less stable than the fod adducts. The pK_a of H-facam (by the same arguement) should be somewhat less than the pK_a of (trifluoroacetyl)acetone, whose pK_a is equal to 6.7.[21] The camphor group should lower the pK_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 pK_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.

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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.

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

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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$_2$M (M = Zn, Cd, Hg; R = Me, Et; and for Cd, R = n-Pr and Me$_3$SiCH$_2$). 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° axial ligand field parameter increases in the order Me ≤ Et < n-Pr < Me$_3$SiCh$_2$. 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$_2$Zn,[2,6] and Me$_2$Cd[7] have been reported. The observed valence-orbital ionization energies for Me$_2$Zn[6] and Me$_2$Cd[7] are in reasonable agreement with those calculated by

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using ab initio methods. The splitting of the outer d levels has been of particular interest. In Hg compounds, it has been concluded that there is a slight amount of Hg 5d involvement in bonding.[2-5] In contrast, for the Zn 3d and Cd 4d spectra, the splitting is due to an electrostatic ligand perturbation (rather than bonding).[6,7] We have shown that the asymmetric part of the crystal field (the C_2° or D_s term) is almost entirely responsible for this splitting, and the ab initio[6,7] and pseudoatomic[8] calculations have confirmed the electrostatic nature of the splitting. We have shown that this ligand field splitting should be observable on the p, d, and f levels of many *main-group* elements.[8c] For example, the $p_{3/2}$ splitting on the 5p level of I in NaI[9] is due to this same effect, and it can be easily calculated just by considering the Na^+ point-charge contribution.[8c]

Recently, He II radiation has been employed to obtain high-resolution spectra of the outer Zn,[10] Cd,[11] and Hg[12] d levels in Me_2M (M = Zn, Cd, Hg) and Et_2Cd, but the He II valence-band spectra have not yet been reported. The increase in the d-level cross sections at higher kinetic energies makes it possible to obtain the d spectra more quickly, often with better resolution with He II radiation than with He I radiation on our high-resolution instrument. The valence-band intensity changes between the two photon energies have often been used as a diagnostic tool to aid in assigning valence-band structure[13-29] and as a probe to understand better the photoionization process.[30-32] Calculations have evolved that rationalize the cross-section changes in spectra of atoms[33-35] and small

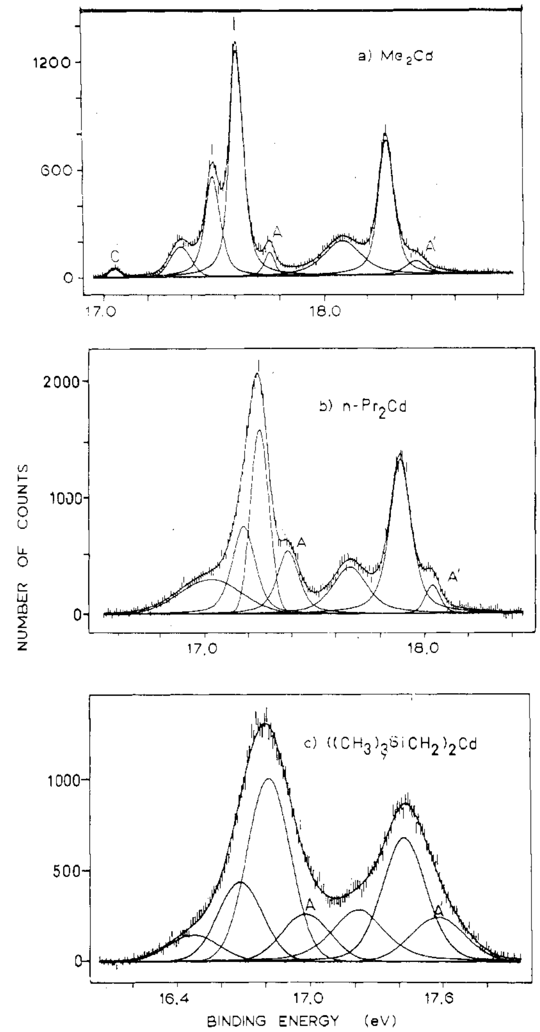

Figure 1. He IIα (40.8 eV) photoelectron spectra of the Cd 4d region in (a) Me_2Cd, (b) n-Pr_2Cd, and (c) $(Me_3SiCH_2)_2Cd$.

