hydrolysis of the complexes are slower than the rate for the free ligand. At high pH the rate for the free ligand drops sharply while the rates for the complexes remain nearly constant.

Discussion

The yield of the α,γ-complex at pH 6.5 has been increased fivefold over the yield originally reported[3] at pH 3.0. The increased yield of the α,γ-complex compared to the β,γ-complex is attributed to the different state of protonation of the incipient phosphate ligand. The relevant p*K* value would be that for a monodentate γ-complex $[Co(NH_3)_4(H_2O)HP_3O_{10}]^{2-}$, which is a likely intermediate in the formation of either isomer. Although no such complex has been isolated, the monodentate complex γ-$Co(NH_3)_5H_2P_3O_{10}$ has been prepared in this laboratory. The highest phosphate p*K* for this complex is 6.7 and should reflect protonation of the terminal uncoordinated phosphate.[17] Such protonation in the tetraammine would discourage coordination of the terminal phosphate group and favor a formation of the β,γ-complex. The different yields at pH 6.5 and 3.0 are consistent with the p*K* value determined for the pentaammine. Higher pH values might increase still further the relative yield of the α,γ-isomer, but the absolute yield would fall due to the autoreduction of the starting cobalt(III) complex.

The values for the apparent equilibrium constant for the isomerization of the chelation isomers of the (dihydrogen triphosphato)tetraaminecobalt(III) complex reveal that the β,γ-complex, **1**, is the thermodynamically preferred species. The thermodynamics are reflected in the yield of each isomer in the synthesis (50% β,γ- and 7% α,γ-complex). The ΔG° value of 1.6 kcal/mol closely matches values reported for the ring-strain energy of other chelating complexes.[11,15] Assignment of this free energy change as due to ring strain, however, would ignore the different energies of hydration of the isomers which would contribute to the difference in free energy change between the two triphosphato–metal complexes.

A positive entropy change is observed for the transformation of the β,γ-complex, **1**, to the α,γ-complex, **2**. Apparently the mobility of the eight-membered ring formed in the α,γ-complex contributes more to the entropy than the mobility of the six-membered ring formed in the β,γ-complex. A decrease in the ordering of solvent molecules in the overall solvation shell would be expected to accompany the increased mobility of the phosphate ring. The combination of these effects explains the entropy increase in the β,γ- to α,γ-isomerization.

The mobility of the ring can also effect the degree of ring strain experienced by each isomer. Flexing and puckering of the ring are accepted as internal factors for decreasing the entropy of the ring system and in turn the ring strain of that system.[15,16] Apparently the α,γ-complex has a mechanism for the partial relief of internal ring strain imposed by the formation of an eight-membered chelate ring.

A large difference in the ring-strain energies between the two isomers would certainly be reflected in their rates of phosphate hydrolysis. The similarity of the hydrolysis rates of the β,γ- and α,γ-complexes suggests that ring strain is not a major contributing factor in determining the rates of hydrolysis.

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Contribution from the Department of Chemistry,
Northern Illinois University, Dekalb, Illinois 60115

Magnetic Circular Dichroism Spectra for the Intense UV Bands of the Tetrachloro- and Tetrabromoplatinate(II) Ions

HUSEYIN ISCI[1] and W. ROY MASON*

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Electronic absorption and magnetic circular dichroism (MCD) spectra are reported for $PtCl_4^{2-}$ in acetonitrile solution in the UV region from 3.9 to 5.1 μm^{-1} and in methanol solution from 3.9 to 5.0 μm^{-1}. Absorption and MCD spectra are also reported for $PtBr_4^{2-}$ in acetonitrile solution from 2.9 to 5.1 μm^{-1}. The two intense bands observed for $PtCl_4^{2-}$ at 4.25 (shoulder) and 4.41 μm^{-1} in acetonitrile have associated with them negative and positive *A* terms, respectively. The bands observed for $PtBr_4^{2-}$ at 3.62 and 4.75 μm^{-1} in acetonitrile also exhibit negative and positive *A* terms, respectively. These bands together with some other features are assigned to a combination of ligand-to-metal charge-transfer (LMCT) and d → p (5d → 6p on Pt) transitions. Comparisons are made with the spectra of $AuCl_4^-$ and $AuBr_4^-$.

