rations of Au(I) lie at relatively low energies compared to other metal ions.[10]

The spectral assignments for AuX_2^- can provide information not only on the relative energies of excited states but also on orbital participation in bonding. The assignments of the d → p bands in all three complexes indicate an orbital energy ordering of $2\sigma_g^+ > \delta_g$, but the separation of the two d → p transitions is relatively small ranging from 0.24 to 0.32 μm^{-1}. Apart from differences in electron repulsions, this small separation suggests only a small difference in energy between the σ-antibonding $2\sigma_g^+$ orbital and the nonbonding δ_g orbitals and thus a very low participation of the $5d_{z^2}$ orbital in σ bonding. Although the d → p transition from the $2\pi_g$ orbitals was not located, the $2\pi_g$ orbitals are expected to be more weakly antibonding than the $2\sigma_g^+$ and to be located energetically between the $2\sigma_g^+$ and δ_g orbitals. A similar conclusion concerning the involvement of the Au 5d orbitals in bonding was drawn from the detailed study of the $Au(CN)_2^-$ spectra where only a small 5d orbital splitting was inferred.[2] The small splitting of the Au 5d orbitals may therefore be regarded as a general feature of two-coordinate Au(I) complexes since it is found for such widely different ligands as CN^- and halides. Since the filled 5d orbitals are presumed to have little involvement, the main contributions to bonding in two-coordinate Au(I) complexes must rest with the empty 6s and 6p orbitals. The $3\sigma_g^+$ and $2\sigma_u^+$ are expected to be strongly σ antibonding and thus may be visualized as forming the basis for two sp_z hybrid orbitals on Au. The use of sp_z hybrid orbitals on Au to describe the bonding in linear two-coordinate Au(I) complexes has received considerable support recently from ^{197}Au Mössbauer studies.[22–25] The large isomer shift (s-orbital participation) and quadrupole splitting (p_z-orbital participation) observed for a variety of Au(I) complexes both increase with the donor strength of the ligand. This observation can be explained easily in terms of sp_z hybridization of Au but appears to be inconsistent with an earlier proposal involving $d_{z^2}s$ hybridization.[26]

The lack of 5d orbital participation tends to rule out significant halide → 5d π bonding so that the $1\pi_g$ ligand orbitals should be virtually nonbonding. Further, the observation of d → p transitions in AuX_2^- at energies anticipated from atomic spectral data[10] for the free ion strongly suggests that halide → 6p π bonding is weak. Strong π bonding involving the 6p orbitals on Au would be expected to destabilize $2\pi_u$ considerably and thus shift d → p transitions to higher energy. This conclusion is further supported by photoelectron spectra of HgX_2 which suggest only a small (but not zero) degree of halide → 6p π bonding in these compounds.[14] π donation from halide ligands to Au(I) is expected to be less than for Hg(II) due to the lower charge on the metal. Thus the contribution to the overall bonding in AuX_2^- from halide to metal π bonding is expected to be small. Consequently σ bonding must be the dominant type of bonding in these complexes and primarily responsible for their stability.

Because of a lack of information concerning relative differences in electron repulsions, it is difficult to draw firm conclusions from the relative energies of the LMCT excited states for $AuBr_2^-$ and AuI_2^-. However, the pattern of LMCT bands observed for AuI_2^- indicates approximately 0.8 μm^{-1} energy difference between the π-LMCT and σ-LMCT band systems. This difference is comparable to that found for HgI_2 (0.74 μm^{-1}) and $HgBr_2$ (0.65 μm^{-1}) but is somewhat smaller than found for typical square-planar MX_4^{n-} or octahedral MX_6^{n-} halide complexes.[18,27,28] As noted earlier[28] this difference between the σ- and π-LMCT can be viewed qualitatively as a "ligand field splitting" of the energies of the *n*p halide orbitals by the metal ion. However, as shown here in Figure 6 the splitting magnitude observed in the electronic spectra also depends upon electron repulsion and spin–orbit coupling differences between the excited states involving the σ- and π-donor orbitals—differences which may be considerable for heavy-metal ions and Br^- or I^- ligands.

Registry No. $[(n\text{-}C_4H_9)_4N][AuCl_2]$, 50480-99-4; $[(n\text{-}C_4H_9)_4N][AuBr_2]$, 50481-01-1; $[(n\text{-}C_4H_9)_4N][AuI_2]$, 50481-03-3; $HgCl_2$, 7487-94-7; $HgBr_2$, 7789-47-1; HgI_2, 7774-29-0.

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Angular-Overlap Calculation of the Jahn–Teller Stabilization Energies for f-Orbital Degeneracies

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The angular-overlap model is applied to the calculation of the linear Jahn–Teller coupling constants for f-orbital degeneracies. The MX_6, O_h, chromophore is treated as representative of the highest symmetry commonly occurring in the lanthanide and actinide series, and it is shown that, even when spin–orbit effects are taken into account, 5f orbital degeneracies may lead to significant Jahn–Teller stabilization energies. The operation of this effect for f^1 Γ_8 states is considered.