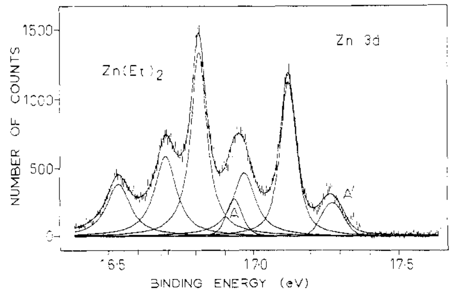

Figure 2. He IIα (40.8 eV) photoelectron spectra of the Zn 3d region in Et_2Zn.

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Table I. Crystal Field and Spin–Orbit Coupling Parameters (eV)[a]

compd	level	C_2°	C_4°	C_2°/C_4°	spin–orbit splitting ($^5/_2\lambda$) exptl	spin–orbit splitting ($^5/_2\lambda$) free atom[b]	E_{nd}
Me_2Zn	3d	−0.0169 (7)	−0.0007 (2)	24	0.335 (5)	0.337	17.109
Et_2Zn	3d	−0.0175 (7)	−0.0001 (4)		0.333 (5)	0.337	16.843
Me_2Cd	4d	−0.0225 (8)	−0.0008 (1)	28	0.685 (10)	0.699	17.747
Et_2Cd	4d	−0.023 (2)	−0.0012 (4)	19	0.688 (20)	0.699	17.497
n-Pr_2Cd	4d	−0.025 (2)	−0.0011 (5)	23	0.679 (10)	0.699	17.44
$(Me_3SiCH_2)_2Cd$	4d	−0.030 (3)	−0.0012 (5)	25	0.698 (15)	0.699	16.90

[a] At least five separate spectra were obtained for each compound and computed separately. The standard deviations were obtained in the normal way after the spectra were averaged. If λ is constrained at the free-ion value, the standard deviations decrease substantially. [b] Reference 40.

molecules.[34-36] For large molecules, theoretical problems make it very difficult to calculate the valence-band cross-section behavior. Most of the literature[13-29] discusses molecular cross sections in qualitative terms by using known atomic cross-section variations.[13,27,28]

In this paper, we extend our previous high-resolution He II studies of ligand field splittings in alkylzinc and -cadmium compounds. We show, for the first time, that this ligand field splitting is sensitive to rather small changes in the alkyl group bonding properties. Moreover, the changes in ligand field splittings correlate with chemical shifts and the relative σ-donor strengths of the R groups. The pronounced changes in the relative intensities of the valence band and outer d orbitals in alkylzinc, -cadmium, and -mercury compounds using He I or He II radiation are discussed by using partial atomic cross sections.

Experimental Section

Me_2Zn was prepared by the reaction of MeI and activated zinc.[37] The activated zinc was prepared by heating zinc powder and cupric acetate under nitrogen with a Bunsen burner until a permanent rust color was obtained. Methyl iodide was then added dropwise to the zinc and refluxed under nitrogen for 30 h. Vacuum distillation yielded Me_2Zn. Purity was checked by NMR and ESCA. Et_2Zn was obtained from Alfa Chemicals and used without further purification. Me_2Cd, Et_2Cd, and *n*-Pr_2Cd were prepared by a standard Grignard reaction.[7,38] Me_2Hg and Et_2Hg were purchased from Alfa Chemicals. $(Me_3SiCH_2)_2Cd$ was kindly supplied by Dr. S. Stobart.

