were calculated from the enhancement of the $^5D_0 \rightarrow {}^7F_2$ Eu(III) transition wherever such an enhancement was observed; a lack of intensity enhancement was taken to imply the adduct between chelate and substrate did not form. The extent of adduct formation was found to depend primarily on the Lewis acidity of the lanthanide chelate, and the strongest adducts were observed with the most highly fluorinated β-diketone systems. Steric effects in both the chelates and substrates were found to play only a secondary role and appeared to be of minor importance for β-diketone complexes containing only simple alkyl substituents on the chelate ring. Substantial steric effects were observed for lanthanide chelates prepared from β-diketone derivatives of *d*-camphor, and the formation constants of these adducts appeared to be influenced by the size of the substrates.

Introduction

The usefulness of β-diketone complexes with lanthanide ions as shift reagents in NMR spectroscopy has been amply demonstrated,[1-4] and the use of these complexes in the simplification of overlapping resonances cannot be overstated. It has been recognized in the past that the usefulness of these shift reagents is related to the ease with which adducts are formed between the lanthanide chelate and the substrate. The theoretical analysis of the induced shifts has been limited somewhat by a lack of precise knowledge regarding the stoichiometry and geometry of the complexes in fluid solution. Information from solid-state crystal structures is not always useful and indeed may even be misleading (in the solid state the Pr(III) complex of 2,2,6,6-tetramethylheptane-3,5-dione exists as a dimer,[5] while all lanthanide chelates of this ligand are known to be monomeric in solution[6]).

We have taken advantage of the fact that most Eu(III) complexes of β-diketones display sharp-line luminescence when excited by UV light to study the nature of the chelate–substrate adducts. It is well-known that the intensity of the emitted light is strongly dependent both on the geometry of the complex[7] and on the possible presence of adducts.[8] High-resolution spectra of the adducts at low temperature has also proved useful in the determination of chelate geometries.[9] In this laboratory, we have observed that when Eu(III) chelates are dissolved in noncoordinating CCl_4, the emission tends to be quite weak, but that addition of a substrate which is capable of forming an adduct with the chelate typically results in a marked intensification of the luminescence. By carrying out these luminescence titrations, it has been possible to determine the formation constants of a wide variety of lanthanide chelate–substrate adducts.[10-12]

In the present work, further emission titration studies are reported involving adduct formation between six lanthanide β-diketonate complexes and four phosphate esters. Tri-*n*-butyl phosphate has been used extensively as an extractant for lanthanide ions[13-15] and has also been used in the synergic extraction of lanthanide ions with thenoyltrifluoroacetone.[16] In this last study, the formation of complexes having two molecules of phosphate ester per molecule of chelate was noted, and a formation constant was calculated from the extraction data. These extraction results parallel the trends observed for lanthanide complexes in that a discontinuity in extraction coefficients was noted at Gd(III), a pattern that is frequently noted in the formation constants of lanthanide ions with a particular ligand.[17]

We report results for the trimethyl phosphate (TMP), triethyl phosphate (TEP), tributyl phosphate (TBP), and triphenyl phosphate (TPP) adducts of Eu(fod)$_3$ (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione), Eu(dpm)$_3$ (dpm = 2,2,6,6-tetramethylheptane-3,5-dione), Eu(facam)$_3$ (facam = (trifluoroacetyl)-*d*-camphor), and Eu(hfpc)$_3$ (hfpc = ((3-heptafluoropropyl)hydroxymethylene)-*d*-camphor). Emission titrations were also attempted for Eu(bzac)$_3$ (bzac = 1-phenylbutane-1,3-dione) and Eu(dbm)$_3$ (dbm = 1,3-diphenylpropane-1,3-dione), but no emission enhancements were noted with any of the phosphate esters. Structures of the Eu(III) chelates are shown in Figure 1. In addition to the titrations, the stoichiometries of the adducts were determined by using Job's method of continuous variations. With the adduct stoichiometry known, it was possible to calculate formation constants for the lanthanide chelate–substrate adducts.

