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Proton Magnetic Resonance Spectra of Some Actinide β-Diketone Complexes

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The nmr spectra of several actinide β-diketone complexes have been obtained in chloroform solution. As opposed to the solid-state structure, the structure in solution of the thorium and uranium dibenzoylmethane complexes is an undistorted square antiprism. Using the ligand 1-phenyl-1,3-hexanedione, the isotropic shifts of the uranium complex were separated into a pseudocontact shift and a contact shift. The contact shift was related to spin delocalization *via* the π orbitals indicating the interaction of the f orbitals with these β-diketone ligands. The spin delocalization is a small effect being only about one-fifth of that observed for the transition metal ions.

Introduction

The β-diketone complexes of the actinide elements are of considerable interest. They have been used in solvent extraction procedures,[2a] the volatility of some of these compounds may make them useful in fractional sublimations,[2b] and it has been reported that they have high thermal and radiation stabilities suggesting their use as organic moderators.[3] Recently, intramolecular energy transfer has been observed in several actinide β-diketone complexes and these have potential applications as liquid lasers.[4]

A considerable amount of useful knowledge about the stereochemistry, electronic structure, and magnetic properties of complexes can be obtained from a study of the nuclear magnetic resonance spectra of paramagnetic metal complexes. Since the required condition for the observation of the nmr spectra of paramagnetic molecules, namely, T_1^{-1} or $T_e^{-1} \gg A_n$, is generally satisfied with the nickel and cobalt complexes, the isotropic shifts of complexes involving these ions have been extensively studied. In addition to studying electron delocalization in several ligand systems,[5-7] the nature of the base adducts with nickel and cobalt acetylacetonates[8] and ion pairing in some anionic nickel and cobalt complexes[9] have been investigated.

It is generally accepted that the β-diketone chelate ring is a conjugated system[10] and that unpaired spin density from the paramagnetic transition metal is transferred throughout the ligand.[11] With the rare earth and actinide ions, however, it is generally stated that the f orbitals are well shielded by the outer s and p orbitals and do not participate in bonding. In the rare earth–dibenzoylmethane complexes Burkert, *et al.*,[12] failed to observe a contact shift substantiating the failure of the f electrons to participate in bonding.

Moeller[13] studied the rare earth–EDTA complexes and, from their magnetic susceptibilities and absorption spectra, concluded that no covalent bonding occurred in these complexes. Hart, Shaw, and Newberry[14] drew the same conclusions from an nmr study of the rare earth–2,2′-bipyridyl complexes. Large chemical shifts were observed in the nmr spectrum of the uranium diethyldithiocarbamate complex; however, the nature of these shifts was not discussed.[15]

The present report describes the nmr spectra of several thorium and uranium β-diketone complexes. The isotropic shift observed is separated into the respective contact and pseudocontact terms.

Experimental Section

Ligands.—Dibenzoylmethane (HDBM) was purchased from City Chemical Corp. and used as received.

1-Phenyl-1,3-hexanedione (Hphd) was prepared by a Claisen condensation of acetophenone and ethyl butyrate. Sodium methoxide (0.75 mol) was prepared by dissolving 17.23 g of sodium in methanol and then removing the excess methanol. A slurry was prepared using 300 ml of diethyl ether. After adding 87 g (0.75 mol) of ethyl butyrate to the slurry over a period of 2 hr, it was refluxed for 1 hr. After cooling, 90 g of acetophenone (0.75 mol) was added dropwise over a period of 2.5 hr. The dark brown solution was neutralized with 2 *N* H_2SO_4 and the ether fraction was separated. After the aqueous layer was washed with several portions of ether and the ether fractions were combined, the ether was removed by distillation. The straw yellow ligand was obtained by vacuum distillation with the fraction distilling between 160 and 170° (~20 mm) being collected (lit.[16] bp 167–170° (20 mm)).

1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyl-4,6-octanedione (Hfod) was also prepared by a Claisen condensation. Ethyl heptafluorobutyrate and pinacolone were allowed to react according to the procedure of Scribner,[17] and the fraction distilling between 35 and 45° (~20 mm) was collected. The initial distillate was clear but it soon developed a pale yellow tinge even when stored at ice temperature in a dark bottle. The nmr spectrum showed no impurity, however, and the ligand was used without further purification.