The gas-phase photoelectron spectra were recorded on our McPherson ESCA 36 spectrometer. A hollow-cathode lamp[12] was used to generate the helium resonance lines. The spectra were calibrated with the Ar 3p lines (Ar $3p_{3/2}$ at 15.759 eV) that gave observed line widths (fwhm) of 17 and 27 meV for the He I and He II radiation excited lines, respectively. The d-level spectra were computed to Lorentzian–Gaussian peak shapes by using an iterative procedure described previously.[39]

Results and Discussion

(a) Ligand Field Splitting on Core d Orbitals. In previous papers [6,7,10,11] we have reported the He I and He IIα spectra of the Cd 4d levels of Me_2Cd and Et_2Cd and the Zn 3d levels of Me_2Zn. The Cd 4d spectra of Me_2Cd, *n*-Pr_2Cd, and $(Me_3SiCH_2)_2Cd$ are shown in Figure 1, and the Zn 3d spectrum of Et_2Zn is shown in Figure 2. Five main peaks (the $^2D_{5/2}$ triplet and $^2D_{3/2}$ doublet) are visually resolved in the four R_2M (M = Zn, Cd; R = Me, Et) spectra. In addition, two small peaks (A and A′) are resolved, and these have been assigned to the RM· radical species.[7] All of these spectra have been computer-fitted to seven peaks without any position constraints. Some line-width and intensity constraints were required to get convergence for the $(Me_3SiCH_2)_2Cd$ spectrum (Figure 1c). In the fit shown, all line widths have been constrained to be between 250 and 300 meV. This compares with the line widths found in an unconstrained fit for Me_2Cd between 70 and 220 meV. The relative intensities of the five $(Me_3SiCH_2)_2Cd$ peaks in Figure 1c have been constrained to be the same (±20%) as those found for the Me_2Cd spectrum. The broad lines in the *n*-Pr_2Cd and $(Me_3SiCH_2)_2Cd$ spectra are associated with the bulky R groups and may be due to larger vibrational or relaxation broadening in theses two compounds.

The five-peak spectra arise from the splitting of the d^9 hole state due to the combined effect of spin–orbit coupling and the ligand field from the R groups. Effectively, we are creating a transition-metal ion in these main-group elements and observing the normal splittings seen in transition-metal ions—albeit with different relative magnitudes for these core orbitals. The complete crystal field Hamiltonian for a d^9 state in $D_{\infty h}$ or $C_{\infty v}$ crystal field is[7]

$$\begin{aligned} H = E_{nd} + C_2^\circ[3L_z^2 - L(L+1)] + \\ C_4^\circ[35L_z^4 - 30L(L+1)L_z^2 + 25L_z^2 - 6L(L+1) + \\ 3L^2(L+1)^2] + \lambda[\tfrac{1}{2}(L_+S_- + L_-S_+) + L_zS_z] \quad (1) \end{aligned}$$

In the above equation, E_{nd} is the Cd 4d or Zn 3d binding energy, C_2° and C_4° are axial and cubic components of the crystal field, respectively, λ is the spin–orbit coupling constant, and the *L*'s and *S*'s are the orbital and spin angular momenta and operators.[7] The Hamiltonian matrix has been diagonalized in the d-electron subspace, and equations for the five energies have been obtained.[7] Using these equations, we can readily solve for the four variables E_{nd}, C_2°, C_4°, and λ.

Table I gives the E_{nd}, C_2°, C_4°, and $^5/_2\lambda$ values for the six compounds. With use of these parameters in Table I, the calculated and observed peak positions are in excellent agreement—within 0.02 eV, except for two lines of the *n*-Pr_2Cd spectrum. In the *n*-Pr_2Cd spectrum, observed and predicted positions differ by as much as 0.04 eV. Moreover, the derived values for the spin–orbit splittings $^5/_2\lambda$ are all very close to the free-ion values for Zn and Cd atoms[40] (Table I). This good agreement is one more strong indication that the peak fits are reasonable, even for the two more poorly resolved spectra. Also, the C_4° value is found to be consistently small compared to the C_2° term—i.e., C_2°/C_4° is always about 20. The C_2° term is expected to be much larger than C_4°.[8c,41]