Experimental Section

Eu(fod)$_3$, Eu(dpm)$_3$, Eu(facam)$_3$, and Eu(hfpc)$_3$ were all purchased from Aldrich and dried for a prolonged period over P_4O_{10} in a vacuum desiccator. Eu(bzac)$_3$[18] and Eu(dbm)$_3$[19] were prepared and purified

---

(1) R. E. Sievers, Ed., "Nuclear Magnetic Resonance Shift Reagents", Academic Press, New York, 1973.

(2) A. F. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, **73**, 553 (1973).

(3) J. Reuben, *Prog. Nucl. Reson. Spectrosc.*, **9**, 1 (1973).

(4) B. C. Mayo, *Chem. Soc. Rev.*, **2**, 49 (1973).

(5) C. S. Erasmus and J. C. A. Boeyens, *Acta Crystallogr., Sect. B*, **26**, 1843 (1970).

(6) Chapter 14 in ref 1.

(7) H. Samelson, C. Brecher, and A. Lempicki, *J. Mol. Spectrosc.*, **19**, 349 (1966).

(8) F. Halverson, J. S. Brinen, and J. R. Leto, *J. Chem. Phys.*, **41**, 157 (1964).

(9) G. A. Catton, F. A. Hart, and G. P. Moss, *J. Chem. Soc., Dalton Trans.*, 221 (1976).

(10) H. G. Brittain and F. S. Richardson, *J. Chem. Soc., Dalton, Trans.*, 2253 (1976).

(11) H. G. Brittain, *J. Am. Chem. Soc.*, **101**, 1733 (1979).

(12) H. G. Brittain, *J. Chem. Soc., Dalton, Trans.*, 1187 (1979).

(13) D. Scargill, K. Alcock, J. M. Fletcher, E. Hesford, and H. A. C. McKay, *J. Inorg. Nucl. Chem.*, **4**, 304 (1957).

(14) D. F. Peppard, W. J. Driscoll, R. J. Sironene, and S. McCarthy, *J. Inorg. Nucl. Chem.*, **4**, 326 (1957).

(15) E. Hesford, E. E. Jackson, and H. A. C. McKay, *J. Inorg. Nucl. Chem.*, **9**, 279 (1959).

(16) H. Irving and D. N. Edgington, *J. Inorg. Nucl. Chem.*, **21**, 169 (1961).

(17) T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel, and W. J. Randall, *Chem. Rev.*, **65**, 1 (1965).

(18) R. G. Charles, *Inorg. Synth.*, **9**, 37 (1967).

0020-1669/80/1319-0640$01.00/0

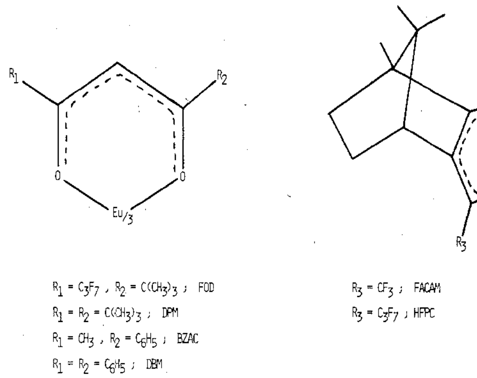

Figure 1. Structures of the Eu(III) β-diketone chelates used in this study.

by literature methods and were also dried in the desiccator. Spectroquality CCl_4 was used as the solvent in all titrations and was dried over molecular sieves before use. TMP, TEP, TBP, and TPP were also obtained from Aldrich and were used as received. Failure to observe rigorous exclusion of water from solutions containing fluorinated chelates resulted in rather irreproducible results, but water proved less of a problem for nonfluorinated chelates.