Introduction

In 1971 Jørgensen[1] could, with some justification, note that although many f^x systems were in principle Jahn–Teller active, there was no convincing experimental evidence for the operation of the effect in such species. Thus Eisenstein and Pryce[2] had earlier suggested that the higher Γ_8' excited state of the $5f^1$ NpF_6 system could show Jahn–Teller splitting, and evidence for such activity had also been adduced[3] for the $5f^2$ U^{4+}

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system at a cubic site in ThO_2. However, in the last decade much interest has been shown[4–9] in the f–f electronic spectra of several O_h hexahalo complexes of the $5f^1$ Pa^{IV} and U^V systems, and the observed splittings of one of the f–f bands ($\Gamma_7 \rightarrow \Gamma_8'$) have been tentatively attributed to the Jahn–Teller activity of the upper state.[7,8]

Unfortunately it is a matter of some difficulty to estimate the potential magnitudes of f-orbital Jahn–Teller effects, and hitherto, when this question was posed, it seems usually to have been tacitly assumed that such contributions would be negligible. Thus Bersuker's[10] review scarcely mentions f-orbital systems, while Sturge,[11] in a similar survey, dismisses the 4f species from consideration on account of their very weak involvement in chemical bonding. Indeed, even Englemann's[12] comprehensive treatise cites only the one f-orbital system (U^{4+} in ThO_2) previously mentioned.[3]

For 4f species this pessimism is not altogether unjustified since the $|LSJM_J\rangle$ basis set here affords the best description of a situation in which the ligand field is very small and its effects are much less than either the spin–orbit or the electron-repulsion terms. On the other hand the ligand-field splittings for many actinide complexes are substantially greater than for the lanthanides, and recent studies of the O_h MX_6 $5f^1$ complexes of Pa^{IV} and of U^V have underlined this point. Thus in the 5f series a typical intermediate coupling situation obtains, with ligand-field, spin–orbit, and electron-repulsion, terms all of comparable magnitude (although in the higher oxidation states the ligand-field contributions give indications of beginning to predominate), and Judd[13] has lately considered the possible operation of the Jahn–Teller effect in such circumstances.

Furthermore, it was recently demonstrated[14] that the angular-overlap model could be successfully applied to the treatment of σ and π bonding in O_h MX_6 f-orbital complexes, in which geometry the f-orbital manifold yields the three irreducible representations a_{2u}, t_{1u}, and t_{2u}. Thus, in principle, it is possible, in contrast to d-orbital O_h systems, to determine both e_σ and e_π via the angular-overlap technique, and Bacci[15] has just presented an ingenious method for the calculation of the Jahn–Teller coupling constants for a given orbital degeneracy in terms of expressions involving only the angular-overlap parameters (e_λ) and the internuclear distance (R) or their derivatives ($\partial e_\lambda/\partial R$). Consequently, the magnitudes of the appropriate Jahn–Teller quantities may now quite readily be estimated.

In this work therefore the Jahn–Teller coupling constants have been evaluated for O_h MX_6 f-orbital systems, in the linear adiabatic approximation, in terms of the e_σ and e_π parameters; because of the large ξ values encountered (especially for 5f species) the effects of spin–orbit coupling have been specifically considered and calculations made of the Jahn–Teller stabilization energies (E_{JT}) to be anticipated for $4f^1$ and $5f^1$ species. The available experimental evidence is then surveyed and brief consideration given to those systems likely to show Jahn–Teller-active f^x ground states.

Table I. Linear Jahn–Teller Coupling Constants for f Orbitals in O_h MX_6 Systems

Trigonal Coupling[a]

$^2T_{1u}(t_{1u}) \otimes \tau_{2g}$

$$\langle z^3|\partial V/\partial Q^{\tau}{}_{\xi}|x^3\rangle = -3(e_\sigma - e_\pi)/R$$

$^2T_{2u}(t_{2u}) \otimes \tau_{2g}$

$$\langle z(x^2-y^2)|\partial V/\partial Q^{\tau}{}_{\xi}|x(z^2-y^2)\rangle = 5e_\pi/2R$$

Tetragonal Coupling[a]

$^2T_{1u}(t_{1u}) \otimes \epsilon_g$

$$\langle z^3|\partial V/\partial Q^{\epsilon}{}_{\theta}|z^3\rangle = 3^{1/2}[(2/3)(\partial e_\sigma/\partial R) - (1/4)(\partial e_\pi/\partial R)]$$

$^2T_{2u}(t_{2u}) \otimes \epsilon_g$

$$\langle z(x^2-y^2)|\partial V/\partial Q^{\epsilon}{}_{\theta}|z(x^2-y^2)\rangle = -3^{1/2}(5/12)(\partial e_\pi/\partial R)$$

[a] The results given for the τ_{2g} and the ϵ_g coupling correspond respectively to the B and C constants of Bersuker.[10]

Theory

Consider a given chromophore, ML_N, where N is the number of coordinated ligands L, and let l be the azimuthal quantum number for the metal M orbitals, with λ denoting the component of angular momentum of any given molecular orbital about the internuclear axis (λ = 0, 1, 2, 3, ... corresponding to σ, π, δ, φ, ... interactions). If ω runs over both components of the (not necessarily degenerate) $\pm m_l$ pair and j over the N ligands, with positions defined by the polar angles θ_j and φ_j, the general ligand-field matrix element is given by

$$\langle\psi_a|V|\psi_b\rangle = \sum_\lambda\sum_\omega\sum_{j=1}^{N} e_{\lambda\omega}F^l{}_{\lambda\omega}(\psi_a)F^l{}_{\lambda\omega}(\psi_b)$$

where the $F^l{}_{\lambda\omega}$ are the elements of the general angular-transformation matrix, given for f orbitals by Clack and Smith.[16]

The linear Jahn–Teller coupling constants may be defined[10,12,17] as

$$c = \langle\psi_a|\partial V/\partial Q^{\Gamma}{}_{\gamma}|\psi_b\rangle$$

where $Q^{\Gamma}{}_{\gamma}$ is a Jahn–Teller-active normal coordinate, being the component γ of the Γ representation. If R_j represents the metal–ligand bond distance, then one may write[15]

$$c = \sum_\lambda\sum_\omega\sum_{j=1}^{N} \frac{\partial[e_{\lambda\omega}F^l{}_{\lambda\omega}(\psi_a)F^l{}_{\lambda\omega}(\psi_b)]}{\partial(R_j,\theta_j,\varphi_j)} \frac{\partial(R_j,\theta_j,\varphi_j)}{\partial Q^{\Gamma}{}_{\gamma}}$$

However, $e_{\lambda\omega}$ and $F^l{}_{\lambda\omega}$ depend respectively on R and on θ and φ. Moreover, for the coupling constants representing purely stretching vibrational modes only $\partial R/\partial Q$ terms will be nonvanishing, so that these will be functions of $\partial e_{\lambda\omega}/\partial R$, while similarly, for those representing purely bending modes only, $\partial\theta/\partial Q$ and $\partial\varphi/\partial Q$ are nonzero, and the resulting quantities will simply involve $e_{\lambda\omega}/R$.