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There are three important trends immediately apparent in Table I: first, the R_2Zn compounds have substantially smaller $C_2°$ values than their Cd analogues; second, the $|C_2°|$ values for the Cd compounds increase as the size of R increases; and third, the chemical shift decreases as $|C_2°|$ increases. These compounds are predominantly covalent with the R groups donating electron density mainly into the Zn $4p_z$ and Cd $5p_z$ orbitals.[6,7] Consider the approximate formula[8c]

$$|C_2°| \overset{\propto}{\sim} F^2(\Delta\rho) \qquad (2)$$

where F^2 is the Slater–Condon integral between valence p and core d levels and $\Delta\rho$ is the excess p-orbital population along the molecular z axis—in this case just the p_z population. The lower Zn $C_2°$ values are due to the smaller F^2 and $\Delta\rho$ values for the Zn compounds relative to their Cd analogues. Considering Me_2Zn and Me_2Cd, the theoretical F^2 values are 0.0715 and 0.0830 Ry,[8c] while the ab initio calculated $\Delta\rho$ values are 0.39 and 0.43 e, respectively.[6,7] The ratio of $(F^2(\Delta\rho))_{Me_2Zn}/(F^2(\Delta\rho))_{Me_2Cd}$ becomes 0.78, and this is in good agreement with the experimental $C_2°$ ratio of 0.75.

The increase in $|C_2°|$ for the Cd compounds can be attributed to the increase in Cd $5p_z$ electron density in the order Me < Et $\lesssim$ *n*-Pr < Me_3SiCH_2. This order is totally consistent with the known same order of increasing donor strengths of these ligands.[42,43]

The third trend—the decrease in Cd 4d chemical shift with increase in $|C_2°|$—further substantiates the above treatment on the basis of changes in σ-donor strengths. As the electron density in the Cd $5p_z$ orbital ($\Delta\rho$) increases, the chemical shift should decrease,[44] and the lower binding energy is a generally observed effect of increasing the alkyl-chain length and the donor strength of the alkyls.[5,45] An increase in $\Delta\rho$ should thus lead to the observed decrease in binding energy and increase in $C_2°$. However, contributions to core-level binding-energy shifts should include final-state relaxation effects as well as the above-mentioned ground-state electron distributions, and Martin and Shirley's paper[47] indicates that the final-state effects dominate for deep core levels. Relaxation shifts for core levels near the valence region (such as Cd 4d) are expected to be an order of magnitude smaller, and it is reasonable then to rationalize the chemical shift–$C_2°$ trend by using just ground-state effects.

Approximate calculations indicate that the ground-state treatment for d levels comes close to rationalizing the changes in $C_2°$ and binding energy. From the $\langle 1/r \rangle$ value for Cd 5p electrons of 12.5 eV,[44] a decrease in binding energy of 0.85 eV from Me_2Cd to $(Me_3SiCH_2)_2Cd$ corresponds to an increase in Cd $5p_z$ population of ~0.07 e. Since $C_2°$ is very approximately linear with $\Delta\rho$ and a $C_2°$ of −0.0225 eV in Me_2Cd corresponds to a $5p_z$ population of 0.40,[7] the 0.07 e change should result in an increase in $C_2°$ of ~0.004 eV, compared to the observed change of 0.007 ± 0.003 eV.

Finally two other chemical shift–$C_2°$ correlations should be mentioned. From the Zn 3d spectra of the zinc dihalides,[49] the binding energies decrease from $ZnCl_2$ (19.3 eV) to $ZnBr_2$ (19.0 eV) and ZnI_2 (18.3 eV), while the ligand field splitting increases in the above order. In contrast, for the I 5p level of the alkali iodides, the binding energy and $C_2°$ increase from Cs to Na; and both binding energies and $C_2°$ values can be calculated readily by using point charges and known bond lengths.[8c]

