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NONCOVALENT CHARACTER IN THE CHEMICAL BONDS OF THE LANTHANIDE(III) AND THE ACTINIDE(III) TRICYCLOPENTADIENIDES*

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SUMMARY

The absorption and UV-excited emission spectra of several micro-crystals of $^{248}Cm(C_5H_5)_3$ have been measured throughout the visible region of the spectrum. One line-group in each spectrum can be clearly assigned to the transition: $J=7/2$ (first-excited state) $\leftrightarrow J=7/2$ (ground state). This group shows a large (~1680 cm^{-1}) ligand-field splitting and a baricenter of intensity at 15,920 cm^{-1}. By comparing the latter with the corresponding value for Cm^{III}_{aq}, the nephelauxetic parameter $d\beta$ for Cm^{III} in $Cm(C_5H_5)_3$ is estimated to be 0.050 ± 0.004; this corresponds to a covalency in these organometallic bonds of about $2.5 \pm 0.2\%$ relative to the corresponding bonds of Cm^{III}_{aq}. Similar considerations based on the published absorption spectrum of $Am(C_5H_5)_3$ lead to an organometallic bond covalency in the latter of about $2.8 \pm 0.2\%$ relative to the corresponding bonds of Am^{III}_{aq}.

The above covalancies for $Am(C_5H_5)_3$ and $Cm(C_5H_5)_3$, representative of the actinide series, are compared with those for $Pr(C_5H_5)_3$, $Nd(C_5H_5)_3$, and $Er(C_5H_5)_3$, representative of the lanthanide series; and it is concluded that although the actinides are more covalent than the lanthanides, as expected, all of these compounds are highly ionic in their organometallic chemical bonding. They should, therefore, be designated as lanthanide or actinide tricyclopentadienides, rather than as tricyclopentadienyls as has been the practice among various authors in recent publications.

1. INTRODUCTION

Crystals of the actinide tricyclopentadienides $^{248}Cm(C_5H_5)_3$, $^{249}Bk(C_5H_5)_3$, and $^{249}Cf(C_5H_5)_3$ were recently originally synthesized in this laboratory[1,2]. Microgram amounts were obtained and the identifications were based on the results of X-ray diffraction measurements. Mass-spectral evidence for the existence of $^{244}Cm(C_5H_5)_3$ was also independently reported by Baumgärtner *et al.*[3] and reports have

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recently appeared on the preparations and absorption spectra of $U(C_5H_5)_3$[4] and $Np(C_5H_5)_3$[5]. Previously only $Pu(C_5H_5)_3$ and $Am(C_5H_5)_3$ were known in the $An(C_5H_5)_3$* series[6,7], and recently spectral data on these have appeared in the literature[8,9]. The analogous lanthanide tricyclopentadienides are all known, and with the known exception of $Tm(C_5H_5)_3$ their reported crystal structures, so far[10], are isomorphous with the $An(C_5H_5)_3$ compounds**: $Am(C_5H_5)_3$[11], $Cm(C_5H_5)_3$[1], $Bk(C_5H_5)_3$, and $Cf(C_5H_5)_3$[2]. The physical and chemical properties[12–15] and the known nephelauxetic spectral shifts[16] for the $Ln(C_5H_5)_3$* compounds indicate that they are primarily ionic in their organometallic chemical bonding; thus Cotton and Wilkinson[17,18] have classified them as the ionic cyclopentadienides, in contrast to the more covalently connotated "cyclopentadienyl" classification for some of the corresponding compounds of the main *d*-block transition-element series.

We expect the compounds of the $An(C_5H_5)_3$ series to be more covalently bonded than the analogous compounds of the $Ln(C_5H_5)_3$ series because a fair amount of evidence exists suggesting this to be generally true of actinide compounds relative to the corresponding lanthanide compounds[19], and it is attributed to the greater extension of the 5*f* orbitals relative to the 4*f* orbitals, thereby allowing greater overlap with resultant higher covalency for the former. The following question then arises: In which class, ionic cyclopentadienide or covalent cyclopentadienyl, should the $An(C_5H_5)_3$ compound be placed? It is the primary purpose of this paper to settle this question on the basis of spectral evidence from which the percent *f*-electron covalency in the $Am(C_5H_5)_3$ and $Cm(C_5H_5)_3$ compounds can be determined. We select these particular $An(C_5H_5)_3$ compounds because their absorption spectra have recently been measured and some of the *J* assignments and ligand-field splittings are clearly evident so that our method can be reliably applied. From our results and similar results for the $Ln(C_5H_5)_3$ series, we show that the $An(C_5H_5)_3$ compounds are

