complex occurs at a rate 0.22 that found with glycine. The reason for this decrease is ambiguous. The presence of the bulky ethanol groups may act as a steric hindrance; or, as suggested by Chaberek, *et al.*,[14] the mono complex might be tridentate and the slower rate of reaction would then be due to the longer time required to form a tridentate chelate compared with a bidentate chelate. Formation of the bis complex with bicine occurs at a rate ~0.03 that seen with glycine. This may be due to the necessity for displacement of one of the coordinating groups of a tridentate mono complex to form the bis-bidentate chelate, which could result in a very substantial decrease in the rate of bis complex formation. An alternative explanation may be found in a close examination of the crystal structure of Cu(II) α-amino acid complexes.[9] In these complexes, Cu(II) is coordinated to a carboxyl oxygen and the amino nitrogen. Groups on the α carbon, such as is found in α-alanine, glutamic acid, and histidine, all point in a direction away from the nitrogen and oxygen bonds. Thus, substitutions on this carbon would not be expected to have large effects on chelation rates. Indeed, this has been confirmed experimentally. On the other hand, the amino nitrogen is directly involved in the chelate bond. Bulky groups attached to this atom might lie in a direction that would interfere with the addition of a second chelate. The magnitude of steric effects on the formation rate constants would depend not only upon the nature of the bulky group introduced into the molecule but also upon the position of such a group in relation to the location of the bonds formed.

The *reverse* rate constants, k_{nr}, are generally obtained from the forward rate constants and the corresponding stability constant. As a consequence, they could be inaccurate due to the resulting accumulation of errors. Nevertheless, some interesting differences and comparisons are to be seen in Table III. The bis complexes generally dissociate more rapidly than the corresponding mono complexes (sarcosine appears to be an exception). If one examines the effect of aliphatic substituents on the α carbon, it is seen that the values of k_{1r} for glycine, alanine, leucine, and valine decrease progressively, paralleling the behavior of k_{1f}. The monosarcosine complex is less stable than that of glycine, presumably due to distortions produced by the presence of the CH_3 group on the nitrogen. This effect should be still more evident in bicine if the alcohol groups did not participate in binding. The fact that k_{1r} is *less* is consistent with the possibility mentioned earlier, *viz.*, that the ethanolic OH groups are participating in the chelate, thus increasing the stability of the complex. Further support for this hypothesis is provided by comparing the values of k_{2r} for sarcosine and bicine: that for bicine is in this case much larger, indicating the presence of repulsive effects which are not compensated for by binding of the OH groups. For the series of aliphatic α substituents, the order for k_{2r} is gly > ala > leu, val. If, as suggested earlier, the rate constants for the second step reflect the rate of inversion of axial–equatorial water molecules, then the value of k_{2r} would be expected to decrease as the α substituents become larger.

In conclusion, we have studied the formation of Cu(II) with two sterically hindered amino acids. These data, when compared with values from other laboratories as well as previous work in this laboratory, allow several conclusions to be reached. First, there is a small but definite reduction of k_{1f} as steric hindrance increases. Such effects on k_{1f} values are relatively small, amounting to a factor of 4 or less. Second, for bis complexation, these effects are considerably larger than for the formation of the mono complex and approach reductions of two orders of magnitude. Finally, substitution on the amino nitrogen is much more effective in reducing k_{2f} than substitution on the α carbon.

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Registry No. Cu(glycine)$_2$, 13479-54-4; Cu(α-alanine)$_2$, 14263-10-6; Cu(L-valine)$_2$, 14267-13-1; Cu(bicine)$_2$, 39465-57-1.

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Covalency Effects on the Ligand Field Splittings of Octahedral 5f^1 Compounds[1]

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Optical spectra have been recorded for $(NEt_4)_2PaCl_6$ and $(NEt_4)_2PaBr_6$ (0.4–2.2 μ) and the experimental results interpreted in terms of two ligand field parameters and the spin–orbit coupling constant. Similar interpretations are provided for data available on uranium(V)-hexahalogeno complexes and NpF_6. Trends in the ligand field parameters can be explained qualitatively in terms of molecular orbital theory with large variations in σ bonding dominating the total ligand field splittings as the halide ion is varied.