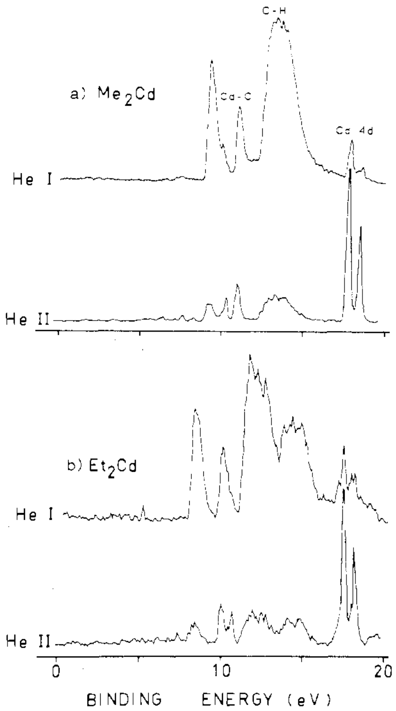

Figure 3. He I and He II spectra of the valence band and Cd 4d regions in (a) Me_2Cd and (b) Et_2Cd. The three major regions of the spectra are noted on the top spectrum: the two Cd–C σ_u and σ_g levels, the C–H σ region, and the Cd 4d region.

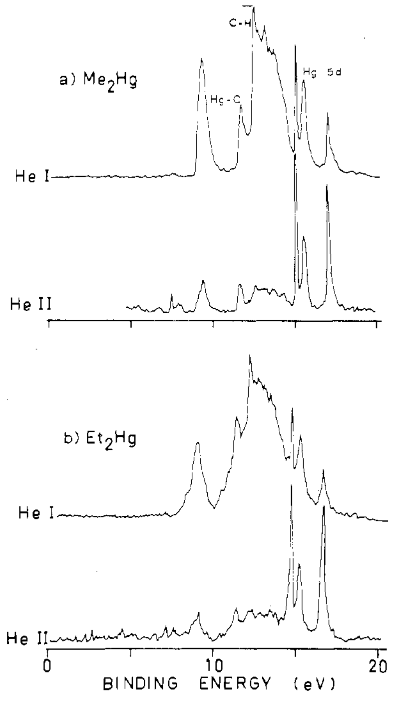

Figure 4. He I and He II spectra of the valence band and Hg 5d regions in (a) Me_2Hg and (b) Et_2Hg.

(b) Variation of Valence-Band Intensities. The He I and He II spectra of R_2M (M = Cd, Hg; R = Me, Et) are shown in Figures 3 and 4, and the binding energies are summarized in Table II for all the dialkyl compounds. The spectral features

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Table II. Comparison of Valence-Level Cross Sections for R_2M (R = Me, Et, *n*-Pr; M = Zn, Cd, Hg)[a]