Introduction

In contrast to the weaker, low-energy ligand field (LF) bands, where band assignments seem well established,[2,3] the interpretation of the intense bands in the UV spectra above 4.0 μm^{-1} for $PtCl_4^{2-}$ and above 3.0 μm^{-1} for $PtBr_4^{2-}$ has presented difficulties. There has been a lack of agreement as to assignment in spite of considerable experimental and theoretical work. Two types of electronic excitation have been proposed for these intense bands: allowed d → p transitions and ligand-to-metal charge-transfer (LMCT) transitions. The former are visualized as excitation from the occupied 5d orbitals of Pt(II) (labeled $b_{2g}(xy)$, $e_g(xz, yz)$, and $a_{1g}(z^2)$ in D_{4h} symmetry) to the empty out-of-plane π MO (a_{2u}), which is mainly $6p_z$ (z axis is taken perpendicular to the molecular

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plane). The latter involves excitation from halide-based MO's to the lowest energy empty σ^* orbital $b_{1g}(x^2 - y^2)$, which is predominantly $5d_{x^2-y^2}$ on Pt(II). The LMCT assignments for the intense bands of $PtCl_4^{2-}$ and $PtBr_4^{2-}$ were suggested from the energy ordering of $Cl^- > Br^-$ for corresponding bands, from their analogy to similar bands in a variety of nd^6 hexahalo complexes,[4] and from their relative energies compared to analogous intense bands at lower energy for the isoelectronic, isostructural $AuCl_4^-$, and $AuBr_4^-$ ions.[5] LMCT bands are expected to be sensitive to the metal orbital stability and red shift as the metal oxidation state is increased from Pt(II) to Au(III). Some MO calculations[6] also placed LMCT excited states lower in energy than d → p states for $PtCl_4^{2-}$. The same conclusion was reached on the basis of the photolysis behavior of $PtCl_4^{2-}$.[7] Photolysis at 1849 Å (5.4 μm^{-1}) was interpreted as producing photoelectrons via a d → p excitation while photolysis at lower energy led to photohydrolysis via population of the σ^* $b_{1g}(x^2 - y^2)$ orbital by LMCT and LF transitions. The assignment of the intense band at 4.6 μm^{-1} to a d → p process was first made by Chatt, Gamlen, and Orgel[8] and was later supported by extended Hückel MO calculations.[9] Credibility was also given to the d → p process in planar Pt(II) complexes by the magnetic circular dichroism (MCD) spectrum in the region of an intense band at 5.1 μm^{-1} for the $Pt(NH_3)_4^{2+}$ ion.[10] A positive *A* term[11] was observed, which is required by the $e_g(xz, yz) \rightarrow a_{2u}(p_z)$ transition. Some polarized reflection spectra for single crystals of K_2PtCl_4 showed the intense band at 4.6 μm^{-1} to be strongly out-of-plane (*z*) polarized.[12] This result was interpreted by a $a_{1g}(z^2) \rightarrow a_{2u}(p_z)$ assignment, which gives rise to a *z*-polarized $^1A_{2u}$ excited state. Further, some MCD measurements for $PtCl_4^{2-}$ in 0.5 M HCl showed an apparent negative *B* term for the 4.6-μm^{-1} maximum and a weaker negative *A* term for the lower energy shoulder at 4.3 μm^{-1}.[13] These results were interpreted as indicating both a nondegenerate d → p transition presumably $a_{1g}(z^2) \rightarrow a_{2u}(p_z)$ (for the 4.6-μm^{-1} band) and a degenerate $Cl^-\ \pi \rightarrow b_{1g}(x^2 - y^2)$ LMCT transition (for the 4.3-μm^{-1} shoulder). Also, studies of polarized crystal spectra for K_2PtBr_4 showed that the intense-band region was substantially different from that for the $PtCl_4^{2-}$ ion, even though there was a close parallel between the LF bands of $PtCl_4^{2-}$ and $PtBr_4^{2-}$.[3] The intense bands for $PtBr_4^{2-}$ were assigned to a combination of d → p and LMCT, while those for $PtCl_4^{2-}$ were ascribed to d → p. Finally, a systematic examination of the spectra of the complexes $PtCl_{4-n}(H_2O)_n^{n-2}$ (n = 0–4) showed a blue shift for the intense bands as Cl^- was replaced by H_2O, which was interpreted as evidence for a d → p process.[14]