M(DBM)₄.—The dibenzoylmethane complexes of thorium

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[1] Mound Laboratory is operated by Monsanto Research Corp. for the U. S. Atomic Energy Commission under Contract No. AT-33-1-GEN-53.

[2] (a) J. Rydberg, *Arkiv Kemi*, **9**, 95 (1955); (b) C. Springer, D. Meek, and R. Sievers, *Inorg. Chem.*, **6**, 1105 (1967).

[3] A. Comyns, Great Britain Atomic Energy Research Establishment Report C/M-320, Harwell, Berks, England, 1957.

[4] L. Nugent, *et al.*, paper presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

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[16] F. Swamer and C. Hauser, *J. Am. Chem. Soc.*, **72**, 1352 (1960).

[17] W. Scribner, Report MRC-DA-141, Monsanto Research Corp., Dayton, Ohio, 1967, p 40.

TABLE I

ANALYTICAL RESULTS OF Th AND U COMPLEXES

Compound	Color	Mp, °C	% C Calcd	% C Found	% H Calcd	% H Found	% M Calcd	% M Found	Mol wt Theoret	Mol wt Exptl	$10^6\chi$
$Th(DBM)_4$	Yellow	198–200[a]	...	...	...	...	...	...	1124	1060	Diamag
$U(DBM)_4$	Dark brown	200–202[b]	...	...	...	...	...	...	...	...	2015
$Th(phd)_4$	Cream	96–98	58.30	57.12	5.30	5.31	23.46	23.36	989	980	Diamag
$U(phd)_4$	Brown	106–108	57.94	56.81	5.27	5.24	23.92	23.80	...	...	2020
$Th(fod)_4$	White	147–148	34.01	34.27	2.85	2.88	16.42	15.96	1413	1280	Diamag
$U(fod)_4$	Olive-brown	148–150	33.86	33.93	2.84	2.82	16.78	16.37	...	...	2045

[a] Lit.[17] mp 196° dec. [b] Lit.[17] mp 198–200°.

and uranium were prepared according to the method of Forsling.[18] Both compounds were recrystallized from CCl_4 and their melting points agree with those reported in the literature.

M(phd)$_4$.—The thorium complex with 1-phenyl-1,3-hexanedione was prepared by neutralizing an alcoholic solution of 0.55 g (1 mmol)) of $Th(NO_3)_4 \cdot 5H_2O$ and 0.76 g (4 mmol) of Hphd with NH_3 in ethanol. After the precipitate had dried, it was recrystallized by dissolving it in a minimum of toluene and then adding hexane until precipitation appeared imminent. The complex was crystallized by cooling the solution to Dry Ice temperature with rapid stirring to prevent the complex from simply oiling out. The uranium complex was prepared similarly using UCl_4.

M(fod)$_4$.—The thorium and uranium complexes of 1,1,1,-2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione were prepared by dissolving 1 mmol of the respective metal salts in a minimum of alcohol. After adding 4 mmol of Hfod, the alcoholic solution was diluted with a large excess of water. The complexes which immediately precipitated were collected by filtration, vacuum dried, and recrystallized from ethanol.

Physical Measurements.—The nmr spectra of deuteriochloroform solutions of the metal complexes were obtained on a Varian Associates HA-60 spectrometer. The spectra were standardized using TMS and in several cases were checked with $CHCl_3$.

The C and H analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and the metal analyses were determined in this laboratory either by igniting to the metal oxide or by spectrophotometry. Melting points were obtained with a Mel-Temp apparatus and are reported uncorrected. Molecular weights were determined with a Perkin-Elmer Hitachi vapor pressure type of molecular weight instrument on chloroform solutions using benzil as the standard. Infrared spectra were obtained using a Beckman IR-12. Magnetic moments were obtained by the Faraday method using $Hg[Co(SCN)_4]$ as the standard.