			rel intens	
compd	level	BE, eV	He Iα	He IIα
Me_2Zn	Zn–C σ_u	9.4	0.82	0.35
	Zn–C σ_g	11.3	0.55	0.17
	C–H σ	~13	1.39	0.43
	Zn $3d_{5/2}$	17.0	1.00[b]	1.53[b]
	Zn $3d_{3/2}$	17.3	0.75	0.96
Et_2Zn	Zn–C σ_u	8.6	0.94	0.38
	Zn–C σ_g	10.5	0.75	0.33
	C–H σ	~13	2.41	0.91
	Zn $3d_{5/2}$	16.7	1.00[b]	1.53[b]
	Zn $3d_{3/2}$	17.0	0.71	0.95
Me_2Cd	Cd–C σ_u	8.8	0.81	0.28
	Cd–C σ_g	10.6	0.60	0.25[c]
	C–H σ	~12.5	1.11	0.48
	Cd $4d_{5/2}$	17.5	1.00[b]	3.52[b]
	Cd $4d_{3/2}$	18.2	0.37	2.12
Et_2Cd	Cd–C σ_u	8.2	0.43	0.17
	Cd–C σ_g	9.9	0.33	0.10
	C–H σ	11–15	1.04	0.66
	Cd $4d_{5/2}$	17.2	1.00[b]	3.52[b]
	Cd $4d_{3/2}$	17.9	0.74	2.24
n-Pr_2Cd	Cd–C σ_u	8.2	0.73	0.40
	Cd–C σ_g	9.9	0.68	0.30[a]
	C–H σ	12–16	2.70	1.10
	Cd $4d_{5/2}$	17.2	1.00[b]	3.52[b]
	Cd $4d_{3/2}$	17.9	0.76	2.16
$(Me_3SiCH_2)_2Cd$	Cd–C σ_u	8.8	1.0	0.5
	Cd–C σ_g	10.9	4.1	1.6
	C–H σ	14.0	7.5	2.0
	Cd $4d_{5/2}$	16.6	1.0	3.1
	Cd $4d_{3/2}$	17.3	1.4	2.1
Me_2Hg	Hg–C σ_u	9.3	0.58	0.19[c]
	Hg–C σ_g	11.6	0.39	0.30
	C–H σ	~13	1.14	0.27
	Hg $5d_{5/2}$	15.0	1.00[b]	1.72[b]
	Hg $5d_{3/2}$	16.9	0.73	1.57
Et_2Hg	Hg–C σ_u	8.9	0.36	0.12[c]
	Hg–C σ_g	11.3	0.30	0.25
	C–H σ	12–14	1.17	0.30
	Hg $5d_{5/2}$	14.7	1.00[b]	1.72[b]
	Hg $5d_{3/2}$	16.6	0.64	1.59

[a] Experimental intensities are divided by the peak kinetic energy and normalized to the atomic $^2d_{5/2}$ cross section. [b] The $d_{5/2}$ relative cross sections are taken from ref 30. [c] Corrected for overlap with d level excited with He IIβ radiation.

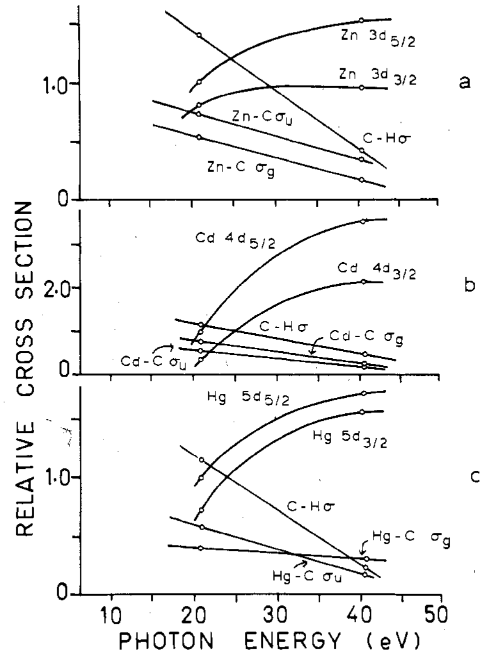

Figure 5. Plots of relative cross sections (normalized to the M $nd_{5/2}$ peak) for (a) Me_2Zn, (b) Me_2Cd, and (C) Me_2Hg.

for these compounds are very similar to those of Me_2Zn and Me_2Cd,[6,7] and the peaks can be readily assigned. There are two M–C bonding orbitals visible at low binding energies (8–12 eV), followed by a characteristically broad and intense (He I) band assigned to the C–H bonding orbitals (12–14 eV). For the longer chain alkyl compounds there is a higher energy band (~15 eV) associated with the alkyl group.[13] And, finally, the "corelike" d levels are seen as a series of peaks at high binding energy (15–19 eV). The most prominent feature in these spectra is the dramatic increase in intensity of the d levels (Zn 3d, Cd 4d, and Hg 5d) relative to the valence-level intensities between He I and He II photon spectra.