Introduction

Over the past 30 years the problem of covalency in d transition metal complexes has been thoroughly studied both theoretically and experimentally.[2] For octahedral complexes the simple model of d-electron orbitals interacting with ligand orbitals within a molecular orbital framework has proved useful since it enables parameters which describe the bonding in the complex to be determined from experimental data.

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[1] This work was supported by the U. S. Atomic Energy Commission.

[2] J. Owen and J. H. M. Thornley, *Rep. Progr. Phys.*, 29, 675 (1966).

This same model has been applied to f transition ions in octahedral symmetry but there have been very few experimental measurements.[3,4] We have now obtained the optical spectra of two octahedral Pa(IV) compounds. The results, combined with earlier measurements by Ryan[5] and others[6,7] on U(V) complexes and the analysis of spectral data available[3a] for NpF_6, have enabled us to provide a preliminary, qualitative analysis of the trends in bonding in these $5f^1$ compounds.

Experimental Section

$(NEt_4)_2PaCl_6$ and $(NEt_4)_2PaBr_6$ ($Et = C_2H_5$) were prepared as reported previously.[8] Absorption spectra were recorded with a Cary Model 14 spectrophotometer using the technique recently described elsewhere.[9] Spectra were recorded for $(NEt_4)_2PaCl_6$ at 85, 300, and 500 K and for the hexabromo analog at 77 and 300 K.

Results and Discussion

The spectra obtained for $(NEt_4)_2PaCl_6$ are illustrated in Figure 1, and the measured peak positions and assignments for this compound and for $(NEt_4)_2PaBr_6$ are listed in Table I. The estimated accuracy of measurement is ±20 Å. The two groups of peaks at *ca.* 1.7 μ were present in the spectrum of NEt_4Cl and in that of $(NEt_4)_2UCl_6$ and are attributed to transitions within the tetraethylammonium cation.

Formally the Hamiltonian to describe the system is[10,11]

$$\mathcal{H} = H_{SO} + H_{CF}$$

$$H_{SO} = \zeta(r)(\vec{s}\cdot\vec{l})$$

$$H_{CF} = B_0{}^4[C_0{}^{(4)} + \sqrt{(5/14)}(C_{-4}{}^{(4)} + C_4{}^{(4)})] + B_0{}^6[C_0{}^{(6)} - \sqrt{(7/2)}(C_{-4}{}^{(6)} + C_4{}^{(6)})] \quad (1)$$

where $\zeta(r)$ (from now written as ζ), the spin-orbit coupling constant, and $B_0{}^4$ and $B_0{}^6$, the crystal field parameters, are used as parameters to be evaluated from the experimental data. The operators $\vec{s}$ and $\vec{l}$, the spin and orbital angular momentum, respectively, and the $C_q{}^{(k)}$, the tensor operators used to describe the crystal field, depend only on the angular coordinates, and the matrix elements of these operators may be readily evaluated.[11]

The energy level diagram derived from the above Hamiltonian (for the special case $B_0{}^6 = 0$ and used for illustrative purposes only) is shown in Figure 2. The right-hand side of the figure represents the limit of strong spin-orbit coupling and no crystal field while the left-hand side represents the limit of strong crystal field and zero spin-orbit coupling. The splittings of the f orbitals in a strong crystal field may be represented by the two parameters θ and Δ which are linearly related to the previously defined crystal field parameters by eq 2.