Results

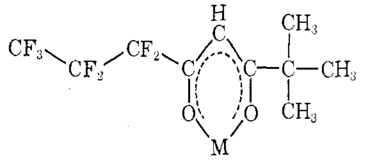
The dibenzoylmethane complexes of thorium and uranium have been previously reported and were therefore characterized only by their melting points. The analytical data for the thorium and uranium complexes of phd and fod are presented in Table I. Molecular weights of the uranium complexes could not be determined since oxidation to the uranium(VI) complexes apparently occurred on the thermistor. The failure to observe the asymmetric stretching peak of the uranyl group in the infrared spectrum indicated that oxidation did not occur upon simply dissolving the complexes, even after standing for several hours.

The nmr spectra of the $Th(phd)_4$ and $U(phd)_4$ complexes are shown in Figures 1 and 2 with the assignments indicated. The nmr spectra of the free ligands were the same as those of the thorium complexes with shifts of several cps observed. In the alkyl region the α and γ protons are triplets, split by the two β protons with relative areas of 2:3, while the β proton is a multiplet (sextet) split by the five α and γ protons and has the same area as the α-proton peak. In the aromatic region of the thorium complex there are two sets of peaks with the one at lower field having a relative area of 2 and corresponding to the *ortho* proton, and the multiplet at higher field corresponding to the *meta* and *para* protons with a relative area of 3. This assignment is in agreement with the aromatic region of benzoylacetone as given by Horrocks and Kluiber.[19]

The uranium complex shows large shifts for all of the protons. By comparison to the uranium dibenzoylmethane complex the aromatic protons can be assigned to the three peaks to the immediate left of TMS. The relative areas from low- to high-field strength are 1:2:2. Allowing splitting only by adjacent protons, one would expect a doublet for the *ortho* proton and triplets for the *meta* and *para* protons. The assignments are therefore straightforward.

The alkyl protons in the uranium complex have the same splitting pattern as the thorium complex, but the peaks are all shifted upfield from TMS. The assignments were made by the splitting patterns and the relative areas of 3:2:2 for the peaks from low field to high field.

The $Th(DBM)_4$ and $U(DBM)_4$ complexes exhibit spectra corresponding to the aromatic region of $Th(phd)_4$ and $U(phd)_4$, respectively. From the structure of the fod complexes only one peak due to the *t*-butyl group is expected and observed.



The chemical shifts for the complexes and ligands are given in Table II. The isotropic shifts, ΔH, for the uranium complexes are also given. The term ΔH is defined as the shift of the paramagnetic ion minus the shift of the diamagnetic ion with the thorium complex used as the diamagnetic ion so as to eliminate any coordination effects.

Discussion

Wolf and Barnighausen[20] have found the crystal structure of $U(DBM)_4$ and $Th(DBM)_4$ to be isomorphic

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[18] W. Forsling, *Acta Chem. Scand.*, **3**, 1133 (1949).

[19] R. Kluiber and W. D. Horrocks, *Inorg. Chem.*, **6**, 166 (1967).

[20] V. Wolf and W. Barnighausen, *Acta Cryst.*, **13**, 778 (1960).