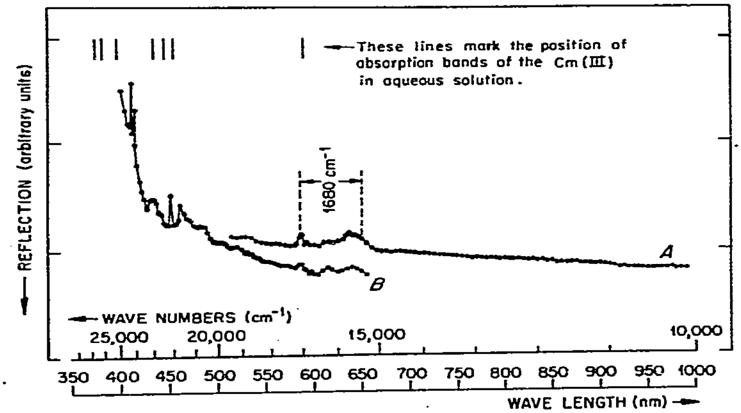

Fig. 1. Reflection spectrum of a microcrystalline sample of $^{248}Cm(C_5H_5)_3$ at room temperature. Curve A was taken with dry ice cooled S-1-surface photo detector; curve B was taken with an S-5-surface photo detector.

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* An = actinide(III); Ln = lanthanide(III).

** It should be noted that no crystal structure information is available yet for $La(C_5H_5)_3$, $Ce(C_5H_5)_3$, $Dy(C_5H_5)_3$, $Er(C_5H_5)_3$, or $Yb(C_5H_5)_3$.

properly placed in the same primarily ionic cyclopentadienide class as the $Ln(C_5H_5)_3$ compounds, and we conclude, therefore, that they should not be designated as cyclopentadienyls as has been the practice among various authors[1-4,6,7,10,14,15] in recent publications.

2. NEW DATA AND ANALYSIS OF $Cm(C_5H_5)_3$

In Fig. 1 we present the reflectance spectrum of $^{248}Cm(C_5H_5)_3$ measured from a colorless submicrogram crystal at room temperature[*,20]. The main features in this spectrum are: weak $f \rightarrow f$ lines in the 15,000–17,000 cm^{-1} region arising from the transition $J = 7/2$ (ground state)$\rightarrow J = 7/2$ (first excited state) with an unusually large ~ 1680 cm^{-1} ligand field splitting, and other weak to strong ligand-field split $f \rightarrow f$ transitions from 20,500 cm^{-1} to 25,000 cm^{-1} and beyond. Each of these line groups roughly matches the corresponding absorption line of Cm^{III}_{aq} in 1 M $HClO_4$ solution[21], drawn-in for reference at the top of Fig. 1, but the $Cm(C_5H_5)_3$ line groups are bathochromically shifted and ligand-field split to a greater extent due to the relatively low (~ 2.4) electronegativity[22] and resultant greater covalent-bonding tendency of the cyclopentadienide ligands.

Our attention focuses in Fig. 1 on the group of lines in the 15,000–17,000 cm^{-1} region, corresponding to the transition from the ground state to the first excited electronic state. This is the only group clearly isolated from neighboring groups so that the J quantum numbers for the transition are definitely identified. The observed line splittings here are undoubtedly due primarily to the ligand field splitting of the energy levels of the $J = 7/2$ first excited electronic state, since for Cm^{III} in $LaCl_3$ the corresponding splitting is known to be 100 times greater than the splitting of the relatively insensitive (nominal) $^8S_{7/2}$ ground state[23]. The baricenter of intensity of this group of lines in Fig. 1 is at 15,920 cm^{-1}; the baricenter of intensity for the corresponding Cm^{III} transition in 1 M $HClO_4$ solution is[21] at 16,830 cm^{-1}; and the 910 cm^{-1} difference between these band centers is due primarily to the nephelauxetic effect.

In order to treat the nephelauxetic effect on a convenient quantitative basis, Jørgensen[24] proposed the approximate relation:

$$\sigma - \sigma_{aq} = d\sigma - (d\beta)\sigma_{aq} \qquad (1)$$

where σ is the baricenter of intensity of an absorption line-group for the compound of interest, σ_{aq} is the corresponding σ for the aquo ion, $d\beta$ is one minus the nephelauxetic ratio, β, for the compound of interest relative to the aquo ion, and $d\sigma$ is a temperature-dependent correction term relating to the ground-J ligand-field energy levels and accounting for ligand-field-splitting differences and corresponding population differences between the compound of interest and the aquo ion[**].