To carry out the luminescence titrations, we pipetted 3.0 mL of a 2.0×10^{-3} M solution of one of the lanthanide chelates into a fluorescence cuvette and recorded its emission intensity. Microliter quantities of phosphate esters were then added directly to the cuvette from stock solutions whose concentration was 0.100 M. The luminescence of the $^5D_0 \rightarrow$ Eu(III) transition (615 nm) was followed as substrate was added, and the intensity was taken as the integrated area under the luminescence peak. Reproducibility in intensity measurements was monitored by periodically recording the emission intensity of a 5×10^{-4} M solution of $Ru(bpy)_3^{2+}$ in 1 M H_2SO_4 and then correcting for fluctuations in instrument response when necessary.

All emission measurements were made on a high-resolution luminescence spectrometer recently constructed in this laboratory. Samples were excited by the 365 nm output of a 200-W Hg–Xe arc lamp, whose output was selected by a combination of UV transmitting "black" glass filters and a grating monochromator (Model H-10UV-V, Instruments SA). The excitation energy was mechanically chopped at 808 Hz (Princeton Applied Research Model 125A light chopper) to allow phase-sensitive detection of the luminescence. The light emitted by the sample was collected at either 90 or 180 °C to the exciting beam, but it appeared that "head-on" collection gave the most reproducible results. The emitted light was passed through a saturated solution of K_2CrO_4 to remove any transmitted excitation light and then analyzed by a 0.5-m Czerny-Turner grating monochromator (Model 1870, Spex Industries). The light was finally detected by an EMI 9798B photomultiplier tube (S-20 response), whose output current was converted to a voltage signal by a Model 181 current-sensitive preamplifier (Princeton Applied Research). Since the emitted light was found at the same frequency as the chopped excitation beam, processing of the output was possible with a PAR Model 5101 lock-in amplifier before displaying the result on a potentiometric recorder (Houston Instruments). The use of phase-sensitive detection resulted in much more favorable signal-to-noise ratios and also made it possible to observe the very weak luminescence of several of the Eu(III) chelates.

Results

Addition of one of the phosphate esters dissolved in CCl_4 to a CCl_4 solution containing one of the Eu(III) β-diketonate complexes usually resulted in a marked increase in Eu(III) luminescence intensity, but this was not always the case. When an increase in intensity was noted, the shape of the titration curve displayed little detail and simply rose until the intensity reached a limiting value, as may be seen in the typical example shown in Figure 2. This limiting intensity was found to depend on the nature of the β-diketone ligand in the lanthanide complex and on the particular substrate used in the titration.

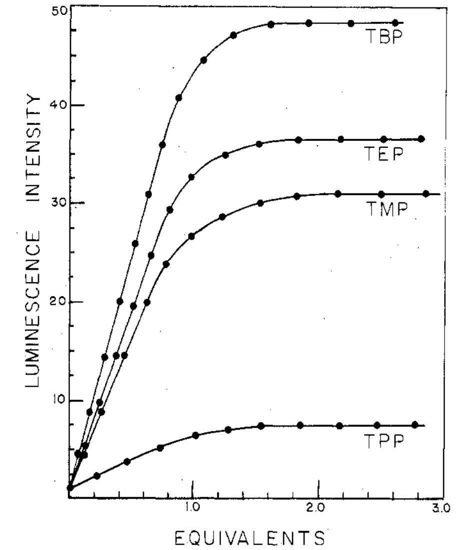

Figure 2. Luminescence titrations of $Eu(hfpc)_3$ with the four phosphate esters. The intensity scale is arbitrary, with the emission intensity of $Eu(hfpc)_3$ in CCl_4 being set equal to 1.0.