For O_h MX_6 species the f orbitals follow the one-electron energy sequence[14] $a_{2u} < t_{2u} < t_{1u}$. If only s and p orbitals of the ligands are considered, the a_{2u} level is nonbonding, the t_{2u} level π antibonding, and the t_{1u} level both σ and π antibonding, so that both λ = 0 and λ = 1 terms must be included. For simplicity the cubic basis functions[14] f_{z^3}, f_{x^3}, f_{y^3}, and $f_{z(x^2-y^2)}$, $f_{y(z^2-x^2)}$, $f_{x(z^2-y^2)}$ were used for the t_{1u} and t_{2u} representations, respectively, so as to minimize the number of ensuing off-diagonal matrix elements. The Jahn–Teller-active vibrational modes for O_h MX_6 species are the ν_2, ϵ_g (θ,ϵ) stretching mode whose components transform as z^2 and as ($x^2 - y^2$), respectively, and the ν_5, τ_{2g} (η,ξ,ζ) bending mode with components transforming as xz, yz, and xy. Both modes may operate on T orbital degeneracies, leading to tetragonal and trigonal distortions, respectively.

In Table I therefore are given the Jahn–Teller coupling constants obtained for the various significant cases for both

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vibrational modes acting within the T states corresponding to the t_{1u} and t_{2u} orbital sets, i.e., within the $^2T_{1u}(t_{1u})$ and $^2T_{2u}(t_{2u})$ states. The expressions listed for the trigonal and tetragonal coupling correspond respectively to the linear vibronic coupling constants B and C as defined by Bersuker.[10] From these coupling constants the values of the Jahn–Teller stabilization energy, E_{JT}, are readily obtained; thus, for the coupling $T_{1,2} \otimes \tau_{2g}$ one has[10,17] $E_{JT} = 2B^2/3K_\tau$, and for $T_{1,2} \otimes \epsilon_g$ one finds $E_{JT} = C^2/2K_\epsilon$, where the K_Γ are the appropriate force constants for the designated vibrational modes. In principle the general couplings, $T_{1,2} \otimes (\epsilon_g + \tau_{2g})$, should be considered, but the simplifying assumption of treating the couplings separately is to some extent justified since the results (vide infra) suggest that the τ_{2g} mode is significantly more effective than the ϵ_g.

Furthermore, for all f-orbital systems the metal spin–orbit coupling constant will be substantial, and the splittings thereby engendered are likely to be appreciably greater than E_{JT}. Thus, in the double group O^* the $^2T_{1u}$ and $^2T_{2u}$ states both yield two fairly well-separated components, giving $\Gamma_6 + \Gamma_8$ and $\Gamma_7 + \Gamma_8$, respecitvely, but the Kramers doublets, Γ_6 and Γ_7, are always Jahn–Teller impotent. In addition, although the Γ_8 levels remain Jahn–Teller active, it is readily shown (cf. Liehr[18]) that for an isolated Γ_8 level E_{JT} is substantially quenched relative to the values deduced for the corresponding $T_{1,2}$ states, being reduced to one-fourth of its former value for both $\Gamma_8 \otimes \epsilon_g$ and $\Gamma_8 \otimes \tau_{2g}$ couplings.

Results and Discussion

As previously shown,[14] the available spectroscopic data for the f–f bands of the 5f^1 $[\mathrm{Pa^{IV}X_6}]^{2-}$ (X = F, Cl, Br, I) and $[\mathrm{U^VX_6}]^-$ (X = F, Cl, Br) systems may readily be analyzed in terms of the angular-overlap parameters, e_σ and e_π. Moreover, Amberger, Rosenbauer, and Fischer[19] have reported a study of the electronic Raman spectrum of the 4f^1 system $\mathrm{Cs_2Na[CeCl_6]}$ in which the ligand-field splittings of the $^2F_{5/2}$ and $^2F_{7/2}$ levels were determined, thus permitting the evaluation of the B_0^4 and B_0^6 parameters and thence the e_σ and e_π quantities. Unfortunately, similar data were not available for the 4f^1 anion $[\mathrm{CeF_6}]^{3-}$, but for the 4f^2 system $[\mathrm{PrF_6}]^{3-}$ the electronic Raman data recorded by Amberger[20] allow the ligand-field and e_λ parameters to be determined. Thus, with the assumption that the e_λ values for the 4f^1 and 4f^2 hexafluoro anions should not differ too greatly, reasonably accurate e_σ and e_π data were available for all the 4f^1 and 5f^1 systems considered.

