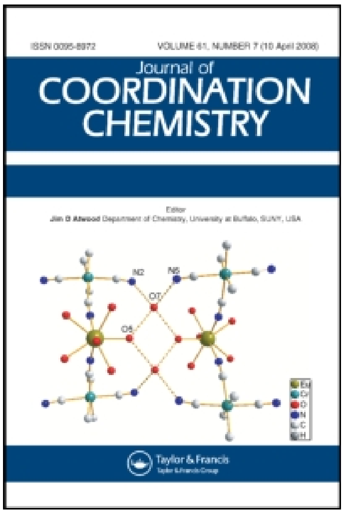

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Dubois, Ronald , Carver, James C. and Tsutsui, Minoru(1977) 'THE X-RAY PHOTOELECTRON SPECTRA OF SIGMA AND Pi BONDED ORGANOGADOLINIUM COMPOUNDS: A SEARCH FOR 4f ORBITAL COVALENCY', Journal of Coordination Chemistry, 7: 1, 31 — 34

To link to this Article: DOI: 10.1080/00958977708073035

URL: http://dx.doi.org/10.1080/00958977708073035

J. Coord. Chem.
1977, Vol. 7, pp. 31–34

THE X-RAY PHOTOELECTRON SPECTRA OF SIGMA AND Pi BONDED ORGANOGADOLINIUM COMPOUNDS: A SEARCH FOR 4f ORBITAL COVALENCY

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(Received December 3, 1976)

The nature of the bonding in a series of *sigma-* and *pi-bonded organogadolinium compounds* ($GdCl_3$, $CpGdCl_2$, Cp_2GdCl, Cp_3Gd, Cp_2GdR where $R{=}CH_3$ and $C{\equiv}CpH$) have been studied by *x-ray photoelectron spectroscopy.* The Gd(3d) region of each compound investigated reveals one *electron "shake-up" photopeak* indicating some covalency due to 4f participation in bonding. The relative areas of the main photopeak and the satellite photopeak show no change between compounds which indicates similar bonding properties for the various sigma- and pi-bonded substituents. As a result, this investigation finds no support for the hypothesis that *sigma-bonded organolanthanide derivatives* are more "covalent" than their pi-bonded analogs.

INTRODUCTION

The last few years have witnessed a rebirth of interest in the organometallic chemistry of lanthanide and acitinide compounds.[2] In particular, the recent successful synthesis and characterization[3–5] of sigma-bonded organolanthanide compounds of the type Cp_2LnR ($Cp = h^5{-}C_5H_5$ and $R = CH_3$, $C{\equiv}CC_6H_5$) has once again posed the question of whether the 4f orbitals of organolanthanide compounds actually participate in covalent bonding. For the lanthanides, it is believed that besides being well *shielded* electrostatically, the 4f orbitals do not extend *far enough spatially* to enter into covalent bonding or to be split by ligand fields to any great extent.[6] In the actinides, the 5f orbitals are much less shielded than the 4f orbitals, the radial function for 5f orbitals is large enough for proper metal–ligand interaction, and the binding energies are lower (i.e. closer to zero) than in the lanthanides. These factors have been attributed to increased covalent bonding for the actinides.[7] Indeed, recent work has established that the bonding in a number of organolanthanide compounds is primarily ionic,[8–10] whereas covalency plays an important role in the bonding of the analogous U(IV) complexes.[11] However, all the lanthanide complexes previously studied contain only pi-bonded ligands in which the negative charge is delocalized over several carbon atoms. By contrast a *monohapto* (sigma) carbanion such as CH_3^- has its electron density concentrated on one carbon atom. This opportunity for a localized interaction between the metal and the ligand could lead to a greater covalency in the lanthanide–carbon sigma bond than for a pi-bond.

This paper summarizes the results of our use of X-ray photoelectron spectroscopy to probe the covalency of a series of sigma and pi bonded organogadolinium compounds. In particular, we monitored the peak area ratios of the Gd $3d_{5/2}$ photopeak and its electron "shake-up" satellite in an effort to qualitatively probe the 4f orbital covalency of a homologous series of organolanthanide compounds. Electron "shake-up" satellite peaks[12] in lanthanide and actinide compounds have been related to ligand to metal (L→M) electron charge-transfer transitions. These transitions are believed to be between bonding and antibonding molecular orbitals having both metal and ligand character and adhering to the monopole selection rules.

If the symmetry remains constant and a series of complexes of the same metal are examined, we would expect that the intensity of the satellite peak would be directly proportional to the overlap integral between the two orbitals involved. This integral will be a measure of the interaction between the metal f-orbitals and the proper ligand orbitals. Therefore the peak area ratio of the main photopeak to its satellite can be used as a *qualitative* gauge of covalency.