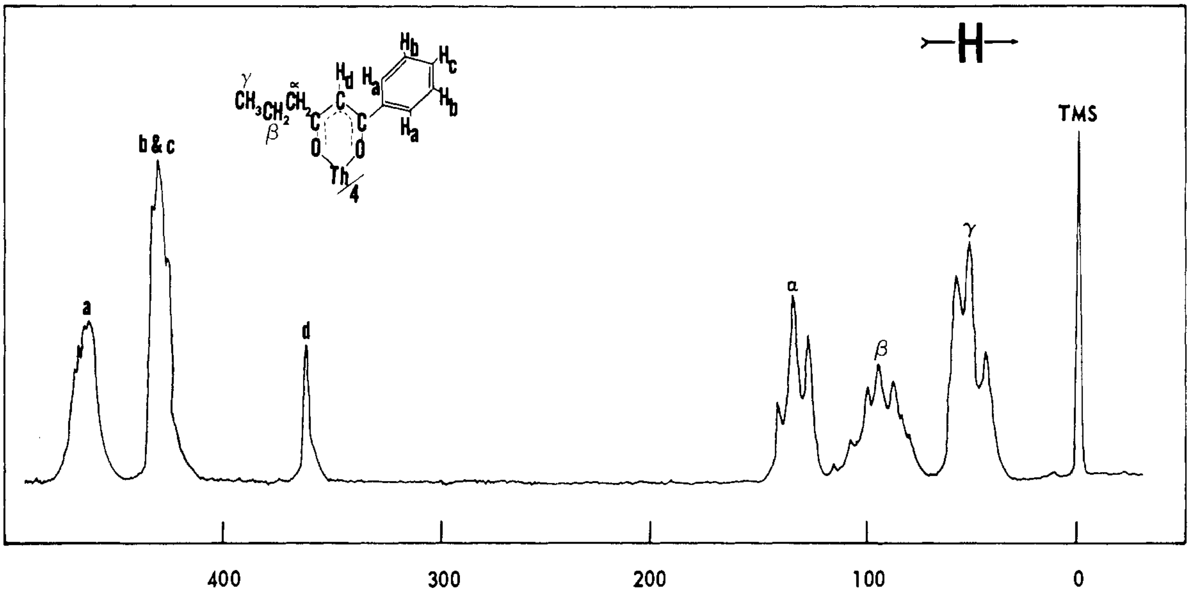

Figure 1.—The nmr spectrum of Th(phd)$_4$ with assignments indicated in cps.

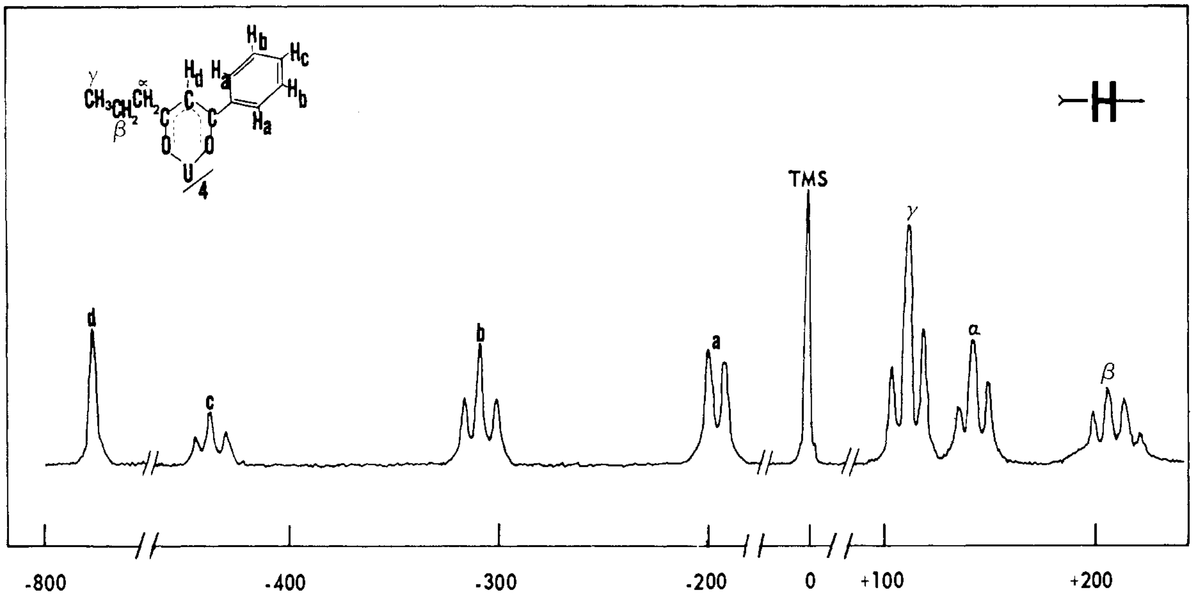

Figure 2.—The nmr spectrum of U(phd)$_4$ with assignments indicated in cps.

Table II

Chemical Shifts and Contact Shifts of Some β-Diketone Ligands and Their Thorium and Uranium Complexes