However, numerical evaluation of the E_{JT} quantities also requires estimates to be made for the derivatives $\partial e_\sigma/\partial R$ and $\partial e_\pi/\partial R$, and this presents somewhat more difficulty. Thus the method adopted by Bacci,[14] which involves the calculation of $\partial S_\lambda^2/\partial R$, would probably be applicable in the 4f series, for which reasonably good analytical radial wave functions are available, but not for the 5f species, for which such data are largely lacking. An alternative approach however is to write the e_σ and e_π quantities in terms of the B_0^4 and B_0^6 parameters. Thus one finds

$$e_\sigma = (2/11)B_0^4 + (56/429)B_0^6$$

$$e_\pi = (4/33)B_0^4 - (56/143)B_0^6$$

so that, if one assumes that the B_0^4 and B_0^6 quantities show the distance dependence predicted by the electrostatic model (varying as R^{-5} and as R^{-7}, respectively), there follow

$$\partial e_\sigma/\partial R = -(10/11)(B_0^4/R) - (392/429)(B_0^6/R)$$

$$\partial e_\pi/\partial R = -(20/33)(B_0^4/R) + (392/143)(B_0^6/R)$$

By this method therefore the required values of $\partial e_\lambda/\partial R$ could readily be obtained, and although it has been suggested[21] that the electrostatic model underestimates these derivatives, the resulting R^{-5} dependence of Dq has been found[22] to give good results for a number of d-orbital systems. For f-orbital systems experimental data are scarce, but for $\mathrm{Tm^{2+}}$ in $\mathrm{CaF_2}$ the electrostatic approach was found[23] to account for about 75% of the observed distance dependence of the splitting parameters. Moreover, calculations of E_{JT} for d-orbital systems, using the $\partial e_\lambda/\partial R$ values obtained in this way, yielded results in quite good agreement with those listed by Bacci,[15] and it would in any case appear likely that any errors arising from this source will be no greater than those accruing from the uncertainties in the values of the K_Γ parameters (vide infra).

Thus the calculation of E_{JT} for the various couplings here considered requires data for the force constants K_ϵ and K_τ relating to the stretching ϵ_g and bending τ_{2g} modes, respectively. For the lanthanides Choca, Ferraro, and Nakamoto[24] have surveyed the available information for $[\mathrm{LnCl_6}]^{3-}$ species (Ln = Nd, Eu, Gd, Dy, Er, Yb), giving tables of results calculated for the K_Γ by using various force-field approximations, showing clearly that the K_Γ varied very little along the 4f series. Thus, the results obtained for $[\mathrm{NdCl_6}]^{3-}$ could be assumed for $[\mathrm{CeCl_6}]^{3-}$ with very little error. Moreover, the values of K_ϵ, relating to the stretching mode, were not strongly dependent on the nature of the force field assumed, so that the MOVFF results, which gave the best fit to the experimental data, were probably reliable to within ±10%. On the other hand the values for K_τ, relating to the bending mode, were much smaller than the corresponding K_ϵ values and varied considerably with the force field adopted; thus, typically, one might find $K_\tau \approx 0.06 \pm 0.03$ mdyn Å^{-1}, so that the uncertainty in K_τ was unlikely to be less than 50% of the average of the calculated quantities.

In the 5f series there are fewer results available for the calculation of the K_Γ values, although both $[\mathrm{UCl_6}]^{2-}$ and $[\mathrm{NpCl_6}]^{2-}$ have been studied[25,26] and the data for the neutral $\mathrm{MF_6}$ species (M = Th, Pa, U, Np) have also been analyzed.[26] Consequently, it has been necessary in many cases to assume that the K_Γ do not vary appreciably along the earlier part of the actinide series and, in addition, that the dependence of the K_Γ on metal oxidation state and on the nature of the halogen involved follows a similar pattern to that found[27] for other octahedral hexahalo systems. Thus the results listed for the K_Γ of the actinide complexes could often only be derived by such interpolations and must again contain appreciable uncertainties, which will be at least comparable to those indicated for the 4f systems.

Finally, it has also been necessary to estimate values for R, the metal–ligand bond length, since crystallographic results are lacking. For the 4f series R may reasonably be equated to the sum of the appropriate $\mathrm{M^{3+}}$ and $\mathrm{Hal^-}$ ionic radii, and a similar procedure was adopted for the $\mathrm{M^{IV}}$ species of the 5f series; for the $\mathrm{M^V}$ 5f complexes the appropriate distances were derived by interpolation between the $\mathrm{M^{IV}}$ and $\mathrm{M^{VI}}$ distances, the latter being taken from data listed by Brown.[28-30]

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Table II. Ligand-Field Parameters and Calculated Jahn-Teller Stabilization Energies for $4f^1$ and $5f^1$ Species