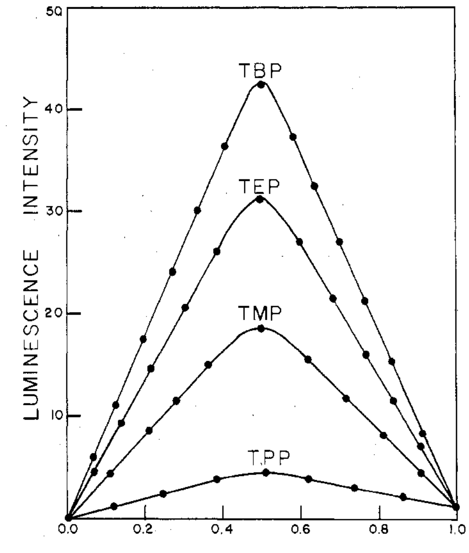

Figure 3. Job's plots illustrating the formation of 1:1 complexes between $Eu(hfpc)_3$ and all four phosphate esters. The intensity scale is the same as Figure 2.

Table I. Limiting Intensities Reached in the Titration of Eu(III) Chelates with Substrates[a]

	intensity			
substrate	Eu-(fod)$_3$	Eu-(dpm)$_3$	Eu-(facam)$_3$	Eu-(hfpc)$_3$
none	1340	95.8	3.76	1.00[a]
TMP	5548	129.6	16.74	30.91
TEP	6486	123.2	25.92	36.45
TBP	6960	120.5	20.47	48.35
TPP	4125	95.8	3.76	7.41

[a] All intensities are relative to the intensity of $Eu(hfpc)_3$ in CCl_4.

A summary of the limiting intensities reached in TMP, TEP, TBP, and TPP titrations with $Eu(fod)_3$, $Eu(facam)_3$, and $Eu(hfpc)_3$ is shown in Table I, and intensities without substrate present are also found in the table. Data for $Eu(bzac)_3$ and $Eu(dbm)_3$ are not shown since no intensity enhancements were found when any of the phosphate esters were added. The initial intensity of $Eu(bzac)_3$ in CCl_4 was found to be 48.9,

---

(19) R. E. Whan and G. A. Crosby, *J. Mol. Spectrosc.*, **8**, 315 (1962).

Table II. Formation Constants of the $Eu(\beta\text{-diketone})_3$–Substrate Adducts[a]

	formation constant			
substrate	log K $Eu(fod)_3$	log K $Eu(dpm)_3$	log K $Eu(facam)_3$	log K $Eu(hfpc)_3$
TMP	3.302	1.407	1.861	2.881
TEP	3.467	1.660	2.130	3.246
TBP	3.432	1.762	2.270	3.212
TPP	2.940	*b*	*b*	2.720

[a] All formation constants are associated with an estimated error of ±0.005 log units. [b] Could not be determined due to a lack of luminescence enhancement.

and the initial intensity observed for $Eu(dbm)_3$ was 7.30.

Job's method of continuous variations has proved useful in the past and has made it possible to determine stoichiometries of the lanthanide chelate–substrate adducts.[11,12,20] A typical example of the sort of plot that one obtains in the present study is found in Figure 3; the skewed nature of the graph is due to the fact that when the mole fraction of lanthanide chelate equals 1.0, luminescence is still observed, but no emission is seen when the mole fraction of the chelate is 0.0. Studies of this type were carried out in all cases where emission enhancements were observed, and it was determined that 1:1 lanthanide chelate/substrate adducts were formed with all chelates and with all esters used in this work.

The verification of 1:1 chelate/substrate stoichiometry according to the reaction

$$\mathrm{Ln} + \mathrm{S} \rightleftarrows \mathrm{LnS} \qquad (1)$$

(where Ln = lanthanide chelate, S = substrate, and LnS = chelate adduct) makes it possible to calculate the formation constant of the adduct:

$$K = [\mathrm{LnS}]/[\mathrm{Ln}][\mathrm{S}] \qquad (2)$$

The intensity of Eu(III) emission before addition of substrate may be related to the concentration of Eu(III) chelate by

$$I_0 = a_1[\mathrm{Ln}] \qquad (3)$$

and the intensity of Eu(III) emission after the adduct is fully formed (which corresponds to the final limiting intensity) may be expressed as

$$I_f = a_2[\mathrm{Ln}] = a_2[\mathrm{LnS}] \qquad (4)$$

In eq 3 and 4, a_1 and a_2 are merely constants of proportionality. The intensity of Eu(III) emission when both free Ln and LnS adduct are both present in solution is then given by