Now β is defined as the ratio of an interelectronic repulsion parameter for the metal ion in the compound of interest to the corresponding interelectronic repulsion parameter for the metal aquo ion, or, more strictly, for the metal ion in vacuum.

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[*] The microscopic techniques we applied in taking the spectra presented here are described in another publication treating electron-transfer bands in the $Ln(C_5H_5)_3$ and $An(C_5H_5)_3$ series, *cf.* ref. 20.

[**] For a more precise discussion of the treatment of the nephelauxetic effect, see ref. 25.

Consequently, the main reason why eqn. (1) is not exact is because the two Landé parameters, ζ_{5f} and $\zeta_{5f}(\mathrm{aq})$, which account for spin-orbit-interaction-energy contributions to σ and σ_{aq}, respectively, are less sensitive to the environmental changes from the compound of interest to the aquo ion[26] than are the parameters of interelectronic repulsion, which also contribute to σ and σ_{aq}. Our approach to minimizing the effects of this approximation on the results we obtain here with eqn. (1) is to use it directly with the spectral data to get a first approximation to $d\beta$, in each case, and then attempt to set error limits on this by estimating the maximum uncertainty introduced by the ζ_{5f}- and $\zeta_{5f}(\mathrm{aq})$-dependent contributions.

In the present room-temperature work on $\mathrm{Cm(C_5H_5)_3}$ the ligand-field splittings of the ground electronic state are much less than kT so it is a good approximation to take $d\sigma = 0$. We then obtain a first approximation of $d\beta = 0.054$ from eqn. (1) and the spectral data above. Next we set error limits on this by estimating the maximum inaccuracy that can arise via spin-orbit interactions, by assuming ζ_{5f} to be unchanged in the two media and subtracting out its contribution in eqn. (1). Thus, examining the energy level diagram of $\mathrm{Cm^{III}}$[27] we see that the ground state has essentially no contribution from ζ_{5f} while the first excited $J = 7/2$ state is shifted downward by about 3000 $\mathrm{cm^{-1}}$ due to a ζ_{5f} contribution. Accordingly, if we make the limiting assumption that ζ_{5f} is the same in both media, its contribution is approximately the same in σ and σ_{aq}, so it subtracts out on the left side of eqn. (1) leaving its value unchanged at 910 $\mathrm{cm^{-1}}$ as before; but σ_{aq} on the right side must be changed to a value 3000 $\mathrm{cm^{-1}}$ higher at 19,830 $\mathrm{cm^{-1}}$. Then with the latter so modified in eqn. (1), we obtain the lower limit $d\beta = 0.046$ for the $\mathrm{Cm(C_5H_5)_3}$ nephelauxetic parameter.

In the first estimate of $d\beta$ above we implicitly assumed that the fractional change in ζ_{5f} between the two media was the same as for the interelectronic repulsion parameters, while in the second estimate we assumed that ζ_{5f} is unchanged between the two media. Since the actual change in ζ_{5f} must lie somewhere between these extremes, the two values for $d\beta$ above represent approximate upper and lower bounds,

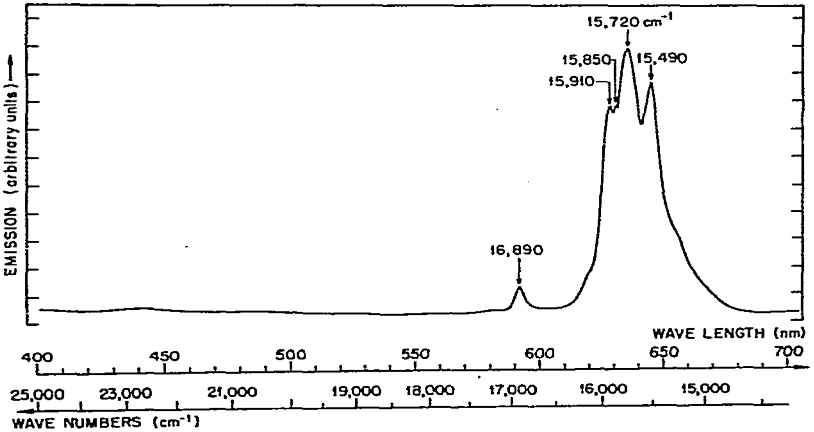

Fig. 2 Emission spectrum of $^{248}\mathrm{Cm(C_5H_5)_3}$-crystals (recorded about 4 h after sublimation of the complex; excited with 3600 Å radiation).

and so the best value for the $Cm(C_5H_5)_3$ nephelauxetic parameter is taken as the midpoint of these, or 0.050±0.004.