Compound	Shift[a] H_0	ΔH_0[b]	Shift H_m	ΔH_m	Shift H_p	ΔH_p	Shift $H\alpha$	$\Delta H\alpha$	Shift $H\beta$	$\Delta H\beta$	Shift $H\gamma$	$\Delta H\gamma$	Shift H_{CH}	ΔH_{CH}
HDBM	−480	...	−448		−448		...		...		...		−410	...
Th(DBM)$_4$	−482		−440		−440		...		...		...		−410	...
U(DBM)$_4$	−143	+339	−293	+147	−433	+7	...		...		...		−809	−399
Hfod[c]	...		...		...		...		−75		...		−359	
Th(fod)$_4$	...		...		...		...		−69		...		−369	
U(fod)$_4$	...		...		...		...		+272	+341	...		−772	−403
Hphd	−472		−442		−442		−141		−101		−56		−367	
Th(phd)$_4$	−471		−440		−437		−136		−97		−52		−366	
U(phd)$_4$	−210	+261	−321	+119	−448	−11	+148	+284	+216	+313	+118	+170	−774	−408

[a] All data are given in cps. The spectra were obtained at 60 Mcps. [b] $\Delta H = H$(paramagnetic) − H(diamagnetic). [c] Values obtained from ref 2b.

and they called the 8-coordinate structure "bis-diphenoid." It may be better described as a distorted square antiprism with each bidentate ligand coordinated to one corner of both square faces with opposite ligands moved up from a mean plane and the remaining pair of ligands moved down from a mean plane parallel to the square faces. The resulting structure has only a twofold axis of rotation and not a fourfold axis which exists in the undistorted square antiprism. Furthermore, in this structure the phenyl rings may be divided into two nonequivalent sets.

The nmr spectrum, however, indicates that, at least in chloroform solution, all of the phenyl rings are equivalent. This may be achieved by forming a perfectly square antiprism where all of the phenyl rings occupy equivalent positions or by a rapid inversion of the distorted structure. However, even if the latter possibility were to prove correct, the average position of each atom would be exactly that of a square antiprism and thus, in future calculations, the square antiprismatic structure will be used as a model for the structure of $U(DBM)_4$ in solution.

The crystal structure also shows the two phenyl rings to be coplanar with the chelate ring and in this rigid position the two *ortho* protons are no longer equivalent. However, since only one signal is observed for the *ortho* protons, the phenyl ring must be rapidly rotating between equal conformers. Thus, the *meta* protons will also be equivalent and only one signal will appear. This situation was also observed in the benzoylacetone complexes of nickel and cobalt.[19]

The structure of the phd and fod complexes are assumed to be the same as that of the DBM complex. This assumption is probably valid since the acetylacetonates also have been shown to have this structure.[21] The nmr spectrum indicates a highly symmetrical structure with all similar protons being equivalent. With these unsymmetrical ligands several possible conformations of the ligands fit the data. However, the conformation of each ligand is not important; it is only important that the over-all structures of these compounds are the same as for the DBM complexes.

Figure 1 shows some rather large isotropic shifts for the ligand protons in the uranium complexes. Isotropic nuclear resonance shifts may be divided into two types: contact shifts and pseudocontact shifts. The contact interaction gives rise to a shift in the resonance from the diamagnetic position due to the presence of unpaired spin density at the resonating nucleus. This spin density may be transmitted through either σ or π orbitals. In an odd-alternant system unpaired spin density in the π orbitals gives alternating positive and negative spin densities at the nucleus and, thus, alternating upfield and downfield nmr contact shifts. The delocalization of spin density in σ orbitals gives rise to shifts in only one direction and these shifts attenuate rapidly as the number of bonds increases.

The nature of the contact shift is well understood and may be described by

$$\left(\frac{\Delta H}{H}\right)_i = -A_i\frac{\gamma_e}{\gamma_H}\frac{g\beta S(S+1)}{3kT} \qquad (1)$$

where A_i is the isotropic hyperfine contact interaction for the ith proton, g is the spectroscopic splitting factor, β is the Bohr magneton, γ_e and γ_H are the gyromagnetic ratios for the electron and proton, respectively, and S is the total spin quantum number. The A_i term is a measure of the amount of spin density at the ith proton which, for delocalization in π systems, may be related to the unpaired spin density, ρ_i, by

$$A_i = \frac{Q_{CH}\rho_i}{2S} \qquad (2)$$

In this equation Q_{CH} is an experimental constant.