$$I_i = X_{\mathrm{Ln}}(a_1[\mathrm{Ln}]) + X_{\mathrm{LnS}}(a_2[\mathrm{Ln}]) \qquad (5)$$

where X_{Ln} is the mole fraction of free lanthanide ion and X_{LnS} is the mole fraction of chelate adduct. It is quite easy to show that

$$X_{\mathrm{Ln}} = (I_i - I_f)/(I_0 - I_f) \qquad (6)$$

Knowledge of the concentration of all starting materials and application of eq 6 enable the calculation of the equilibrium concentrations of Ln, S, and LnS. This enables the calculation of formation constants for the adducts, and these are collected in Table II. The lack of intensity enhancements for $Eu(bzac)_3$ and $Eu(dbm)_3$ made it impossible to compute formation constants for possible adducts formed with these chelates.

Discussion

Various explanations may be advanced to explain the enhanced luminescence intensity as substrate was added, but most of these may be easily disposed of. It is possible that the lanthanide complex absorption at the exciting line (365 nm) increases as the adduct forms and thus yields enhanced emission, but repeated attempts to find such an absorption increase at 365 nm failed. Energy transfer from the substrate to the lanthanide ion was considered, but all the substrates used in this study absorb at much higher energies than was used in this work. It is possible that the geometry of the lanthanide adduct is more conducive toward luminescence, but this possibility was not considered due to repeated observations in previous work[10–12] that small changes in the geometry of a particular lanthanide complex only influence the luminescence intensity to a minor extent. It is known, however, that the predominate mode of luminescence quenching is via the solvent and that protection of the metal ion from the solvent results in greatly enhanced quantum yields.[8] We therefore contend that the enhanced luminescence observed when the lanthanide chelate–adduct is formed is primarily due to protection of the central metal ion from the solvent. This conclusion requires that the substrate binds directly to the metal (and does not form an outer-sphere type of adduct) and that the rise in luminescent intensity may be directly related to the ease with which the adduct is formed and therefore enables the calculation of formation constants from the emission titration data.

Several interesting trends emerge from the results presented in the preceding section. There appears to be a definite correlation between the magnitude of the formation constant of the chelate–substrate adduct and the number of fluorine atoms attached to the β-diketone ring. For a given phosphate ester, very weak complexes are formed with the nonfluorinated $Eu(dpm)_3$ chelate, and apparently no adduct is formed at all with the $Eu(bzac)_3$ and $Eu(dbm)_3$ chelates. Placement of a $-CF_3$ group on the chelate ring yields a definite increase in adduct stability, with an approximate increase by a factor of 3 in passing from $Eu(dpm)_3$ to $Eu(facam)_3$. A further increase by at least 1 order of magnitude is found when a $-C_3F_7$ group is attached to the ring. The approximate stability of the chelate–substrate complex appears to be most dependent on the degree of fluorination, since the $Eu(fod)_3$ and $Eu(hfpc)_3$ chelate adducts with phosphate ester substrates all display formation constants that differ only by 0.2 log units.

An approximate correlation of complex acidity with ligand properties may be made by comparing the ligand pK_a values with the strength of the chelate–substrate adducts: the larger the ligand dissociation constant, the stronger the chelate–substrate complex. The pK_a values for the nonfluorinated ligands are fairly small, pK_a = 9.8 for H-bzac,[21] pK_a = 10.3 for H-dbm,[22] and pK_a = 11.8 for H-dpm,[23] and all of the chelates formed from these ligands form weak (if any) chelates with the substrates of this study. On the other hand, the pK_a for H-fod is 6.7,[24] and chelates of this ligand form considerably stronger adducts with the phosphate esters. The pK_a values of H-facam and H-hfpc have not been reported, but since the pK_a values of similar β-diketones tend to be fairly equal in magnitude, certain predictions can be made. The pK_a values of H-fod and H-hfpc should be about the same, since both possess an alkyl substituent and a $-C_3F_7$ group, and one would predict that the greater electron-donating power of a camphor group relative to that of a *tert*-butyl group would lower the pK_a of H-hfac somewhat. This prediction is borne out by the formation constant trends, since the hfpc adducts are slightly

---

(20) G. A. Catton, F. A. Hart, and G. P. Moss, *J. Chem. Soc., Dalton Trans.*, 208 (1976).