Since we recently considered the LMCT spectra for $AuCl_4^-$ and $AuBr_4^-$ in some detail,[15] we were naturally prompted to reexamine the intense bands of $PtCl_4^{2-}$ and $PtBr_4^{2-}$. We have measured and report herein the MCD spectrum of the tetra-*n*-butylammonium (TBA) salt of $PtCl_4^{2-}$ at 7 T in acetonitrile to 5.1 μm^{-1} and in methanol to 5.0 μm^{-1} and have extended MCD measurements to $(TBA)_2[PtBr_4]$ in acetonitrile. The MCD spectrum of $PtBr_4^{2-}$ has not been reported previously. The solutions of acetonitrile or methanol solvents are stable toward solvolysis and, therefore, did not require excess added halide. The absence of added halide allowed greater penetration into the UV region than possible with aqueous solutions containing halide for hydrolysis suppression.

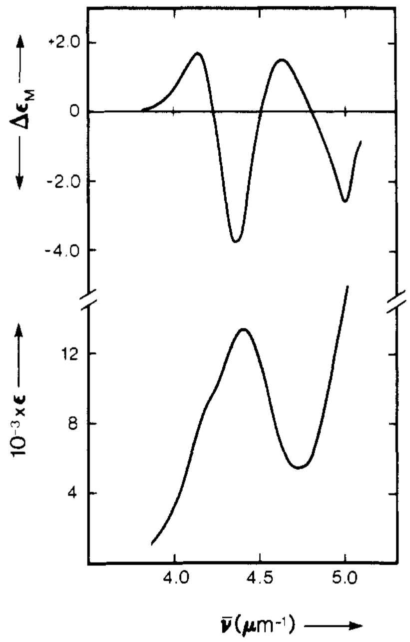

Figure 1. MCD (upper curve) and absorption (lower curve) spectra for $(TBA)_2[PtCl]_4$ in acetonitrile solution.

Table I. Spectral Data

band no.[a]	absorption $\bar{\nu}$, μm^{-1} (ϵ, M^{-1} cm^{-1})	MCD $\bar{\nu}$, μm^{-1} ($\Delta\epsilon_M$, M^{-1} cm^{-1} T^{-1})	excited states
		$(TBA)_2[PtCl_4]$ in CH_3CN	
		4.15 (+1.71)	
V	4.25 (9400)[b]	[c] 4.24 (0)	$2E_u + 7E_u$
		4.36 (−3.83)	
VI	4.41 (13 100)	[c] 4.50 (0)	$8E_u$
		4.63 (+1.52)	
		5.00 (−2.57)	see text
		$(TBA)_2[PtCl_4]$ in CH_3OH	
		4.24 (+1.45)	
V	4.38 (8600)	[c] 4.42 (0)	$2E_u + 7E_u$
		4.59 (−3.91)	
VI	4.63 (9400)	[c] 4.73 (0)	$8E_u$
		4.79 (+0.86)	
		4.93 (−0.54)	see text
		$(TBA)_2[PtBr_4]$ in CH_3CN	
IV	3.35 (3600)[b]	3.28 (+0.35)[b]	$1A_{2u}$
		3.54 (+1.40)	
V	3.62 (8200)	[c] 3.72 (0)	$2E_u$
		4.80 (−0.31)	
		4.22 (−2.84)[b]	$6E_u$, $3A_{2u} + 7E_u$
		4.67 (−5.5)	
VI	4.75 (52 900)	[c] 4.78 (0)	$5E_u + 8E_u$
		4.83 (+1.27)	
VII	4.97 (55 500)	4.98 (−6.4)	Br^- CTTS

[a] LF bands also observed for $PtCl_4^{2-}$ in CH_3CN: I, 2.03 (18); II, 2.49 (59); III, 295 (71); IV, 3.75 (450).[b] In CH_3OH: I, 205 (16); II, 2.54 (58); III, 2.98 (66); IV, 3.80 (450).[b] For $PtBr_4^{2-}$ in CH_3CN: I, 2.33 (126); II, 2.70 (183);[b] III, 3.05 (720).[b] [b] Shoulder. [c] *A* term.