A pseudocontact shift may result if the dipolar interaction between the net electron spin magnetization and the proton fails to average to zero. The metal will then possess an anisotropic g factor. The pseudocontact interaction for a solid may be expressed by[22]

$$\left(\frac{\Delta H}{H}\right)_i = -\frac{1}{3N}(K_\parallel - K_\perp)\frac{3\cos^2\psi_i - 1}{r_i^3} \qquad (3)$$

where $K_\parallel$ and $K_\perp$ are the principal molar susceptibilities parallel and perpendicular to the ligand field axis, ψ_i is the angle between this axis and a radius vector to the proton in question, and r_i is the length of this vector. In a complex containing several protons $i, j, \ldots,$ the distribution of these shifts can be described solely in terms of the molecular geometry

$$\left(\frac{\Delta H}{H}\right)_i : \left(\frac{\Delta H}{H}\right)_j : (\ldots) = \frac{3\cos^2\psi_i - 1}{r_i^3} : \frac{3\cos^2\psi_j - 1}{r_j^3} : (\ldots) \qquad (4)$$

Since the crystal structure of the uranium and thorium complexes with dibenzoylmethane is known, the geometric factors for each proton can be calculated and the relative pseudocontact shifts for the *ortho*, *meta*, and *para* protons can be determined. Although there are several structures which fit the solution spectra, the crystal structure shows that, to a first approximation, the average position of the *ortho* protons and the average position of the *meta* protons and the position of the *para* proton lie on a line passing through the metal atom. Thus, for any structure fitting the spectra the angle ψ for these protons may be taken to be the same and the ratios of the pseudocontact shifts are dependent only on the reciprocal of the distance cubed of the protons from the metal atom. From the information listed in Table III, which shows the calculated pseudocontact shift ratios and observed isotropic ratios, it can be seen that the entire observed isotropic shift is not due to a pseudocontact contribution.

It must be remarked that the crystal structure does indicate a variation of several degrees for ψ for the *ortho*, *meta*, and *para* protons. If the crystal field axis is taken to be the fourfold rotation axis bisecting the two square faces, there is a difference in ψ of less than 5°. Unfortunately, if the crystal field axis is used as defined above, the protons are so situtated that the numerator of the geometrical factor is extremely small and a small change in ψ appears to cause an extremely large change in the geometrical factor.

To determine the actual angular dependency, the β

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(21) D. Grdenic and B. Matkovic, *Nature*, **182**, 465 (1958).

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TABLE III

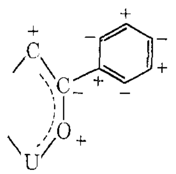
ISOTROPIC SHIFT DATA[a]

	PCS ratios[b]	Obsd isotropic shift ratios		PCS[c]	CS[d]	ρ[e]
			U(phd)$_4$			
p/o	0.226	−0.042	*o*	313	−52	−0.00039
m/o	0.344	+0.440	*m*	107	+12	+0.000089
p/m	0.654	−0.096	*p*	71	−84	−0.00063
			U(DBM)$_4$			
p/o	0.226	0.021	*o*	391	−52	−0.00039
m/o	0.344	0.430	*m*	135	+12	+0.000089
p/m	0.654	0.048	*p*	88	−81	−0.00061

[a] All shifts are given in cps at 60 Mcps. [b] Calculated pseudocontact shift. [c] Pseudocontact shift contribution. [d] Contact shift contribution. [e] Unpaired spin desntiy.

protons of the phd complexes may be compared to the methyl protons of the fod complexes. Since the fod complex contains the bulky heptafluoropropyl substituent at one end of the ligand, a difference in the angle ψ for the methyl groups in this complex from the angle ψ for the β protons in the phd complex most likely exists. Yet there is only a 10% change in the value of the observed isotropic shift. A comparison of isotropic shifts of one molecule to another may be tenuous owing to differing dissociation constants; however, since these are extremely small, this effect would cause only a small change of the shift compared to the fivefold change predicted for a 1° change of ψ in the geometric factor for these protons. Thus, it appears that there is no strong angular dependence on the pseudocontact term, and the approximation of a constant angle for the aromatic protons is valid.

If the observed and calculated ratios of the isotropic shifts in Table III are compared, an upfield bias is noted for the *meta* proton and a downfield bias is noted for the *ortho* and *para* protons. This is the expected pattern of shifts for spin delocalization *via* ligand π orbitals. This same pattern has been observed for the similar phenyl isocyanide ligand.[23] Thus, the observed isotropic shifts appear to be a result of a combination of a pseudocontact interaction and a contact interaction involving the π orbitals



It is interesting to note that the theory for the pseudocontact shifts predicts a large negative shift for the chelate ring CH proton and this is exactly what is observed.