	$4f^1$ [g]		$5f^1$ [h]						
	$[CeF_6]^{3-}$	$[CeCl_6]^{3-}$	$[PaF_6]^{2-}$	$[PaCl_6]^{2-}$	$[PaBr_6]^{2-}$	$[PaI_6]^{2-}$	$[UF_6]^-$	$[UCl_6]^-$	$[UBr_6]^-$
$B_0{}^4$, cm^{-1}	3920[a]	1984[b]	14742[c]	6669[d]	5417[d]	4190[e]	22205[f]	11989[f]	9749[f]
$B_0{}^6$, cm^{-1}	480[a]	38[b]	1422[c]	394[d]	−68[d]	−281[e]	2297[f]	713[f]	20[f]
e_σ, cm^{-1}	775[a]	366[b]	2866[c]	1264[d]	976[d]	725[e]	4337[f]	2273[f]	1775[f]
e_π, cm^{-1}	287[a]	225[b]	1230[c]	654[d]	683[d]	618[e]	1792[f]	1174[f]	1174[f]
R, Å[g,h]	2.4	2.85	2.3	2.75	2.9	3.1	2.15	2.6	2.75
$\partial e_\sigma/\partial R$, 10^{11} cm^{-2}	−1.67	−0.65	−6.39	−2.34	−1.68	−0.96	−10.40	−4.45	−3.23
$\partial e_\pi/\partial R$, 10^{11} cm^{-2}	−0.44	−0.39	−2.19	−1.08	−1.20	−1.07	−3.33	−2.04	−2.13
K_ϵ, mdyn Å^{-1}	1.17[i]	0.70[j]	2.4[k]	1.2[k,l]	0.95[k]	0.85[k]	2.8[k]	1.2[k]	1.0[k]
K_τ, mdyn Å^{-1}	0.03[i]	0.02[j]	0.08[k]	0.05[k,l]	0.05[k]	0.05[k]	0.12[k]	0.06[k]	0.06[k]
$E_{JT}(T_{1u} \otimes \epsilon_g)$, cm^{-1}	26	5	171	39	21	5	396	150	78
$E_{JT}(T_{2u} \otimes \epsilon_g)$, cm^{-1}	1	1	10	5	8	7	21	18	24
$E_{JT}(T_{1u} \otimes \tau_{2g})$, cm^{-1}	164	15	754	117	24	3	1392	355	95
$E_{JT}(T_{2u} \otimes \tau_{2g})$, cm^{-1}	40	26	296	94	92	66	479	281	252
$h\nu(\epsilon_g)$, cm^{-1} [m,n]	335	205	310	225	150	120	380	277	185
$h\nu(\tau_{2g})$, cm^{-1} [m,n]	170	115	170	120	83	65	185	136	90
% $^2T_{1u}$ in $\Gamma_8{}'$	63.5	51.2	75.5	53.4	47.4	43.2	81.0	61.1	53.5
$E_{JT}(\Gamma_8{}')/h\nu(\epsilon_g)$	0.01	0.004	0.11	0.03	0.02	0.01	0.21	0.09	0.07
$E_{JT}(\Gamma_8{}')/h\nu(\tau_{2g})$	0.17	0.04	0.94	0.22	0.18	0.15	1.64	0.60	0.47

[a] Estimated from $[PrF_6]^{3-}$ data.[20] [b] Reference 19. [c] Reference 4. [d] Reference 5. [e] Reference 6. [f] References 7–9. [g] 4f values from ionic radii in F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, 1962. [h] 5f values from ionic radii.[35] [i] Based on $[LaF_6]^{3-}$ data: R. Becker, A. Lentz, and W. Sawodny, *Z. Anorg. Allg. Chem.* **420**, 210 (1976). [j] Reference 24. [k] Estimates based on data from ref 27. [l] Based on $[NpCl_6]^{2-}$ data from ref 26. [m] Based on data from ref 35. [n] Based on data from J. L. Ryan, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One*, 7, 323 (1972).

The R values thus deduced have a likely uncertainty of some ±5% of the listed values and are collected, together with the relevant K_Γ, $\partial e_\lambda/\partial R$, e_λ, $B_0{}^4$, and $B_0{}^6$ quantities, in Table II; also listed there are the values of E_{JT} thereby calculated for the couplings $^2T_{1u} \otimes \epsilon_g$, $^2T_{2u} \otimes \epsilon_g$, $^2T_{1u} \otimes \tau_{2g}$, and $^2T_{2u} \otimes \tau_{2g}$.

However, these values of E_{JT} have been derived without considering the effects of spin–orbit coupling acting within the $^2T_{1u}$ or $^2T_{2u}$ manifolds, and since the effective value of ξ is about 650 cm^{-1} for Ce^{III}, 1500 cm^{-1} for Pa^{IV}, and 1800 cm^{-1} for U^V, these contributions must be appreciable. Furthermore, if the resulting splittings, $^2T_{1u} \rightarrow \Gamma_6 + \Gamma_8$ and $^2T_{2u} \rightarrow \Gamma_7 + \Gamma_8$, are large compared with E_{JT}, one is essentially dealing with an isolated Γ_8 level, thereby quenching the Jahn–Teller activity such that, for the couplings considered, $E_{JT}(\Gamma_8) = (1/4)E_{JT}(T_{1,2})$. In fact, calculations using the strong-field f^1 matrices listed by Brown et al.[4] indicate that this is effectively the situation; thus, for the upper, $\Gamma_8{}'$, level in $[CeF_6]^{3-}$, $[PaF_6]^{2-}$, and $[UF_6]^-$, for example, one finds respectively the (Γ_6–$\Gamma_8{}'$) separations of 635, 1950, and 2710 cm^{-1}, all of which are substantially greater than the largest appropriate E_{JT} values calculated for these species. Of course, the relatively large spin–orbit effects will ensure that the Γ_8 states deriving from the $^2T_{1u}(t_{1u})$ and $^2T_{2u}(t_{2u})$ levels will be substantially mixed, and in Table II the percentage $^2T_{1u}$ character of the upper, $\Gamma_8{}'$, level is also shown; naturally, the larger the values of θ and of Δ (the octahedral splitting parameters) the greater will be the $^2T_{1u}$ contribution. (The opposite composition will clearly obtain for the lower Γ_8 level, but this $\Gamma_7 \rightarrow \Gamma_8$ transition has rarely been observed experimentally.) Thus, keeping in mind all the foregoing considerations, it is now possible to compare the calculated E_{JT} values for the various couplings with the available spectroscopic data for f^1 O_h MX_6 systems.