Experimental Section

Tetra-*n*-butylammonium tetrachloroplatinate(II), $[(n\text{-}C_4H_9)_4N]_2[PtCl_4]$, and tetra-*n*-butylammonium tetrabromoplatinate(II), $[(n\text{-}C_4H_9)_4N]_2[PtBr_4]$, were prepared according to the literature;[5] they gave good elemental analyses, and their electronic spectra in acetonitrile were the same as reported previously.[5,16]

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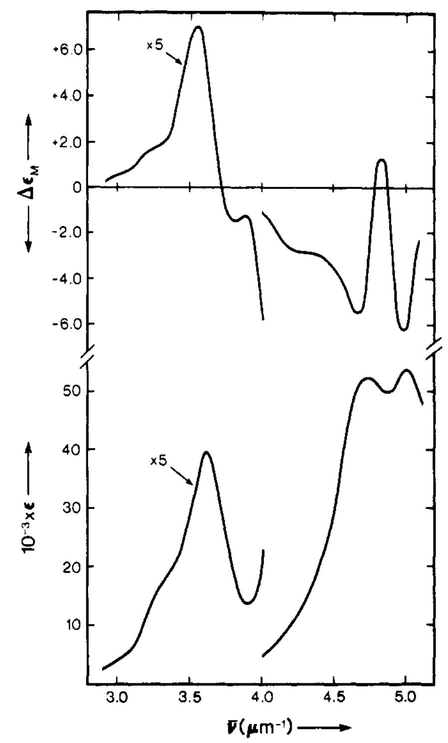

Figure 2. MCD (upper curve) and absorption (lower curves) spectra for $(TBA)_2[PtBr_4]$ in acetonitrile solution.

Spectral grade solvents were used throughout. Absorption spectra were obtained with a Cary 1501 spectrophotometer. Simultaneous MCD and absorption spectra along the same light path were obtained with a computer-controlled spectrometer described elsewhere.[17] The MCD spectra were measured at 7 T with a superconducting magnet system (Oxford Instruments SM2-7, fitted with a room-temperature bore).

Results and Discussion

Absorption and MCD Spectra. Absorption and MCD spectra for $(TBA)_2[PtX_4]$ ($X = Cl^-$ and Br^-) in acetonitrile solution are presented in Figures 1 and 2. Detailed spectral data are summarized in Table I, along with data for $(TBA)_2[PtCl_4]$ in methanol solution. Beer's law was obeyed within experimential error, and there was no evidence of spectral changes due to solvolysis during the time required for the measurements (typically 0.5 h). The energy and absorptivity of the LF bands observed for each complex (see footnote a, Table I) compare favorably with previous studies.[3,5,7,13]

A comparison of the present 7-T MCD results for $PtCl_4^{2-}$ in acetonitrile and methanol with the earlier MCD measurements[13] for 0.5 M aqueous HCl solutions shows similarity in the spectra below the energy of band VI (4.6 μm^{-1}). However above the energy of band VI the present results reveal a clear positive $\Delta\epsilon_M$ maximum and an additional negative feature at higher energy in both acetonitrile and methanol. The earlier measurements[13] show only a return of $\Delta\epsilon_M$ to zero at $\simeq 4.9$ μm^{-1}. It is possible that the 0.5 M Cl^- in the solution interfered at higher energy. The new MCD spectra now suggest two overlapping *A* terms of opposite sign: the lower energy term, associated with band V, being negative and the higher energy term, associated with band VI, being positive. Although the MCD spectra are complicated by the presence of *B* terms (positive for band V and negative for band VI, a moment analysis[11] of the spectra revealed substantial *A* terms of opposite sign. The quantitative reliability of the moments and the A_1 and B_0 parameters derived from them is not very high, however, because of the large degree of overlap between the two MCD features.