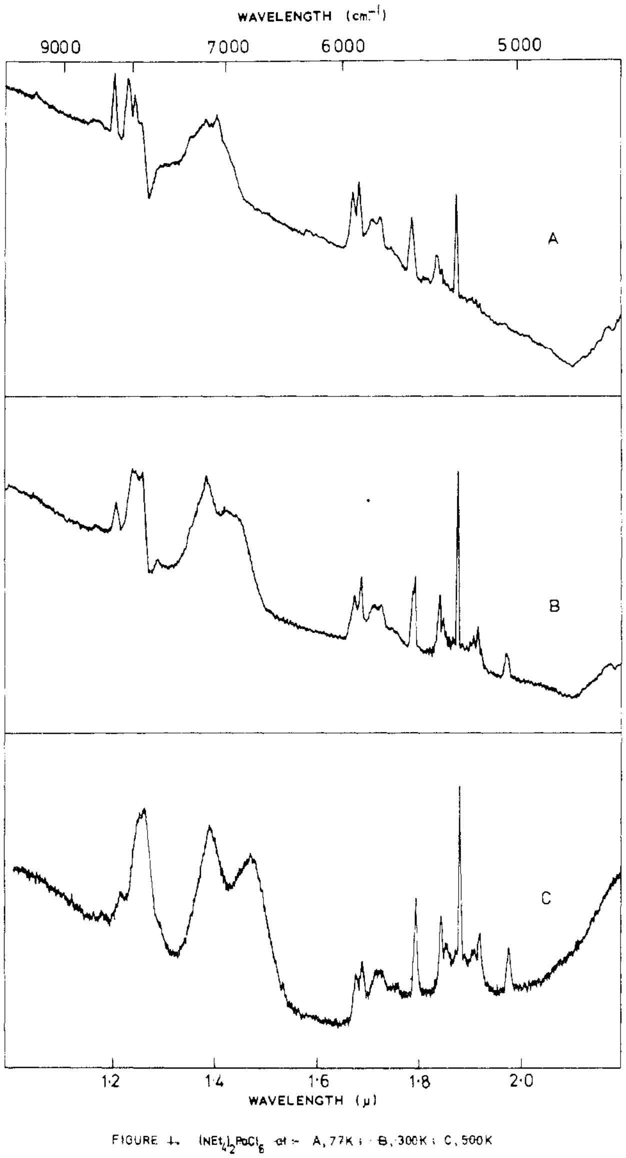

Figure 1. Spectra of $[(C_2H_5)_4N]_2PaCl_6$: A, 77°K; B, 300°K; C, 500°K.

$$b_4 = B_0{}^4/33, \quad b_6 = (-5/429)B_0{}^6$$

$$\theta = 8b_4 - 56b_6 \quad (2)$$

$$\Delta = 10b_4 + 84b_6$$

As the ratio of the spin-orbit coupling constant to the crystal field splitting changes, the levels shift and in the intermediate region are labeled by their group theory representations as shown in Figure 2. This diagram approximately represents the energy levels of the Pa compounds for the ratio

$$\frac{((7/2)\zeta/18b_4)}{1 + ((7/2)\zeta/18b_4)} \simeq 0.6 \quad (3)$$

We assign the optical absorption bands to transitions from the ground Γ_7 level to the Γ_7', Γ_8', and Γ_6 states (Table I). Our spectra are remarkably similar to those of Ryan[5] for UX_6^- compounds (X = F, Cl, Br) and our assignments are based on the arguments which he gave and which we will not repeat. There are two points to note, however.

First, the spectra are dominated by vibronic bands. The

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[10] B. G. Wybourne, "Spectroscopic Properties of Rare Earths," Wiley, New York, N. Y., 1965.

[11] There are a number of different conventions used for the crystal field parameters. We believe the formulation which is used in the theory of tensor operators is the most convenient. For the f^1 system the "operator equivalent" convention has been used most frequently in the literature and the relationship is given by the equations $A_4{}^0\langle r^4\rangle = B_0{}^4/8$; $A_6{}^0\langle r^6\rangle = B_0{}^6/16$.

Table I. Experimental Spectral Results for $PaCl_6{}^{2-}$ and $PaBr_6{}^{2-}$ Complexes