In Fig. 2 we present the room temperature UV-excited luminescence spectrum from several $^{248}Cm(C_5H_5)_3$ micro crystals. We see strong ligand-field-split lines corresponding to the transition from the first excited electronic state to the ground states; these make the crystal appear to glow red under UV excitation, as expected. The ligand field splitting here is essentially the same as in the absorption spectrum of Fig. 1, but the relative intensity of the high-energy line at 16,890 cm^{-1} is decreased due to population discrimination within the first-excited-state ligand-field energy levels, as accounted for approximately by metastable Boltzmann equilibrium among the populations of these states. Since the corresponding high-energy line in absorption in Fig. 1 is comparable in intensity to the neighboring strong lines, it is most likely that we deal here entirely with pure electronic transitions rather than with vibronic transitions, so the latter should not complicate our treatment.

3. PREVIOUS DATA AND ANALYSIS OF $Am(C_5H_5)_3$

Pappalardo, Carnall, and Fields' room temperature absorption spectrum[9] of sublimed thin films of $Am(C_5H_5)_3$ shows a distinct group of lines with a center of gravity at 18,849 cm^{-1} and a total ligand-field splitting of 1187 cm^{-1}. This group can be definitively assigned to the (nominal) $^7F_0 \rightarrow {}^5L_6$ transition. The corresponding absorption band for Am^{III}_{aq} is centered at 19,889 cm^{-1}, so $\sigma-\sigma_{aq}$ here for $Am(C_5H_5)_3$ is 1040 cm^{-1}. Also, since the ground state of Am^{III} is a $J=0$ level the first-order ligand-field splitting is zero and $d\sigma = 0$. Thus the first approximation for $d\beta$ is 0.052 according to the data above and eqn. (1), and for similar reasons as in the Cm^{III} case above this can be taken as a lower limit. We obtain an upper limit by noting from the Am^{III} energy level diagram[27] that the ground ($J=0$) state is depressed by about 6000 cm^{-1} due to ζ_{5f}-energy contributions while the terminal (nominal $^5L_6$)state is depressed by about 4000 cm^{-1} due to ζ_{5f}-energy contributions. If we make the limiting assumption that ζ_{5f} is the same in both media, as we did in the Cm^{III} case above, the left side of eqn. (1) remains approximately at 1040 cm^{-1} but σ_{aq} on the right side must be changed to a value 2000 cm^{-1} lower at 17,889 cm^{-1}. Then with the latter so modified in eqn. (1), we obtain the upper limit $d\beta = 0.058$. So the best value for the $Am(C_5H_5)_3$ nephelauxetic parameter is taken as the midpoint of the above values, or 0.055±0.003.

4. COVALENT CHARACTER IN THE CHEMICAL BONDS OF $Ln(C_5H_5)_3$ AND $An(C_5H_5)_3$ COMPOUNDS

Henrie and Choppin[29] and Tandon and Mehta[30] have recently discussed the combination of metal *f*-electrons with ligand electrons to form partial covalent bonds. They write the corresponding wavefunction as:

$$<\Phi_f| = (1-b)^{1/2} <f| - b^{1/2} <\Phi_{\text{ligands}}| \qquad (2)$$

where $b^{1/2}$, the covalency factor, is a measure of the amount of *f*-electron-ligand mixing, and they show that b is approximately one-half the nephelauxetic parameter $d\beta$. Now it is well known that the fractional covalency involved in an orbital represented by the type of wavefunctions as $<\Phi_f|$ of eqn. (2) can be interpreted as the square of the covalency factor, or approximately $d\beta/2$ from the relationship indicated above*. Therefore we can very simply approximate the percent f-electron covalency in the organometallic chemical bonds of $Ln(C_5H_5)_3$ and $An(C_5H_5)_3$ compounds from measurements of their nephelauxetic parameters.