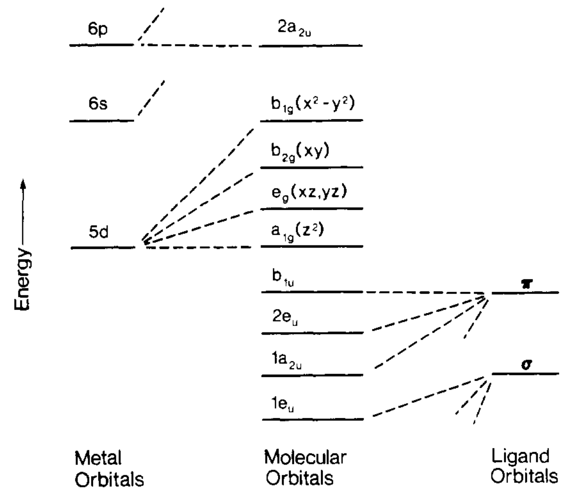

Figure 3. Abreviated molecular orbital diagram showing MO's that will give rise to allowed excited states for LMCT and d → p transitions (see Table II).

Table II. Excited States for LMCT and d → p Transitions

excited confign[a]	no spin-orbit coupling	spin-orbit states[b]	*A* term sign
	LMCT		
$(b_{1u})(b_{1g})$	$^1A_{2u}$	$1A_{2u}$	
	$^3A_{2u}$	$1E_u$	+
$(2e_u)^3(b_{1g})$	^1E_u	$2E_u$	−[c]
	^3E_u	$3E_u$	−[c]
		$2A_{2u}$	
$(1a_{2u})(b_{1g})$	$^3B_{2u}$	$4E_u$	−
$(1e_u)^3(b_{1g})$	^1E_u	$5E_u$	+[c]
	^3E_u	$6E_u$	+[c]
		$3A_{2u}$	
	d → p		
$(b_{2g})(2a_{2u})$	$^3B_{1u}$	$7E_u$	−
$(e_g)^3(2a_{2u})$	^1E_u	$8E_u$	+
	^3E_u	$9E_u$	+
		$4A_{2u}$	
$(a_{1g})(2a_{2u})$	$^1A_{2u}$	$5A_{2u}$	
	$^3A_{2u}$	$10E_u$	+

[a] Filled orbitals omitted. [b] Forbidden states omitted. [c] σ–π mixing required in one-center approximation (see text).

Although they are unsymmetrical in both cases due to the presence of *B* terms, the MCD spectrum for $(TBA)_2[PtBr_4]$ in acetonitrile (Figure 2) shows negative and positive *A* terms for bands V and VI at 3.62 and 4.75 μm^{-1}, respectively. Band IV, which appears as a shoulder at 3.35 μm^{-1} on the low-energy side of band V, has a corresponding shoulder in the MCD and is probably due to a positive *B* term. For band VII at 4.97 μm^{-1}, the term assignment is inconclusive because of the spectral limits of the measurements.

Excited States and MCD Terms. In order to interpret the absorption and MCD spectra for the D_{4h} PtX_4^{2-} ions, an abbreviated one-electron MO energy level diagram that will be helpful in visualizing both the LMCT and d → p transitions is given in Figure 3. The highest occupied level is $b_{2g}(xy)$ so that the ground state for these diamagnetic ions is totally symmetric $^1A_{1g}$. Electric dipole selection rules for D_{4h} dictate that only transitions to A_{2u} (*z*-polarized) and E_u (*xy*-polarized) excited states are allowed; the former gives rise only to *B* terms in the MCD, while the latter can exhibit both *A* and *B* terms (*C* terms will be absent because of the diamagnetic ground

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[16] An error was made in the absorptivity of $(TBA)_2[PtCl_4]$ in acetonitrile for the 4.4-μm^{-1} maximum reported previously.[3] The correct value is half the value reported or 13 100 M^{-1} cm^{-1}.

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state). The sign and magnitude of the MCD terms are, of course, dependent upon the origin of the excited states. Table II presents the LMCT and d → p excited configurations expected to be of lowest energy, together with the singlet and triplet excited states that can lead to A_{2u} or E_u spin–orbit states. For the LMCT states, spin–orbit coupling is due to the halide ligands ($\zeta_{3p\,Cl} = 0.059\ \mu m^{-1}$, $\xi_{4p\,Br} = 0.246\ \mu m^{-1}$) and will be more important for $PtBr_4^{2-}$, but for the d → p states, Pt spin–orbit coupling is the important factor ($\xi_{5d} \simeq 0.40\ \mu m^{-1}$). The MCD A terms for the various $E_u(j)$ states are given in terms of the A_1 parameter by eq 1,[11] where L_z and S_z are