	$(NEt_4)_2PaCl_6$ at 500°K			$(NEt_4)_2PaCl_6$ at 300°K			$(NEt_4)_2PaCl_6$ at 77°K			$(NEt_4)_2PaBr_6$ at 300°K		
	Band position, cm^{-1}	Intens[a]	Vib freq, cm^{-1}	Band position, cm^{-1}	Intens	Vib freq, cm^{-1}	Band position, cm^{-1}	Intens	Vib freq, cm^{-1}	Band position, cm^{-1}	Intens	Vib freq, cm^{-1}
Γ_7-Γ_6	8264	m	+264	8271	s	+260	8306	s	+261	7664	s	+184
	···	···	···	8081	b	+70	8130	s	+85	7539	s	+59
	8000	s	0	(8011)[b]	···	0	8045	w, sh	0	(7480)	···	0
	7936	s	−62	7943	s	−68	7980	m	−65	7422	s	−58
	7760	vw, sh	−240	7752	w	−259				7308	w	−172
										7232	w	−248
Γ_7-$\Gamma_8{}'$							7385	sh				
	7204	b		7273	b		7293	b		6943	vb	
	6840	b		7008	b		7102	b		(6751)	b	
							6978	vw, sh		(6676)	b	
Γ_7-$\Gamma_7{}'$	5593	s	+255	5590	s	+260	5590	s	+257	5547	s	+182
	5444	s	+106	5444	s	+114	5441	s	+108			
	5405	s	+67	5405	sh	+75	5405	sh	+72	5431	b	+66
	5365	vw	+31	5372	vw	+42	5370	vw	+37			
	5338	s	0	5330	s	0	5333	s	0	5365	s	0
	5285	vw	−53	5271	vw	−39						
	5263	s	−75	5256	sh	−76				5307	b	−58
	5225	s	−113	5227	s	−103						
	5079	s	−259	5080	s	−250				5181	s	−184

[a] Key: s; sharp; b, broad; m, medium; w, weak; vw, very weak; sh, shoulder. [b] Values in parentheses are estimated.

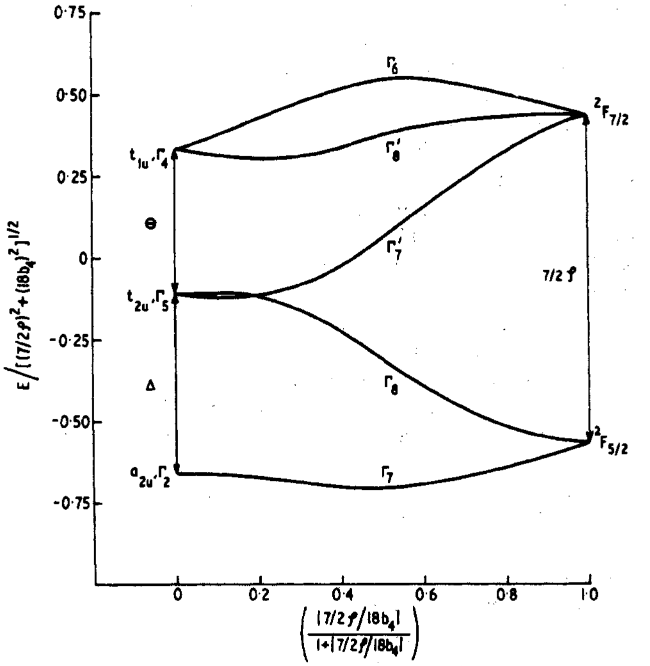

Figure 2. Energy level splittings of the f orbitals in octahedral symmetry *vs.* the ratio of the relative strengths of crystal field splittings and spin-orbit splitting (drawn for $B_0{}^6 = 0$).

vibrational modes which combine with the electronic levels to produce the strongest vibronic bands are those which destroy the center of symmetry of the complex during vibration, *viz.*, $\nu_3(T_{1u})$, $\nu_4(T_{1u})$, and $\nu_6(T_{2u})$, while the totally symmetric vibrational mode $\nu_1(A_{1g})$, which is Raman active, can couple to produce bands of very low intensity. The infrared-active mode ν_3 has been observed directly[8] for $PaCl_6{}^{2-}$ and $PaBr_6{}^{2-}$ salts at 255-266 and 180-182 cm^{-1}, respectively. The mean values of 257 and 183 cm^{-1} obtained from the electronic spectra for the highest vibrational frequencies of the $PaCl_6{}^{2-}$ and $PaBr_6{}^{2-}$ salts, respectively, are in close agreement with these directly observed values. The infrared spectra of hexahalogenoprotactinates(IV) have not yet been investigated below 250 cm^{-1}, but we have observed ν_4 at 118 cm^{-1} for Cs_2UCl_6 and the value 114 cm^{-1} has been deduced for hexachlorouranates(IV) from electronic spectral studies.[12] In addition, ν_4 has been recorded at 117 cm^{-1} for hexachloroneptunates(IV).[13] Consequently, one can confidently assign the mean vibrational frequency of 109 cm^{-1} obtained from vibronic bands observed for $(NEt_4)_2PaCl_6$ to ν_4. The remaining vibrational mode which couples strongly with the electronic transitions, ν_6, is both infrared and Raman inactive. The mean vibrational frequencies obtained for $(NEt_4)_2PaCl_6$ and $(NEt_4)_2PaBr_6$ during the present studies, 72 and 60 cm^{-1}, respectively (Table I), are close to those reported previously[12,13] for ν_6 for the analogous uranium(IV) and neptunium(IV) complexes and are assigned to this vibrational mode. The origin of the very low frequency vibrations observed for $(NEt_4)_2PaCl_6$ is not understood at present. It will obviously be valuable to have complete infrared and Raman data for the protactinium(IV) complexes in order to confirm the above assignments and to investigate further the trends in the positions of the vibrational bands of the hexahalogenoactinides(IV) with increasing mass of the actinide element.