Electron delocalization may occur by either of two mechanisms. According to the calculations of Eaton[11] for acetylacetonates metal to ligand transfer of α spin results in a large positive spin density at the carbon bearing the phenyl group while ligand to metal charge transfer results in a small spin density of indeterminate sign. The apparent spin delocalization mechanism is thus ligand to metal which is opposed to that observed for the transition metal acetylacetonates.

In order to calculate spin densities at a given carbon atom it is necessary to separate the contact contribution from the observed isotropic shift. If the phd complex is considered completely symmetrical, *i.e.*, ψ for the β proton is the same as ψ for the *ortho* proton, then the pseudocontact shift for the β proton (the observed isotropic shift assuming no σ-bond contact shift is present) can be related to the pseudocontact shift of the *ortho* proton, and hence also the *meta* and *para* protons. The phd complexes are probably symmetrical since the "bulkiness" of the phenyl ring and isopropyl group are nearly equal, and, although a very small σ-bond shift appears to exist for the α protons, it is probably negligible for the β proton since this effect attenuates rapidly. The isotropic pseudocontact shifts calculated in this manner are presented in Table III along with the contact contribution and unpaired spin density.

One cannot expect to use the pseudocontact value of the phd complex for the pseudocontact contribution of the DBM complex since dissociation may average the isotropic shifts with the shifts of the free ligand. However, the ratios of the pseudocontact shifts for the *ortho*, *meta*, and *para* protons and the ratios of the unpaired spin densities at these positions should remain constant from one complex to the other. Using these facts, the pseudocontact shifts and contact shifts were calculated for the DBM complex and these results are also listed in Table III.

The observation of a contact shift implies that the electron spin has been delocalized from the metal to the ligand. It appears to be established that the unpaired electrons in actinide ions are in f orbitals[24] and from this study it is concluded that f orbitals are involved in the bonding scheme of actinide compounds. If the splitting of the sevenfold degenerate set of f orbitals in a cubic field is considered, the lowest energy orbitals, $f_{z(5z^2-3r^2)}$, $f_{y(5y^2-3r^2)}$, and $f_{x(5x^2-3r^2)}$, which contain the unpaired electrons, are π-bonding orbitals. Qualitatively, π bonding involving f orbitals is possible. Bearing in mind that the DBM has two phenyl rings over which to delocalize unpaired electrons, the results indicate that these complexes are slightly more efficient in spin delocalization. This delocalization is, however, only about one-fifth of that observed for transition metals.[19]

Using eq 3 it is theoretically possible to calculate the *g* factor from this data; however, the exact form of the molar susceptibility for these uranium complexes is still uncertain. It is certainly true that the common practice of using a spin-only Curie law is not valid,[25] and therefore this calculation was not performed.

Conclusions

The remarkably good consistency between the two ligand systems attests to the validity of the method

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[23] W. D. Horrocks, R. Taylor, and G. LaMar, *J. Am. Chem. Soc.*, **86**, 3031 (1964).

[24] G. Gandila, C. Hutchison, and W. Lewis, *J. Chem. Phys.*, **30**, 246 (1959).

[25] J. Day and L. Venanzi, *J. Chem. Soc.*, *A*, 197 (1966).

used in this study. Although there may be a fairly large error associated with the quantitative calculations, one may see a good qualitative description of the bonding involved in these actinide β-diketone complexes. The f orbitals which have been considered to be inert as far as bonding is concerned have now been shown to be involved in bonding schemes.