EXPERIMENTAL

All of the compounds used in this investigation were

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TABLE I

Summary of photoelectron data for a series of σ and π bonded organogadolinium compounds

Compound	Gd(4f) B.E.(FWHM)[a]	Cl(2p1/2) B.E.(FWHM)	Cl(2p3/2) B E (FWHM)	Gd(4d) B.E.(FWHM)	Gd(5s)[c] B.E.(FWHM)	Gd(5s)[c] (B.E.(FWHM)
All values in electron volts (eV)						
$GdCl_3$	9.0(3.2)	199.2(1.6)	197.6(1.7)	142.3(3.9)	47.8(3.5)	43.8(3.0)
$CpGdCl_2$	8.8(3.1)	200.2(1.8)	198.6(1.8)	142.3(4.1)	48.2(3.5)	44.0(3.6)
Cp_2GdCl	8.8(3.2)	200.3(2.1)	198.6(2.2)	142.3(4.0)	48.6(3.4)	44.0(3.6)
Cp_3Gd	8.8(3.2)	N.O.[b]	N.O.[b]	142.3(4.0)	48.5(3.9)	44.0(4.2)

Compound	Gd(3d5/2) B.E.(FWHM)	Gd(3d5/2)sat B.E.(FWHM)	ΔE[d]	Ratio[e] A_{main}/A_{at}
All values in electron volts (eV)				
$GdCl_3$	1189.7(5.1)	1199.6(3.4)	9.9	13
$CpGdCl_2$	1189.8(5.3)	1200.3(4.3)	10.5	12
Cp_2GdCl	1189.5(5.5)	1198.8(4.2)	9.3	9
Cp_3Gd	1189.9(5.7)	1199.6(4.4)	9.7	12
$Cp_2Gd{\equiv}CPh$	1189.9(5.5)	1198.7(4.3)	9.8	12
Cp_2GdCH_3	1189.6(5.6)	1200.3(5.2)	10.7	12

[a] FWHM = *full width half maximum of photopeak in eV.*
[b] N.O. = not observed
[c] Gd(5s) values represent computer deconvoluted Gd(5s) multiplets splitting photopeaks.
[d] $\Delta E = |\, B.E._{main} - B.E._{sat} \,|$
[e] Ratio of peak area main photopeak relative to the peak area of the satellite photopeak.

handled at all times under strict inert-atmosphere conditions. Anhydrous $GdCl_3$ was purchased from Ventron Corporation and used without further purification. The remaining compounds $CpGdCl_2$, Cp_2GdCl, Cp_3Gd, Cp_2GdCH_3 and $CpGdC{\equiv}CPh$ (where $Cp{\equiv}\pi^5 C_5H_5$) were synthesized and purified using standard literature procedures.

ESCA samples were prepared in a Vacuum-Atmospheres dry box under dry Ar gas. The samples were prepared by brushing each compound on double-stick scotch tape. All spectra reported in this paper were recorded on a Hewlett-Packard 5950A ESCA spectrometer using monochromatized Al K_α radiation ($h\nu$ = 1486.6 eV). The "charging effects" were neutralized by using a thermionic source whose voltage was set at 0.3 eV and emission current which is a measure of electron flux from the gun at 0.04 ma.

Each of the samples were internally calibrated to the Si $2p_{3/2}$ line of the double-stick scotch tape which was previously referenced to the Au $4f_{7/2}$ line (83.8 eV)[12c]. Spectral deconvolution was accomplished both by using a least-squares computer algorithm and a Dupont Curve Resolver Model No. 310. The agreement between the two methods was quite good. Table I summarizes the deconvoluted photoelectron data measured during this investigation.

RESULTS AND DISCUSSION

Examination of the chlorine 2p data reveals that the binding energies of both the Cl $2p_{1/2}$ and Cl $2p_{3/2}$ photopeaks increase slightly as the number of chlorine ions in the molecule are replaced in the series $GdCl_3$ to Cp_2GdCl. The 1 eV increase in binding energy of the Cl $2p_{3/2}$ photopeaks in $CpGdCl_2$ relative to $GdCl_3$ might be interpreted as a small decrease in the electronic charge density located in the chlorine ions in going from $GdCl_3$ to $CpGdCl_2$. Such a result is not surprising since the cyclopentadienyl group can easily accept additional charge density from the chlorine ions. Since no corresponding change occurs in the Gd(III) ion, it must not accept much if any of the charge density. No chemical shift in the C(1s) would be expected since a negative charge which resided on the Cp group would be highly delocalized.