Second, the $\Gamma_8{}'$ quartet level appears to be split by a lower symmetry electric field into two doublets; we have averaged these two levels and assumed this average is a good value for the $\Gamma_8{}'$ level in octahedral symmetry. The apparent splitting of the Γ_7-$\Gamma_8{}'$ transition decreases with decreasing temperature and this is associated with the smaller contribution from vibronic transitions to the low-energy side of the bands at lower temperatures. Consequently the high-temperature spectrum represents the best value for this transition. The other levels are assumed to be unaffected by the lower symmetry field. A similar splitting of this $\Gamma_8{}'$ quartet level has repeatedly been observed in the spectra of uranium(V) compounds. Many of the data are summarized and discussed elsewhere.[14,15]

In addition to the above optical data, *g* value measurements

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Table II. Results of the Fitting of the Spectral Data for 5f^1 Compounds

		Energy, cm^{-1}				Parameters, cm^{-1}		
Compd		Γ_7–Γ_6	Γ_7–Γ_8'	Γ_7–Γ_7'	g	θ	Δ	ζ
$(NEt_4)_2PaCl_6$	Calcd	8,029	6,988	5347	−1.115	1,873	1634	1523
	Exptl[a]	8,011	7,022	5330	−1.141[b]			
$(NEt_4)_2PaBr_6$	Calcd	7,509	6,767	5401	−1.100	1,268	1707	1535
	Exptl[a]	7,480	6,828	5365	−1.150[c]			
$(Ph_4As)UF_6$	Calcd	16,135	13,424	7427	−0.556	6,882	4479	1885
	Exptl[d]	15,900	13,715	7413	−0.700[e]			
$(NEt_4)UCl_6$	Calcd	11,646	9,903	6917	−0.927	3,371	2936	1913
	Exptl[d]	11,470	10,190	6801	−1.1[f]			
$(NEt_4)UBr_6$	Calcd	10,689	9,369	6955	−0.931	2,375	2935	1925
	Exptl[d]	10,555	9,620	6823	−1.1[c]			
NpF_6	Calcd	28,380	24,025	9348	−0.604	17,498	5619	2433
	Exptl[g]	27,000	24,000	9350	−0.604[h]			

[a] This work. [b] Reference 12. [c] Estimated value. [d] Reference 5. [e] Reference 6. [f] Reference 7. [g] Reference 3a. [h] Reference 17.

are available for the ground state for $PaCl_6^{2-}$,[16] UCl_6^-,[7] UF_6^-,[6] and NpF_6.[17] We have assumed for fitting purposes (to be described later) that the bromide complexes have the same g values as the chloride compounds. The g values for Cs_2PaCl_6 and NpF_6 were empirically determined to be negative, so we have assumed all the compounds have negative g values.

In a strong octahedral field the seven f orbital levels are split into two triplets, t_{2u} and t_{1u}, and one singlet a_{2u}. The ordering of the levels from geometric arguments is as shown in Figure 2.