We list the relative intensities of the valence-band and d peaks in the Me compounds in Table II after dividing through by the kinetic energy to correct for analyzer sensitivity and normalizing to the relative atomic d cross sections reported by Süzer et al.[30] We have shown previously that the Zn 3d and Cd 4d levels are atomic-like, i.e., not involved in bonding.[6,7] The Hg 5d levels, however, are slightly involved in bonding.[2,3,12] These "cross sections" are then shown in Figure 5. The lines in this figure are intended to represent (in an approximate way) the smooth variation of the partial cross sections with photon energy. The curves for the $d_{5/2}$ level are set equal to the reported atomic values for Zn 3d, Cd 4d, and Hg 5d.[30]

To interpret Figure 5, we use the known kinetic energy variation of atomic s-, p-, and d-level cross sections.[13,27,28] The photoionization cross section of s electrons is observed to be small near the ionization threshold, with a very slow decrease with increasing photon energy. In contrast, p-type orbitals have high-photoionization cross sections near the ionization threshold which very rapidly falls off with increasing photon energy. Atomic d-orbital cross sections are low near the ionization threshold, and increase rapidly to a maximum around 20–40 eV above the threshold, followed by a slow decrease with increasing photon energy.

We then combine the known atomic cross-section variations above with a Gelius intensity model[50] to discuss the variations in intensities of molecular orbitals. In the high kinetic energy limit, Gelius has shown that the intensity of the *j*th molecular orbital I_j^{MO} is proportional to the linear combination of atomic cross sections $\sigma_A{}^{AO}$ multiplied by the fractional occupancies P_A; i.e.

$$I_j^{MO} \propto \sum_A P_A \sigma_A \tag{3}$$

Although this approach has not been quantitatively successful in the UV region, it can be used in a qualitative way to discuss intensity variations.

The rapid decrease in the C–H σ, C–M σ_u, and C–M σ_g levels (Figure 5) is due to the large C 2p character of these levels. In separate calculations Basch[7] and Topiol et al.[6] calculated the character of the valence levels for Me_2Cd and Me_2Zn, respectively. Each calculation found about 50% C 2p and 45% H 1s population in the C–H σ-bonding orbitals, 20% M *n*p, 73% C 2p, 5% H 1s and 2% C 2s population in the M–C σ_u bonding orbital, and about 35% M *n*s, 60% C 2p, and 5% H 1s population in the M–C σ_g bonding orbital. The C 2p cross section has been calculated[34] to decrease by ~30% between He Iα and He IIα radiations.

There is only one exception to this general behavior. The photoionization cross section of the Hg–C σ_g-bonding level in Me_2Hg decreases only slightly between He Iα and He IIα

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radiations. This behavior is attributed to the mixing of Hg 5d character with the σ_g bonding level.[28] Because the cross section of the Hg 5d level is the only atomic cross section which increases significantly between these energies, the rapid decrease in p cross section is offset by Hg 5d orbital mixing. This same behavior has recently been observed in the valence band of mercuric dihalides, and similar conclusions have been made.[28] In addition to these observations, the splitting patterns of the Hg 5d levels[1,2,10] are further confirmation of the slight bonding nature of the Hg 5d orbitals.

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Registry No. Me_2Zn, 544-97-8; Et_2Zn, 557-20-0; Me_2Cd, 506-82-1; Et_2Cd, 592-02-9; n-Pr_2Cd, 5905-48-6; $(Me_3SiCH_2)_2Cd$, 63835-91-6; Me_2Hg, 593-74-8; Et_2Hg, 627-44-1.

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Electronic Structure and Spectra of Linear Dihaloaurate(I) Ions

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Solution absorption and magnetic circular dichroism (MCD) spectra in the ultraviolet region are reported for $[(n\text{-}C_4H_9)_4N][AuX_2]$ ($X = Cl^-$, Br^-, and I^-) in CH_3CN. Absorption spectra are also reported for unoriented crystalline films of these compounds on quartz plates at 300 and 26 K, with considerable resolution enhancement observed for $AuBr_2^-$ and AuI_2^- at low temperature. The $AuCl_2^-$ spectra are interpreted in terms of a parity forbidden 5d → 6s transition and allowed 5d → 6p transitions, while the spectra of $AuBr_2^-$ and AuI_2^- exhibit in addition ligand to metal charge-transfer (LMCT) transitions. The LMCT spectra for AuI_2^- are interpreted by means of excited configurations which include both ligand and metal spin-orbit coupling. Detailed spectral assignments are presented and the results discussed in terms of gold orbital participation in bonding and the extent of halide to gold σ and π bonding in the AuX_2^- ions.