$$A_1 = i\langle E_u(j)x|L_z + 2S_z|E_u(j)y\rangle D_0(^1E_u) \qquad (1)$$

z-component orbital and spin angular momentum operators and $D_0(^1E_u) = |3^{-1/2}\langle ^1A_{1g}|m|^1E_u\rangle|^2$, is the dipole strength of a fully allowed $^1A_{1g} \rightarrow {}^1E_u$ transition. While the exact magnitude of A_1 cannot usually be calculated reliably from eq 1, the sign of the A term can be determined from the angular momentum matrix element since $D_0(^1E_u)$ will always be positive. The angular momentum matrix element can be evaluated in the standard way by approximating the MO's involved by pure atomic orbitals (5d and 6p on Pt and 3p or 4p on the halide) and retaining only one-centered integrals. The signs of the A terms expected for the various LMCT and d → p E_u states are included in Table II. It should be noted, however, that the one-center approximation for the LMCT states involving $1e_u$ (a σ MO) and $2e_u$ (a π MO) requires nonzero intermixing of these two orbitals (σ–π mixing); otherwise the angular momentum matrix elements reduce to only two-centered integrals, which are expected to be ~0. Also the ***relative*** magnitudes of the A terms for the $2E_u$ and $3E_u$ π-LMCT states, respectively, compared to the $5E_u$ and $6E_u$ σ-LMCT states are dependent upon the extent of the σ–π mixing, with the π-LMCT A terms predicted to be smaller than the σ-LMCT A terms (see ref 15 for details). The d → p states are symmetry analogous to the metal-to-ligand charge-transfer (MLCT) states of $Pt(CN)_4^{2-}$ and related D_{4h} complexes containing π-acceptor type ligands that feature an empty, low-energy orbital of a_{2u} symmetry. Therefore, the results of the A sign determination for the d → p states using eq 1 will be exactly the same as for the MLCT states of $Pt(CN)_4^{2-}$ reported previously.[18,19] Unfortunately the B terms for the A_{2u} and E_u LMCT and d → p states cannot be calculated in a general way, because they involve a summation of terms over all other A_{2u} and E_u states of the molecule and the summation is sensitive to the energy ordering of each individual state.[11]

Spectral Assignments. The interpretation of the absorption of MCD spectra for the PtX_4^{2-} ions is based on the foregoing characteristics of the LMCT and d → p states and is based on spectral comparison with our previous results for the AuX_4^- ions.[15] Excited-state assignments keyed to the notation of Table II are summarized in Table I for each band. The rationale for these assignments is discussed each in turn.

$PtCl_4^{2-}$. The MCD spectrum for $PtCl_4^{2-}$ in the region of bands V and VI is significantly different from the lowest energy intense LMCT band system of $AuCl_4^-$. This difference signals the presence of one or more different transitions for the two ions. Therefore, band VI for $PtCl_4^{2-}$ is assigned to the d → p transition to $8E_u$ on the basis of its intensity and positive A term. A LMCT assignment of this band can be excluded because the positive A term and the band intensity would be consistent only with the σ-LMCT transition to $5E_u$. Analogous LMCT transitions in octahedral complexes generally blue shift 1.0–1.2 μm^{-1} as the metal oxidation state is changed by −1.[4,20] Since the σ-LMCT to $5E_u$ is observed at 4.4 μm^{-1} for $AuCl_4^-$ in acetonitrile, this transition should be well over 5.4 μm^{-1} for $PtCl_4^{2-}$. Band V for $PtCl_4^{2-}$ however is 1.1 μm^{-1} higher in energy than the π-LMCT to $2E_u$ observed at 3.1 μm^{-1} for $AuCl_4^-$ in acetonitrile. The observed negative A term is expected if there is significant σ–π mixing between the $1e_u$ and $2e_u$ orbitals.[15] The assignment of band V to $2E_u$ raises the question of the location of the transition to the allowed LMCT to $1A_{2u}$, which is expected at slightly lower energy. The transition to $1A_{2u}$ although of singlet parentage, is an n → σ^* transition (b_1 is nonbonding) and is predicted to be weak.[15] Such a transition could reasonably be obscured by the more intense absorption of bands V and VI and the associated B term obscured by the stronger A term of band V.