If we use these strong crystal field states as our basis states, the energy matrices are[3a,4,6]

$$\Gamma_7 = \begin{vmatrix} 0 & 3^{1/2}\zeta \\ 3^{1/2}\zeta & \Delta - \tfrac{1}{2}\zeta \end{vmatrix}$$

$$\Gamma_8 = \begin{vmatrix} \Delta + \tfrac{1}{4}\zeta & \tfrac{3}{4}(5^{1/2})\zeta \\ \tfrac{3}{4}(5^{1/2})\zeta & \Delta + \theta - \tfrac{3}{4}\zeta \end{vmatrix}$$

$$\Gamma_6 = \left| \Delta + \theta + \tfrac{3}{2}\zeta \right|$$

The g value for the ground state is[6]

$$g = 2(\cos\alpha)^2 - \frac{8}{3^{1/2}}\sin\alpha\cos\alpha \tag{4}$$

where

$$\tan 2\alpha = \frac{2(3^{1/2})\zeta}{\Delta - \tfrac{1}{2}\zeta}$$

If, instead of this procedure, we had used molecular orbital wave functions[3b,4,6] we would have obtained a similar set of energy matrices which would have included in the most general case four orbital reduction factors plus the parameters Δ, θ, and ζ. The above g value equation would also contain an orbital reduction factor. In this paper we are concerned primarily with the qualitative changes of the parameters as the charge on the central ion is varied or the halide ligand is changed. For this reason, and also because we have insufficient data to justify using more parameters, we have used only the three parameters θ, Δ, and ζ to fit the experimental data. The crystal field parameters θ and Δ incorporate in their empirical values the sum of the electrostatic and covalent effects. Calculations based on the electrostatic point charge model fail to give the correct magnitude, or in some cases the correct trends, to these two parameters for the compounds studied in this work. Similar effects have been found previously in studies of rare earth ions in fluorite type crystals.[18] We therefore assume covalent effects dominate the empirical values of θ and Δ. The values of ζ found empirically will be an average of the spin–orbit interactions in the t_{1u} and the t_{2u} orbitals corresponding to setting the orbital reduction factors equal to unity.

The results of the fitting procedure are shown in Table II. The agreement between the experimental and calculated levels is reasonably good. For UCl_6^- and UBr_6^- the fits are less satisfactory because the g values did not correlate well with the optical data. The calculated magnetic splittings are very sensitive to the value of the orbital reduction factor and this less satisfactory fit could be due to our assumption of unity for this parameter. These discrepancies are now being investigated. However, the most dramatic changes occur in the parameters θ and Δ.

Figure 3 shows the variations of θ and Δ in the 5f^1 compounds. There are three distinct trends. First, as the ligand is fixed, the splittings increase with higher oxidation state, *i.e.*, $\theta + \Delta$ increases as we change from Pa(IV) to U(V) to Np(VI). Second, if we fix the oxidation state the splittings decrease as we change from the most electronegative to the least electronegative halide ion. Third, θ changes much more rapidly than Δ in the second case, for a fixed metal ion oxidation state.

The increase in the total splitting for a fixed halide ion with increasing oxidation state follows qualitatively the trends expected. A more positive metal ion will draw charge from the ligand and result in increased covalent bonding which will increase the ligand field splittings. However we also expect increased covalency as we change the ligand from F^- to Cl^- to Br^-, but the total ligand field splitting $\Delta + \theta$ decreases.

This same trend has been found for 3d transition metal complexes. Owen and Thornley[2] have shown that the ligand field splitting for these ions can be represented approximately as $(\alpha_\sigma^2 - \alpha_\pi^2)(E_d - E_p)$, where α_σ and α_π are the coefficients of the σ and π combinations of ligand wave functions in the molecular orbital wave function. E_d and E_p are the binding energies of the outer d metal ion electrons and the outer p shell ligand electrons. They suggested the quantity $(\alpha_\sigma^2 - \alpha_\pi^2)(E_d - E_p)$ could vary from F^- to Cl^- to Br^- in such a way so as to cause the observed trends. It can readily be shown (following Owen and Thornley[2]) for f^1 compounds in octahedral symmetry that

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(17) C. A. Hutchinson, Jr., and B. Weinstock, *J. Chem. Phys.*, 32, 56 (1960).