As would be expected from the bonding characteristics[14] of the threefold degenerate levels, the Jahn–Teller constants relating to the t_{1u} orbital set involve both e_σ and e_π quantities, or their derivatives, while those describing the t_{2u} level contain only e_π or $\partial e_\pi/\partial R$. Thus, since these quantities usually follow the trends $e_\sigma > e_\pi$ and $\partial e_\sigma/\partial R > \partial e_\pi/\partial R$, it is not surprising that the predicted values of E_{JT} are generally greater for t_{1u} than for t_{2u} orbital degeneracies. Nevertheless, in the 5f series it has been shown[14] for the hexahalo complexes of Pa^{IV} and of U^V (5f^1) that the e_π/e_σ ratio increases markedly along the sequence F, Cl, Br, I. Thus, since the Jahn–Teller constants for the t_{1u} set involve *differences* between e_σ and e_π, or between their derivatives, whereas the t_{2u} terms contain only the appropriate e_π quantities, it is not unexpected that the E_{JT} values for the t_{2u} degeneracy should show signs of beginning to exceed the t_{1u} values for the heavier halogens. However, it is clear that the largest E_{JT} values are to be anticipated for the hexafluoro species, E_{JT} generally decreasing along the halogen sequence, and that in such cases E_{JT} is substantially greater for the t_{1u} than for the t_{2u} set. In addition, even allowing for the appreciable uncertainties involved, especially in the K_τ values, it is evident that trigonal distortion, via the τ_{2g} bending mode, is favored at the expense of tetragonal distortions, via the ϵ_g stretching mode.

In the 4f series both the $[LnF_6]^{3-}$ and $[LnCl_6]^{3-}$ complexes have been shown[31,32] to possess face-centered cubic lattices, in which the LnX_6 unit has O_h site symmetry. For the 4f^1 system the most significant Jahn–Teller activity would be expected for the hexafluoro complex, and although there are unfortunately no experimental spectroscopic data, the results of Table II suggest that (neglecting the ϵ_g coupling) E_{JT} for the upper, $\Gamma_8{}'$, level (mainly $^2T_{1u}$) should be about 30 cm^{-1}. Thus, since the separation between the potential sheets will be $4E_{JT}$, there might be some prospect of optical detection of the splitting of the upper level in the $\Gamma_7 \rightarrow \Gamma_8{}'$ transition, although the region of the spectrum in which this band is likely to fall (ca. 3000 cm^{-1}) is experimentally difficult. On the other hand the electronic Raman spectrum of $[CeCl_6]^{3-}$ obtained by Amberger et al.[19] succeeded in locating all the f–f transitions originating from the Γ_7 ground state. Unhappily, the $\Gamma_7 \rightarrow \Gamma_8{}'$ peak at 2661 cm^{-1} appears to lie close to a region of high background absorption, which may have obscured any possible Jahn–Teller splitting, but the $\Gamma_7 \rightarrow \Gamma_8$ transition resulted in a band clearly split into two components, at 562 and 577 cm^{-1}. This separation of 15 cm^{-1} is eminently consistent with the calculated $E_{JT}(\Gamma_8)$ of about 5 cm^{-1}.

For the 5f^1 hexahalo complexes of Pa^{IV} and of U^V numerous spectroscopic studies have been carried out,[4-9] and the low

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intensities of the f–f transitions and the rich vibronic structure observed leave little doubt that O_h MX_6 units, with a center of inversion, are involved. For the Pa^{IV} systems measurements were made only on solid samples, but for the U^V complexes spectra have been recorded for both solids and solutions. Nevertheless, in all cases one of the most prominent features observed proved to be the pronounced splitting exhibited by the $\Gamma_7 \rightarrow \Gamma_8'$ transition, and several authors have discussed its possible origin.[7–9,33,34] Thus, in essence, three possible explanations have been advanced for the presence of two distinct peaks within this band, namely, (i) that these represent vibronic excitations lying above and below the absent (0,0) transition,[7,8] (ii) that the splittings are brought about by distortions from strict O_h symmetry,[8,33] and (iii) that the feature is due to the Jahn–Teller activity of the upper, Γ_8', level.[7–9]

The first explanation was however shown by Ryan[9] to be untenable. Thus he pointed out that for the U^V species the two components of the $\Gamma_7 \rightarrow \Gamma_8'$ band were of roughly equal intensity, which would not be expected for such a vibronic model, while the separation between the two components decreased much more markedly between the F and Cl species than between the Cl and Br complexes, whereas the opposite result would have been expected for features of vibronic origin. Moreover, the spectra now available[4–6] for the $[PaX_6]^{2-}$ complexes (X = F, Cl, Br, I) appear to follow the same trends. Thus the $[PaF_6]^{2-}$, $[PaCl_6]^{2-}$, and $[PaBr_6]^{2-}$ systems show band splittings of 605, 265, and 75 cm^{-1}, respectively, at 300 K, as against the values of 1050, 620, and 430 cm^{-1} for the corresponding $[UX_6]^-$ species.[7–9] Furthermore, for a vibronic interpretation, decrease in temperature would be expected to lead to a decrease in the relative intensity of the lower energy component of the split band, whereas for the $[PaX_6]^{2-}$ complexes the opposite tendency is, if anything, observed.

A vibronic origin for the splitting of the $\Gamma_7 \rightarrow \Gamma_8'$ band is therefore improbable, but the possibility that this feature represents a measure of the extent of geometrical distortion of the MX_6 unit from strict O_h symmetry must now be considered. Thus, Selbin, Ballhausen, and Durrett[33] noted that in $CsUF_6$, which is rhombohedral with a $KOsF_6$ lattice,[30] the $[UF_6]^-$ anion is somewhat distorted from regular O_h symmetry, and they suggested that such a distortion should be smaller for the $[UCl_6]^-$ and $[UBr_6]^-$ species, containing the bulkier halogens. On this basis therefore they felt able to explain the decrease in the band splitting from $[UF_6]^-$ to $[UCl_6]^-$ and $[UBr_6]^-$. However, it has been pointed out by Brown, Whittaker, and Edelstein[34] that the distortion from strict O_h symmetry in the $[UF_6]^-$ anion is really very small and should certainly be less than for the anion $[UOF_5]^{2-}$. Nevertheless, the band splitting found[9] for $[UF_6]^-$ in $CsUF_6$ (1200 cm^{-1}) proved actually to be *greater* than for the $[UOF_5]^{2-}$ compound (950 cm^{-1}), which must certainly be more distorted. Consequently, geometrical distortion from strict O_h symmetry cannot be a dominant factor as regards the magnitude of the $\Gamma_7 \rightarrow \Gamma_8'$ band splitting, and it is also noteworthy that a similar splitting sequence is also found for the $[UX_6]^-$ species (X = F, Cl, Br) by solution measurements.