(21) M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945).

(22) L. G. Van Vitert and W. C. Fernelius, *J. Am. Chem. Soc.*, **75**, 3862 (1953).

(23) (a) G. A. Gouter and G. S. Hammond, *J. Am. Chem. Soc.*, **78**, 5166 (1956); (b) T. R. Sweet and H. W. Parlett, *Anal. Chem.*, **40**, 1885 (1968).

(24) T. R. Sweet and D. Brengartner, *Anal. Chim. Acta*, **52**, 173 (1970).

less stable than the fod adducts. The $\mathrm{p}K_a$ of H-facam (by the same arguement) should be somewhat less than the $\mathrm{p}K_a$ of (trifluoroacetyl)acetone, whose $\mathrm{p}K_a$ is equal to 6.7.[21] The camphor group should lower the $\mathrm{p}K_a$ by an appreciable amount and thus correlate with the decreased stability of Eu(facam)$_3$ adducts compared to Eu(hfpc)$_3$ adducts.

While the relative acidity of the Eu(III) chelates (as influenced by the ligand $\mathrm{p}K_a$ values) appears to be the main factor governing the extent of chelate–substrate interaction, steric effects are also found to play an important role. The Lewis basicity of the four phosphate esters used as substrates in the present work cannot be expected to differ to any extent in CCl_4, so any variation in formation constants found for a particular chelate system must then be related to the different steric nature of the substrates. It is believed that the substrate binds directly to the lanthanide ion and expands to coordination number of the metal from six to either seven or eight.[25] Since the β-diketone ligands must be pushed closer together to accommodate the substrate, it follows that the steric requirement of the substrate and the steric nature of the bonded β-diketone ligands will influence the extent of adduct formation.

Examination of the formation constants of Table II reveals that the behavior of the fod and dpm chelates is somewhat different than the behavior of the facam and hfpc chelates. Formation constants obtained from the interaction of Eu(fod)$_3$ and TMP, TEP, and TBP are all approximately the same, which indicates that the steric nature of the alkyl substituents on the phsophate ester does not play a significant role in this relatively unhindered chelate. The TPP substrate must present a more severe steric problem for the chelate, and its formation constant is measurably smaller. Similar behavior is noted for the Eu(dpm)$_3$ adducts; formation constants of the TMP, TEP, and TBP adducts are all approximately the same, and the TPP adduct apparently does not form at all. We conclude that both the fod and dpm chelates possess only minor steric requirements, and this property accounts for the great success that has been achieved in NMR spectroscopy using these chelates.

On the other hand, the facam and hfpc chelates clearly have a different steric requirement than do the fod and dpm chelates. A chelate "pocket" of definite size appears to exist on the β-diketone chelates made from the camphor derivatives. TEP and TBP bind equally well to both Eu(facam)$_3$ and Eu(hfpc)$_3$ (as evidenced in the equality of formation constants), but both TMP and TPP do not bind nearly as well. The formation constant of TPP with Eu(hfpc)$_3$ is distinctly lower than the constants found with TEP and TBP, and TPP does not even bind to Eu(facam)$_3$. We interpret these observations to indicate that TPP is too large to fit in the chelate "pocket". The formation constants of TMP with Eu(facam)$_3$ and Eu(hfpc)$_3$ are also much smaller than those obtained with either TEP and TBP, and one is forced to conclude that this substrate is too small for the "pocket" and thus does not present an optimal situation for bonding.