Examination of the Gd 5s region reveals two photopeaks arising from the spin–spin exchange interactions in the final state between the Gd 5s photohole and the partly filled Gd 4f shells.[13] Any changes in this splitting might be relevant to the covalency experienced by the Gd. The gradation of ΔE is quite subtle and in fact the standard deviations between the splittings do not satisfy the 3σ criteria for significance precluding any definitive statement regarding the relevance of the observed multiplet splitting pattern. This uncertainty is approximately ±0.4 eV which is about four times larger than the normal uncertainty because of the exceptionally weak signals arising from the 5s region. The mean splitting observed of 4.3 eV is in relatively good agreement with the value calculated (3.9 eV) for the Gd(III) ion using the Slater model by Herbst, Lowry and Watson.[14]

The binding energies determined for the Gd $4d_{5/2}$ and $3d_{5/2}$ photopeaks are summarized in Table I. Examination of the Gd 4d and 3d data reveals no significant binding energy shifts as the cyclopentadienyl ions are systematically substituted for chlorine ions in the series $GdCl_3$ to Cp_3Gd. The apparent change in BE for Cp_2GdCl when compared with its adjacent series members might be due to the change from a monomer to a dimer. These results coupled with the BE data from Cl 2p region imply that the cyclopentadienyl ion and chlorine ion are very similar chemically. This result is not unexpected when one considers previous work done.[15]

Careful examination of the Gd 3d region reveals a second photopeak of lower intensity located approximately 10 eV higher in bonding energy than the main Gd 3d photopeaks. This additional satellite photopeak is believed to be the result of the transition of a valence band electron to an empty 4f orbital. This process of photoionization and simultaneous outer-shell excitation is referred to as electron "shake-up" or monopole transitions.[16] The "shake-up" satellite intensity will be proportional to overlap and inversely proportional to separation in energy between the occupied and empty orbital involved. "Shake-up" transitions are often enhanced if the transition energies are lowered and the electrons in the initial and final state orbitals tend to occupy the same space.[12] Thus an enhancement of the satellite photopeak relative to the main photopeak might be interpreted as an indication of greater orbital overlap and hence greater covalency between the Gd 4f orbitals and the appropriate sigma and pi bonding ligands. Since there is a known change in geometry for the monochloride species we might expect to see a change here unrelated to covalency.[17] Table I summarizes the relative binding energy differences, ΔE, between the Gd $3d_{5/2}$ photopeak and its electron "shake-up" satellite and the relative peak area ratios (A_{main}/A_{sat}) for all the sigma and pi bonded compounds investigated.

Examination of the peak area ratios yields the following results. First, substitution of a cyclopentadienyl ion for a chloride ion in the series $GdCl_3$ to Cp_3Gd has little or no effect on the peak area ratios except when accompanied by a simultaneous change in structure. This structural dependence is clearly observed in Cp_2GdCl, a compound whose solid state structure is undoubtedly dimeric. Furthermore, the observed decrease in ΔE between the main and satellite photopeaks in Cp_2GdCl can be viewed as collaborative evidence in support of the observed intensity data. Second, a similar comparison with the sigma bonded organogadolinium derivatives, $Cp_2GdC{\equiv}CPh$ and Cp_2GdCH_3, yields similar intensity and ΔE data to the π-bonded species. This result indicates that the substitution of a sigma bonding ligand such as CH_3^- into Cp_2GdCl does not increase the compounds relative 4f orbital covalency. Therefore these sigma bonded moities seem to induce no more f-orbital interaction than does a simple Cl^-.

We would expect "shake-up" transitions to be involved for each satellite and when the symmetry is changed the relative probabilities of the various transitions could be altered. Such an occurance might result in the most intense part of the satellite peak being changed. The changes in ΔE for these satellites do not seem to reflect any apparent trends and since no corresponding intensity changes occur (except for Cp_2GdCl which has already been discussed) we can only suggest that these variations might be due to changes in symmetry. $GdCl_3$ and $GdCp_3$ are approximately C_{3v} while the compounds are C_{2v} or lower symmetry. Therefore a full explanation of the details of the satellite structure awaits corresponding cross section and molecular orbital calculations.

In conclusion, these results indicate that the cyclopentadienyl ion and chlorine ions are very similar in ionicity and that coordination of a sigma-bonded alkyl or alkynyl derivative does not increase 4f orbital covalency. Evidence for these conclusions is based on constant electron "shake-up" transitions probabilities. These results do not eliminate the possibility that a sigma bonded compound might be more covalent, but only that the f-orbital participation in such bonds is minimal. Evidence is also presented for utilizing ESCA "shake-up" as a means of detecting structure changes.

ACKNOWLEDGEMENT

We gratefully acknowledge the financial support of the Robert A. Welch Foundation (Grant No. A-420) and NSF Grant No. GP-41563 under which the ESCA spectrometer was purchased. We also acknowledge helpful discussions with Dr. M. K. Hall.

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