The unequivocal assignment of band V to the π-LMCT transition to $2E_u$ is complicated by the prediction of a negative A term for the d → p transition to $7E_u$ ($^3B_{1u}$) also. The $7E_u$ state is likely to be at lower energy than $8E_u$ since the ordering of the occupied orbitals is known to be $b_{2g}(xy) > e_g(xz, yz)$ from LF spectra.[2] Even though $7E_u$ is of triplet parentage, the transition could gain intensity via Pt spin–orbit coupling with $8E_u$, which is of singlet parentage and close in energy. There is also a significant solvent shift (0.18–0.22 μm^{-1} to higher energy, see Table I) for both bands V and VI as the solvent is changed from acetonitrile to methanol (a similar solvent shift has been reported by others[7]). Such a solvent shift is more easily explained for d → p transitions than for LMCT because the acceptor $2a_{2u}$ orbital is more exposed to solvent interaction than the halide-based σ- and π-bonding orbitals or the $b_{1g}(x^2 - y^2)$ σ^* orbital. Very little solvent shift is observed for the LMCT bands of AuX_4^- for example.[21] Clearly the assignment of band V to the d → p transition to $7E_u$ cannot be excluded, nor can an unresolved combination of transitions to both the π-LMCT $2E_u$ state and the d → p $7E_u$ state, though we favor the π-LMCT assignment on the basis of the band position argument in comparision with AuX_4^-.

Finally, a negative MCD feature is observed at high energy in both acetonitrile and methanol, but no corresponding absorption band is clear. The term assignment and the origin of this feature are not known, but it is probably associated with the higher energy band system (5.2–5.4 μm^{-1}) reported using very short-path cells.[7] This band may be the high-energy σ-LMCT transition to $5E_u$, and the negative feature observed in the MCD may be the negative low-energy portion of the positive A term.

$PtBr_4^{2-}$. In the $PtBr_4^{2-}$ spectrum, band V is found 0.58 μm^{-1} to lower energy than band V for $PtCl_4^{2-}$ in acetonitrile. This red shift is nearly the same as observed for the π-LMCT to $2E_u$ between $AuBr_4^-$ and $AuCl_4^-$ in the same solvent (0.56 μm^{-1}).[15] The assignment of band V for $PtBr_4^{2-}$ to the π-LMCT to $2E_u$ is thus logical. The weaker low-energy shoulder on this band (band IV) is assigned as the LMCT transition to $1A_{2u}$; the corresponding shoulder in the MCD would then be due to a positive B term analogous to that observed for $1A_{2u}$ for $AuBr_4^-$.[15]

The assignment of the high-energy bands for $PtBr_4^{2-}$ (bands VI and VII) is more difficult because there are several possibilities that cannot be distinguished unambiguously from the present results. First, the σ-LMCT transition of singlet parentage to $5E_u$ in $AuBr_4^-$ is observed 1.38 μm^{-1} higher in energy than the π-LMCT to $2E_u$, and the band has a high absorptivity (ϵ = 52 500). This pattern is typical of LMCT observed for octahedral complexes: the σ-LMCT is 1.0–1.5 μm^{-1} to higher energy and is more intense than the π-

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LMCT.[4,20] If a comparable separation is applicable to PtBr$_4^{2-}$, then either band VI or band VII (1.13 and 1.35 μm^{-1}, respectively, higher than band V) could be assigned to the σ-LMCT, with the absorptivity quite comparable to that of AuBr$_4^-$. Second, the d → p transition to 8E$_u$, being a metal-atom-localized transition, is not expected to exhibit a strong shift, as Cl$^-$ is replaced by Br$^-$ so that band VI at 4.75 μm^{-1} could reasonably be assigned to this transition. Finally, the Br$^-$ ion exhibits strong absorption bands in this energy region in acetonitrile that have been assigned to charge transfer to solvent (CTTS), and the lowest energy CTTS transitions are characterized by positive *A* terms in the MCD.[22] It is likely that coordinated Br$^-$ will also exhibit such transitions. Thus, the observed positive *A* term for band VI of PtBr$_4^{2-}$ (the term assignment for band VII is not possible from the present data) is consistent with any of these possibilities. Because they would be internally consistent with the other assignments presented here for PtCl$_4^{2-}$ and previously for AuX$_4^-$,[15] we assign band VI as the unresolved combination of the σ-LMCT to 5E$_u$, the d → p transition to 8E$_u$, and band VII as Br$^-$ CTTS. The shoulder observed in the MCD at 4.22 μm^{-1}, which has no corresponding band in the absorption spectrum, is then assigned to the d → p transition to 7E$_u$ and the σ-LMCT transitions to 6E$_u$ and 3A$_{2u}$. The *A* term for band VI renders the term assignment(s) for these transitions obscure.