In addition the $[PaX_6]^{2-}$ data provide further evidence against an explanation of this type. Thus the measurements on these systems were all carried out on the $(NEt_4)_2$ salts, which for the Cl and Br anions show orthorhombic crystal lattices.[29] In these compounds therefore the site symmetry of the MX_6 unit is lower than octahedral, but $(NEt_4)_2PaF_6$ may be obtained in two crystalline modifications,[5] namely, the α form, with a face-centered cubic lattice and O_h site symmetry, and the β form, which is again orthorhombic. Nonetheless, for both forms of $(NEt_4)_2PaF_6$ an identical spectrum was obtained, and the band splittings again followed the sequence F > Cl > Br.

There remains therefore the possibility that the observed band splitting is of Jahn–Teller origin. As noted earlier, the separation between the two Jahn–Teller potential sheets for a Γ_8 level derived from a T_1 or a T_2 state should be $4E_{JT}(\Gamma_8)$. Thus, although the band contour and the peak separation will be a complex function of E_{JT}, temperature, and the energy of the Jahn–Teller active mode, the calculated E_{JT} quantities from Table II are clearly of the proper order of magnitude to correspond to the known features of the $\Gamma_7 \rightarrow \Gamma_8'$ bands. Moreover, the nature of the transition $\Gamma_7 \rightarrow \Gamma_8$ (to the lower Γ_8 level) is also in accordance with the foregoing arguments. Thus, this transition which is expected to lie at very low energies is not often observed experimentally but was found[7] at about 3300 to 3800 cm^{-1} in $[UCl_6]^-$, while a similar feature near 5000 cm^{-1} is apparent in Ryan's[9] spectrum for $[UF_6]^-$ in the solid phase. In both cases the band is rather broad, although not actually split, but again this is not entirely surprising. Thus the lower Γ_8 level should of course also be Jahn–Teller active, but since it will generally represent a mainly $^2T_{2u}(t_{2u})$ state, the splitting should be appreciably less than for a $^2T_{1u}(t_{1u})$ level because of the smaller E_{JT} values usually resulting from the t_{2u} orbital degeneracy.

However, for the more significant Jahn–Teller effects associated with the upper, Γ_8', level it is possible to make rough estimates of the strength of the Jahn–Teller coupling as defined by the ratio $E_{JT}(\Gamma_8)/h\nu$, where $h\nu$ is the energy of the appropriate Jahn–Teller-active mode. For the $4f^1$ species it is clear that the coupling is rather weak, even for the most favorable case ($\Gamma_8' \otimes \tau_{2g}$, $[CeF_6]^{3-}$), but for the $5f^1$ complexes appreciably larger values are predicted. Thus, for the fluoro compounds the calculated $E_{JT}(\Gamma_8')/h\nu(\tau_{2g})$ ratio in fact approaches or exceeds unity respectively for $[PaF_6]^{2-}$ and $[UF_6]^-$ and is still appreciable for the hexachloro species. The strength of the coupling is also seen to decrease with increasing halogen atomic weight, most markedly between F and Cl, and the attribution of the Γ_8' splitting to Jahn–Teller activity is thus fully consistent with the available experimental evidence.

Finally, it is appropriate to comment briefly on the possibility of Jahn–Teller activity for ground states within the 5f series. Thus both $5f^1$ and $5f^2$ systems, with $^2F_{5/2}$ and $^3H_4$ free-ion ground states, yield Jahn–Teller impotent ground levels for O_h MX_6 species, Γ_7 and Γ_1 components respectively lying lowest. However, for the $5f^3$ configuration a Γ_8 component of $^4I_{9/2}$ will almost certainly be the ground level, but as yet the only experimental evidence relating to possible Jahn–Teller effects for such systems is provided by a study by Stone and Karraker[36] of the low-temperature magnetic susceptibilities and Mössbauer spectra of Cs_2NpCl_6, $(NMe_4)_2NpCl_6$, and $(NEt_4)_2NpCl_6$. The results were consistent with a Γ_8 ground state for all three species, but the susceptibilities indicated a small (ca. 5–10 cm^{-1}) splitting of this level for the Cs and NEt_4 salts, which do not have O_h site symmetry but possess trigonal and orthorhombic lattices, respectively.[28–30] However, although the NMe_4 salt, which does have a face-centered cubic lattice, showed no detectable splitting, it alone exhibited an anomalously low magnetic moment, which could be of Jahn–Teller origin, while the Mössbauer spectrum showed a temperature dependence demonstrated by Bersuker[10] to be characteristic of Jahn–Teller-active ground levels.

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It must however be borne in mind that the Jahn–Teller effects for the 5f^3 ground state may well be much smaller than for the 5f^1 Γ_8' level since not only are the ligand-field parameters reported[37] to be considerably smaller than for the earlier [AnCl$_6$]$^{2-}$ systems but in addition the Γ_8 ground level of $^4I_{9/2}$ should correlate most strongly with the strong-field states showing t_{2u} rather than t_{1u} orbital degeneracies, i.e., with the Γ_8 levels of $^2T_{2u}(a_{2u}{}^2t_{2u})$ and of $^2T_{1u}$ and $^4T_{1u}(a_{2u}t_{2u}{}^2)$. Nevertheless, further studies of the Np^{IV} hexahalo species and of the isoelectronic CsPuF$_6$ would obviously be of interest since the present work clearly indicates that f-orbital Jahn–Teller effects need not always be negligible.