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CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORIES,
AJINOMOTO COMPANY, INC., KAWASAKI, JAPAN

Spectroscopic Studies on Coordinated Acetylene

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The structure and bonding of acetylene in $CH\equiv CHCo_2(CO)_6$ was studied by means of spectroscopic methods. The assignments of the infrared absorption bands were established unequivocally by the use of some isotope-substituted molecules: $CH\equiv CDCo_2(CO)_6$, $CD\equiv CDCo_2(CO)_6$, and $^{13}CH\equiv CHCo_2(CO)_6$. The frequency of the C≡C stretching vibration of coordinated acetylene was found to be lower than that of free acetylene by about 570 cm^{-1}, and such a marked change in the vibrational frequency implies a large distortion of the coordinated acetylene from its free state. A structure with the C_{2v} symmetry of coordinated acetylene can well explain the observed infrared and nmr spectra. The similarity of the vibrational spectrum of coordinated acetylene to the electronically excited molecule is suggested, and the nature of the bond between acetylene and cobalt is discussed.

Introduction

The reaction of acetylene with cobalt carbonyl has been studied by many investigators.[1,2] In these reactions, $CH\equiv CHCo_2(CO)_6$ is one of the most frequently encountered complexes. In the present study, we attempted to obtain information on the molecular structure of the acetylene molecule in such a complex. Greenfield and his coworkers[3] observed infrared spectra of $CH\equiv CHCo_2(CO)_6$ and discussed the possible structures. This assignment of the absorption bands, however, was not conclusive. Sly[4] showed that the diphenylacetylene of $C_2(C_6H_5)_2Co_2(CO)_6$ has a nonlinear structure from X-ray analysis. However, information on the structure of acetylene itself, instead of diphenylacetylene, is still wanted.

We have observed not only the infrared and nmr spectra of the complex $CH\equiv CHCo_2(CO)_6$ itself, but also those of $CH\equiv CDCo_2(CO)_6$, $C\ \equiv CDCo_2(CO)_6$, $^{13}CH\equiv CHCo_2(CO)_6$, and $CH\equiv CHCo_2(CO)_5P(C_6H_5)_3$. On the basis of these observations, unequivocal assignments of the absorption bands of the acetylene molecule have been established. A number of definite conclusions on the structure of the acetylene molecule are now drawn from such assignments. Comparison of the vibrational frequencies in the coordinated state with those in the electronically excited state seems to be very interesting.

Results and Discussion

Assignment of Infrared Spectra.—Figure 1 illustrates the infrared spectrum of $CH\equiv CHCo_2(CO)_6$ from 4000 to 200 cm^{-1}. The five strong bands observed at 2097.8, 2058.5, 2033.7, 2028.1, and 2016.6 cm^{-1} can be assigned to the C≡O stretching mode,[3] a series of bands in the far-infrared region to metal–ligand vibrations, and progressions from 2300 to 2600 cm^{-1} to their combination bands. A comparison of $CH\equiv CHCo_2(CO)_6$, $CH\equiv CDCo_2(CO)_6$, and $CD\equiv CDCo_2(CO)_6$ (Figure 2) shows that the bands at 3116.0 (m), 3086.0 (m), 1402.5 (s), 894.0 (s), and 768.0 (s) cm^{-1} are due to the coordinated acetylene. Judging from isotope shifts given in Table I, 3116.0 (m) and 3086.0 (m) cm^{-1} can be assigned to CH stretching modes, the band at 1402.5 (s) cm^{-1} is almost a pure C≡C stretching mode (Figure 3), and the bands at 894.0 (s) and 768.0 (s) cm^{-1} can be assigned to CH bending modes (Figure 4), respectively. In the far-infrared region (Figure 4), two absorptions at 605.0 and 551.0 cm^{-1} must be due to the acetylene–cobalt bond on the basis of their shifts.

Broad 1530-cm^{-1} bands may be tentatively assignable to difference bands between C≡O stretching bands and metal–ligand bands since the above-mentioned combination bands from 2300 to 2600 cm^{-1} show considerable intensity.

Symmetry of the Coordinated Acetylene Molecule.—The appearance of two CH stretching modes and one C≡C stretching mode in the infrared spectrum suggests that the symmetry of the coordinated acetylene is lower than that of free acetylene, that is, C_{2v}, C_{2h}, C_2 (Figure 5), or asymmetric. In the nmr spectrum of the complex, the acetylene protons show a singlet signal at δ −4.0 ppm; therefore the possibility of the asymmetric structure can be eliminated.

Furthermore, infrared and nmr spectra of the mono-triphenylphosphine-substituted complex $CH\equiv CHCo_2(CO)_5P(C_6H_5)_3$ were examined. In the infrared spec-

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