TABLE 1

NEPHELAUXETIC PARAMETERS FOR SOME MEMBERS OF THE $Ln(C_5H_5)_3$ AND $An(C_5H_5)_3$ SERIES

M (atomic No.)	Nephelauxetic parameter, $d\beta$ (%)	Ref.
Pr (59)	5.0	16
Nd (60)	3.8	16
Er (68)	2.8	16
Am (95)	5.5 ± 0.3	Present work
Cm (96)	5.0 ± 0.4	Present work

In Table 1 we present the nephelauxetic parameters determined above for $Am(C_5H_5)_3$ and $Cm(C_5H_5)_3$ with those determined previously[16] for $Pr(C_5H_5)_3$, $Nd(C_5H_5)_3$, and $Er(C_5H_5)_3$. The corresponding percent covalency, relative to the metal aquo ions, for each of the above compounds is plotted against atomic number in Fig. 3, with one smooth curve for the $Ln(C_5H_5)_3$ series and another for the $An(C_5H_5)_3$ series. These curves are plotted so that each point on the abscissa corresponds approximately to equal radii for the Ln^{III} and An^{III} ions[34], rather than to equal numbers of f-electrons. This better illustrates the enhanced covalent bonding character of $5f$-electrons relative to $4f$-electrons, and it suggests the following procedure for extrapolating from the two presently known $Am(C_5H_5)_3$ and $Cm(C_5H_5)_3$ points through the entire $An(C_5H_5)_3$ series: For equal An^{III} and Ln^{III} radii the rate of change of the percent covalency with atomic number is assumed to be the same in both series. This assumption is somewhat arbitrary, but the few data points of Fig. 3 suggest such a trend, and it is not physically or chemically unreasonable; so in the absence of more information we apply it in Fig. 3 to obtain a first approximation for the other otherwise undetermined percent covalencies in the $An(C_5H_5)_3$ series.

The only other previously available $Ln(C_5H_5)_3$ points, in addition to those shown on the smooth curve in Fig. 3, are from the $Tm(C_5H_5)_3$ work of Fischer and Fischer[35]. These workers analyzed the room-temperature absorption spectrum of $Tm(C_5H_5)_3$ in benzene solution and concluded three possibilities for this nephelauxetic parameter, corresponding to cases (1a), (1b), and (2c) indicated in Fig. 3. On the basis of our smooth $Ln(C_5H_5)_3$ curve in Fig. 3, we would accept case (2a) and discard cases (1a) and (1b); however, a note of caution must be sounded here. Pappalardo[36] recently measured the absorption spectra of sublimed films of $Tm(C_5H_5)_3$ at 300° K, 78° K, and at 4° K, and he reports that the unusually large ligand-field splittings claimed by Fischer and Fischer are accounted for by "hot bands" in their room temperature spectrum. Since this disagreement has not been settled yet it is better to reserve judgement on the covalent character in the chemical bonding of $Tm(C_5H_5)_3$ until more work is done.

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* See ref. 31; for a good discussion of this LCAO–MO ligand-field approach to metallo-organic chemical bonding, see ref. 32; see also ref. 33 for a more detailed discussion of the approximations and resultant limitations involved in the relationship $b \sim d\beta/2$.

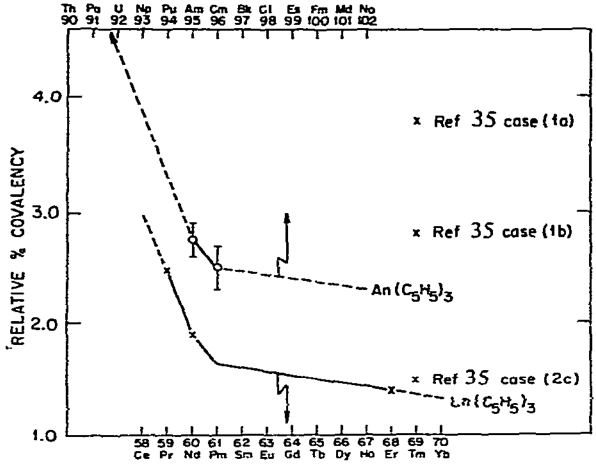

Fig. 3. The percent *f*-electron covalency in the chemical bonds of $An(C_5H_5)_3$ and $Ln(C_5H_5)_3$ compounds relative to the metal aquo ions. The dashed lines represent extrapolations.

5. CONCLUSION

From the results shown in Fig. 3 it appears that the covalency in the organometallic chemical bonds of the compounds of the $Ln(C_5H_5)_3$ and $An(C_5H_5)_3$ series is in every case less than 5% and in most cases less than 3%. Although these are percent covalencies relative to the metal aquo ions, judging from the Pr^{III}_{aq} case where the aquo ion covalency relative to the free metal ion is less than 2%[37], the actual absolute covalencies should not in any case be any more than 1 or 2% greater than those of Fig. 3. Thus there is very little justification for continuing to classify the compounds of either of these series as tricyclopentadienyls. The present evidence indicates that they are all highly ionic so they should be classified as tricyclopentadienides under similar designations as Cotton and Wilkinson give for the members of the $Ln(C_5H_5)_3$ series.

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