One may conclude, therefore, that the relative Lewis acidity of the lanthanide chelate and the Lewis basicity of the substrate dominate the extent of adduct formation but that steric effects play an important role. Complete understanding of the processes involved in NMR shift reagent work will be aided by continued investigation of the nature of shift reagent adducts.

The effectiveness of a given lanthanide chelate to function as an NMR shift reagent is clearly dependent on the degree to which the chelate–substrate complex is formed. Other factors such as spin relaxation,[2–4] magnetic anisotropy,[26] and chelate solubility play a large role in governing the magnitude of induced shifts, but it is clear that if the adduct formed is weak, then any induced shift in a proton resonance will be small. Formation constants calculated from absorption[20] and luminescence[12] measurements often differ with those calculated from NMR techniques, and it thus appears that spectroscopic results will aid considerably in the further development of shift reagent methods.

Acknowledgment. This work was supported by a Cotrell grant from the Research Corp. (Grant No. 8926) and by the National Science Foundation (Grant CHE 78-03402).

Registry No. Eu(fod)$_3$·TMP, 72346-93-1; Eu(fod)$_3$·TEP, 72346-94-2; Eu(fod)$_3$·TBP, 72346-95-3; Eu(fod)$_3$·TPP, 72346-96-4; Eu(dpm)$_3$·TMP, 72346-97-5; Eu(dpm)$_3$·TEP, 72360-46-4; Eu(dpm)$_3$·TBP, 72346-98-6; Eu(facam)$_3$·TMP, 72360-47-5; Eu(facam)$_3$·TEP, 72346-99-7; Eu(facam)$_3$·TBP, 72360-48-6; Eu(hfpc)$_3$·TMP, 72360-49-7; Eu(hfpc)$_3$·TEP, 72347-00-3; Eu(hfpc)$_3$·TBP, 72360-50-0; Eu(hfpc)$_3$·TPP, 72347-01-4; Eu(fod)$_3$, 17631-68-4; Eu(dpm)$_3$, 15522-71-1; Eu(facam)$_3$, 34830-11-0; Eu(hfpc)$_3$, 34788-82-4; Eu(bzac)$_3$, 14459-33-7; Eu(dbm)$_3$, 14552-07-9.

---

(25) S. P. Sinha, *Struct. Bonding (Berlin)*, **25**, 69 (1976).

(26) B. Bleaney, *J. Magn. Reson.*, **8**, 91 (1972).

Contribution from the Department of Chemistry, University of Western Ontario,
London, Canada N6A 5B7

Photoelectron Studies of Dialkyl Group 2B Compounds: Ligand Field Splittings and Intensity Variations with Photon Energy

D. K. CREBER and G. M. BANCROFT*[1]

Received July 31, 1979

High-resolution He Iα (21.2 eV) and He IIα (40.8 eV) gas-phase photoelectron spectra have been obtained for the group 2B dialkyl compounds, R_2M (M = Zn, Cd, Hg; R = Me, Et; and for Cd, R = *n*-Pr and Me_3SiCH_2). The five observed Zn 3d and Cd 4d peaks are caused by the combined effect of spin–orbit splitting and the axial ligand field from the R groups. The magnitude of the derived C_2^0 axial ligand field parameter increases in the order Me ≤ Et < *n*-Pr < Me_3SiCh_2. The Cd 4d binding energies decrease in the above order. These trends correlate with the donor strength of the alkyl groups. A pronounced intensity dependence on photon energy is found in the He I and He II valence-band spectra of these compounds. The relative changes in intensity of the valence and core levels are described by using partial atomic cross sections. Further evidence for Hg 5d orbital involvement in bonding in the alkylmercury compounds is presented.

Introduction

The He I photoelectron spectra of the valence band and outer metal d levels of a number of alkylmercury compounds,[2–5] Me_2Zn,[2,6] and Me_2Cd[7] have been reported. The observed valence-orbital ionization energies for Me_2Zn[6] and Me_2Cd[7] are in reasonable agreement with those calculated by

---

(1) To whom correspondence should be addressed.