Registry No. [CeF$_6$]$^{3-}$, 72283-25-1; [CeCl$_6$]$^{3-}$, 27796-27-6; [PaF$_6$]$^{2-}$, 49864-66-6; [PaCl$_6$]$^{2-}$, 44463-14-1; [PaBr$_6$]$^{2-}$, 44463-09-4; [PaI$_6$]$^{2-}$, 44463-23-2; [UF$_6$]$^{-}$, 48021-45-0; [UCl$_6$]$^{-}$, 44491-58-9; [UBr$_6$]$^{-}$, 44491-06-7.

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Spin-State Isomerism of Tris(2-picolylamine)iron(II). The Diiodide and the Hydrated Dichloride

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Crystal structure determinations of tris(2-picolylamine)iron(II) dichloride dihydrate and tris(2-picolylamine)iron(II) diiodide have accounted for the anomalous magnetic susceptibility of the diiodide and have demonstrated that both the *fac* and *mer* isomers of this complex can exhibit spin-equilibrium behavior. The influence of the complex geometry on the thermodynamics of the spin transformation is discussed. In the dichloride dihydrate lattice the tris(2-picolylamine)iron(II) cation, Fe(2-pic)$_3{}^{2+}$, adopts the *fac* configuration with approximate threefold symmetry and an average iron–nitrogen bond length at 115 K of 1.997 (2) Å indicative of the low-spin state. A three-dimensional hydrogen-bonding network links the noncoordinating chloride ions, the water molecules, and all six amine hydrogens of the complex. At 115 K the dichloride conforms to space group $P\bar{1}$ with $Z = 2$, $a = 10.099$ (4) Å, $b = 10.541$ (3) Å, $c = 11.272$ (4) Å, $\alpha = 114.11$ (3)°, $\beta = 98.77$ (3)°, $\gamma = 94.05$ (3)°, $V = 1071$ (1) Å^3, $R = 0.030$, and $R_w = 0.042$ for 4377 observed reflections. Two crystallographically independent isomers of the Fe(2-pic)$_3{}^{2+}$ complex are found in the diiodide lattice. The unsymmetrical *mer* isomer, with an average iron–nitrogen bond length of 2.200 (7) Å, is high spin, while the *fac* isomer, with an average bond length of 2.064 (6) Å, exists as an interconverting mixture of high-spin and low-spin species at room temperature. The *mer* and *fac* isomers are linked together through hydrogen-bonding interactions between the iodide ions and the amine hydrogen atoms of both isomers. At room temperature the diiodide conforms to space group $P\bar{1}$ with $Z = 4$, $a = 11.649$ (3) Å, $b = 16.933$ (6) Å, $c = 16.271$ (5) Å, $\alpha = 116.86$ (2)°, $\beta = 92.92$ (2)°, $\gamma = 120.02$ (2)°, $V = 2314$ (1) Å^3, $R = 0.038$ and $R_w = 0.045$ for 4362 observed reflections.

Introduction

Observation of spin isomerism in certain transition-metal complexes has prompted a number of efforts to appraise those factors that influence the energetics of spin-state transformations. Changes in nonmagnetic and noncoordinating counterions and molecules of solvation have been found to produce pronounced changes in the magnetic properties of both iron(II) and iron(III) complexes. Among the complexes that have been investigated are [Fe^{II}paptH$_2$]X$_2$,[1,2] Fe^{II}(pyim)$_3$(ClO$_4$)$_2$,[3] [Fe^{II}(pyben)$_3$]X$_2$,[4] [Fe^{III}(sal)$_2$trien]X,[5] Fe^{III}(S$_2$CNC$_4$H$_8$O)$_3$,[6] and Fe^{II}(2-pic)$_3$Cl$_2$·S[7-9] where S = 2H$_2$O, MeOH, and EtOH. The energy differences responsible for these magnetic changes are relatively small (a few kcal), and as a result, such factors as hydrogen bonding, geometric isomerism, and van der Waals interactions can all play significant roles.

The study reported herein is the second in a series of investigations of the solid-state spin transformations of the Fe^{II}(2-pic)$_3{}^{2+}$(2-pic = 2-picolylamine) dication. Multiple-temperature structural investigations of the *mer* isomer of this ion, described in the initial report,[9] demonstrated the feasibility of crystallographic resolution of spin isomers and elucidated the structural relationships between the ethanol and methanol solvates of tris(2-picolylamine)iron(II) dichloride. In the present investigation structural observations pertinent to the spin dynamics of the *fac* isomer are reported and related to those previously provided.

Experimental Section

Preparation of Compounds. Fe(2-pic)$_3$I$_2$. To a 0.1 M aqueous solution of FeCl$_2$·4H$_2$O was added, under N$_2$, 3 equiv of 2-picolylamine (Aldrich Chemicals, 99%) whereupon a dark red solution formed. A 20-fold excess of KI dissolved in a minimum volume of deoxygenated (N$_2$) water was added to this solution. Dark red diamond-shaped crystals of Fe(2-pic)$_3$I$_2$ formed when the resulting solution was cooled in an ice-salt water bath.

Fe(2-pic)$_3$Cl$_2$·2H$_2$O. To a concentrated aqueous solution of FeCl$_2$·4H$_2$O was added, under N$_2$, 3 equiv of 2-picolylamine. The dark red solution was evaporated under nitrogen. Red crystals of the dihydrate formed after approximately 1 week.

Data Collection. Fe(2-pic)$_3$I$_2$. A tetrahedrally shaped crystal of volume 0.0064 mm^3 was attached to a glass fiber and mounted on a Syntex $P\bar{1}$ diffractometer. Automatic centering of 15 strong reflections with graphite-monochromatized Mo Kα radiation (λ 0.71070

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