Introduction

Gold(I) forms some of the best examples of linear two-coordinate complexes which can be considered as prototypes of this very simple coordination geometry. Consequently electronic spectra of linear two-coordinate Au(I) complexes are of interest in providing an experimental basis for the study of electronic structure of two-coordination in general. However, except for the $Au(CN)_2^-$ ion, whose spectra have been studied in some detail,[1,2] little is known about electronic spectra of two-coordinate gold(I) complexes. This may be partly due to experimental difficulties encountered with many Au(I) complexes in aqueous solution. For example, simple dihalo complexes, AuX_2^- ($X = Cl^-$, Br^-, and I^-), are unstable with respect to disproportionation in aqueous solution.[3] Many other complexes containing P, S, or As donor ligands are simply not soluble; those that are disproportionate or hydrolyze. Although some of these problems may be avoided by the use of nonaqueous solvents, molecular Au(I) complexes generally exhibit spectra in the UV region which have often been obscured by strong ligand or counterion absorptions.[4,5]

As part of a systematic investigation of electronic spectra of two-coordinate Au(I) complexes, the present paper reports spectral measurements for the dihaloaurate(I) complexes, $AuCl_2^-$, $AuBr_2^-$, and AuI_2^-. Simple discrete linear ions are presumed for these three complexes, analogous to isoelectronic HgX_2 ($X = Cl^-$, Br^-, and I^-) complexes which are known to be linear. Structural studies of AuX_2^- salts are limited,[5,6] but in each case linear two-coordination about the gold is indicated. Infrared and Raman spectra have been interpreted in terms of ions of $D_{\infty h}$ symmetry,[3,7] and single ^{35}Cl and ^{37}Cl nuclear quadrupole resonances are observed for $AuCl_2^-$, indicating equivalent chloride ligands.[7,8] Previous electronic spectral measurements for AuX_2^- in acetonitrile, although incomplete, revealed a single weak band ($\epsilon < 250$) for each complex, which was assigned to a parity forbidden 5d → 6s transition.[9] In the present paper we report acetonitrile solution spectra for tetra-n-butylammonium salts of $AuCl_2^-$, $AuBr_2^-$, and AuI_2^-, which extend to the high-energy solvent cutoff (5.1 μm^{-1}). In addition, magnetic circular dichroism (MCD) spectra were obtained for acetonitrile solutions. Spectra were also recorded for thin crystalline films of the tetra-n-butylammonium salts on quartz plates at 300 and 26 K.

Experimental Section

The tetra-n-butylammonium dihaloaurate(I) salts, $[(n\text{-}C_4H_9)_4N][AuX_2]$, where $X = Cl^-$, Br^-, and I^-, were prepared by the methods described by Braunstein and Clark.[3] Excellent yields of the dibromo and diiodo complexes were obtained, but difficulties were encountered with the synthesis of the dichloro complex via phenylhydrazine hydrochloride reduction of $[(n\text{-}C_4H_9)_4N][AuCl_4]$ in ethanol. Only small amounts of product were obtained in each of several experiments. In several other cases the product was severely contaminated with either unreacted starting material or gold metal. Attempts to improve the synthesis by changing the reducing agent or solvent were unsuccessful. However, enough pure product was obtained from multiple preparations for analysis and spectral measurements. All three compounds gave satisfactory elemental analysis.

Absorption spectral measurements were made by using a Cary Model 1501. Spectroquality acetonitrile was used throughout for solution spectra. The MCD spectra were recorded on a JASCO

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