(18) J. D. Axe and G. Burns, *Phys. Rev.*, **152**, 331 (1961).

$$\theta \simeq (\alpha_\pi^2 + \alpha_\sigma^2 - \alpha_\pi'^2)(E_f - E_p)$$
$$\Delta \simeq (\alpha_\pi'^2)(E_f - E_p) \tag{5}$$

where α_π and α_σ are the ligand admixture coefficients for the t_{1u} state, α_π' is the ligand admixture coefficient for the t_{2u} state, and E_f is the binding energy of the outermost f electrons.

Equation 5 states the total ligand field splitting ($\theta + \Delta$) depends on $(\alpha_\pi^2 + \alpha_\sigma^2)(E_f - E_p)$. We suggest that similarly to the d series this quantity could vary in such a way so as to explain the gross variations of ($\Delta + \theta$) as the halide ion is changed and the metal ion oxidation state is kept fixed.

Let us now consider the changes in θ and Δ as the metal ion is fixed but the halide ion changes. The fact that θ changes much more rapidly than Δ suggests from eq 5 that $(\alpha_\pi^2 + \alpha_\sigma^2 - \alpha_\pi'^2)$ changes much more rapidly than $\alpha_\pi'^2$. Now α_π and α_π' both involve the same ligand orbital so we expect changes in π bonding to leave θ relatively unaffected since these effects will tend to cancel. The quantity Δ will depend directly on π-bonding effects. However experimentally Δ does not vary drastically compared to θ. It appears, therefore, that there are large changes in σ bonding as the halide ion is changed and the π bonding is relatively unaffected. Jorgenson, *et al.*,[19] have suggested that σ-antibonding effects could adequately explain ligand field splittings in f electron compounds. Our results again point out the importance of σ antibonding.

Further work is now in progress to extend the number of compounds and the spectral range for which observations have been made, to perform accurate magnetic measurements on all the compounds, and to use the molecular orbital theory to fit the observations.

Summary

We have fitted the spectral data of $5f^1$ compounds in terms of three parameters θ, Δ, and ξ and assumed covalent effects provide the dominant contribution to the ligand field parameters. Qualitatively, the trends in the ligand field parameters can be explained in terms of molecular orbital theory with large variations in σ bonding dominating the total ligand field splitting as the halide ion is varied.

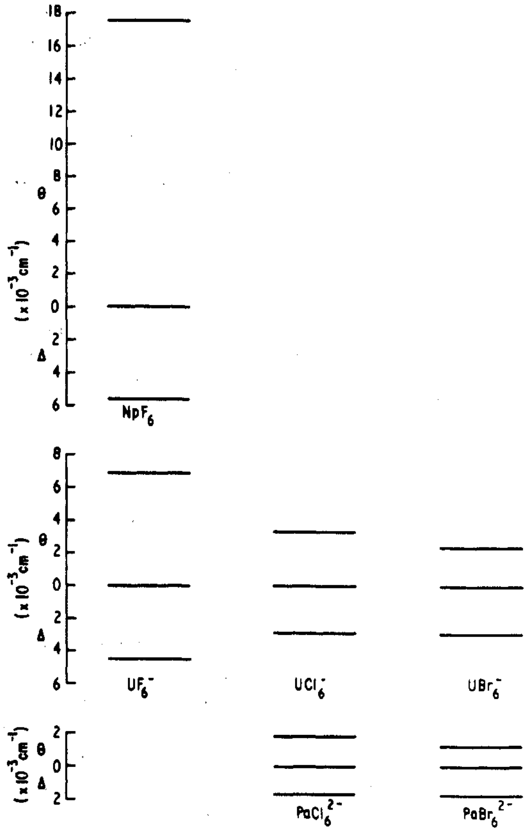

Figure 3. Ligand field splittings Δ and θ for various octahedral $5f^1$ compounds.

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Registry No. $(NEt_4)_2PaCl_6$, 12080-92-1; $(NEt_4)_2PaBr_6$, 49772-07-8; $(Ph_4As)UF_6$, 31183-09-2; $(NEt_4)UCl_6$, 17141-96-7; $(NEt_4)UBr_6$, 25630-17-5; NpF_6, 14521-05-2.

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