Conclusions. The assignment of the intense bands in the PtX$_4^{2-}$ ions to both d → p and LMCT transitions is consistent with the present results. Thus, the PtX$_4^{2-}$ spectra can be visualized as resulting from the blue shift of LMCT transitions accompanied by the red shift of d → p transitions from AuX$_4^-$. Both shifts are consonant with the expected changes in orbital stability as the oxidation state is changed from Au(III) to Pt(II).

The negative *A* terms for the π-LMCT transitions to 2E$_u$ are clear in the MCD spectra of the PtX$_4^{2-}$ ions, but they are obscured by *B* terms in the MCD spectra of AuX$_4^-$. This indicates a greater relative magnitude of these *A* terms for Pt(II) than for Au(III). This together with the greater relative intensity for the π-LMCT transitions compared to the σ-LMCT observed for PtBr$_4^{2-}$ compared to AuBr$_4^-$ can be attributed to greater σ–π mixing of the 1e$_u$ and 2e$_u$ halide orbitals. Stronger mixing might be expected if there is a smaller energy difference between these orbitals in the Pt(II) complex compared to the Au(III) complex. An analogous trend was noted earlier from some comparisons among several octahedral halo complexes[20] and was interpreted as an enhancement of σ donation over π donation as the metal oxidation state was increased.

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Contribution from the City University of New York, John Jay College and Graduate School,
New York, New York 10019, Institut für Organische Chemie, Friedrich-Alexander-Universität Erlangen-Nürnberg,
D-8520 Erlangen, Federal Republic of Germany, and Organisch-Chemisches Institut, Universität Heidelberg,
D-6900 Heidelberg, Federal Republic of Germany

Structures and Energies of Lithium Amide Dimers and Trimers: An ab Initio Study

ANNE-MARIE SAPSE,*[1a] ELMAR KAUFMANN,[1b] PAUL VON RAGUÉ SCHLEYER,*[1b] and ROLF GLEITER[1c]

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The structures and energies of LiNH$_2$ dimers and trimers were investigated by ab initio and semiempirical (MNDO) molecular orbital theory. In agreement with X-ray structure results on derivatives, (LiNH$_2$)$_2$ and (LiNH$_2$)$_3$ prefer symmetrical D_{2h} and D_{3h} geometries (**4** and **5**, respectively), with all hydrogen atoms perpendicular to the planar heavy-atom rings. The LiNH$_2$ dimerization (–62.5 kcal/mol) and trimerization (about –120 kcal/mol) energies are at least as large as the related values for LiOH and LiF. The LiCH$_3$ dimerization and trimerization energies are much smaller. Since these association energies generally follow electronegativity trends, specific nitrogen lone pair–lithium interactions are indicated in **4** and **5**. When all NH$_2$ groups are rotated by 90°, these interactions are lost and the resulting isomers, **8** and **9**, are much less stable. Further energetic relationships and the nature of lithium bonding are discussed.

Introduction

Association is a principal characteristic of lithium compounds.[2-4] The energies involved are very large, and aggregated species, rather than monomers, are typical. While this paper is concerned with oligomers of LiNH$_2$, the simple alkyllithiums are the best known examples. Thus, methyllithium is a tetramer, (CH$_3$Li)$_4$, in ether solvents,[2,4] in the crystal,[5] and even in the gas phase.[6] The association energy is not known experimentally, but values (kcal/mol) for the formation of the dimer (42), trimer (82), tetramer (128), and higher oligomers are available from a number of calculations.[7] Gas-phase association energies for (LiF)$_2$ (61.4 ± 8 kcal/mol), for (LiF)$_3$ (116.8 ± 12 kcal/mol), and for (LiOH)$_2$ (62.4 ±

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(1) (a) City University of New York. (b) Friedrich-Alexander-Universität Erlangen-Nürnberg. (c) Universität Heidelberg.

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