Electronic Absorption and Magnetic Circular Dichroism Spectra for the Linear Two-Coordinate Bis(tri-*tert*-butylphosphine)platinum(0) Complex in 2-Methylpentane at 295 and 80 K

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Electronic absorption and 8.0 T magnetic circular dichroism (MCD) spectra are reported for $Pt(P(t\text{-}Bu)_3)_2$ in 2-methylpentane solutions at 295 K and in glasses at 80 K. The intense bands observed in the 2.4−5.0 μm^{-1} ($1\ \mu m^{-1} = 10^4\ cm^{-1}$) region are assigned as 5d → 6p/metal-to-ligand charge-transfer transitions to dipole-allowed $\Sigma_u{}^+$ and Π_u spin−orbit states of $5d^{10} \rightarrow 1\pi_u$ excited configurations. The enhanced resolution of the spectra at low temperatures reveals several previously unresolved spectral features in both absorption and MCD spectra, which strengthen the assignments and relative orbital energy ordering concluded from them.

Introduction

This laboratory has had an interest in the electronic structures of low coordination number complexes for many years and has examined the electronic spectra previously for the linear two-coordinate $Au(P(t\text{-}Bu)_3)_2{}^+$ complex in an acetonitrile solution and the isostructural $Pt(P(t\text{-}Bu)_3)_2$ complex in both acetonitrile and *n*-hexane solutions.[1] Two-coordinate Pt(0) complexes ($5d^{10}$) are not common and usually require sterically demanding ligands, such as $P(t\text{-}Bu)_3$, to prevent higher coordination numbers (three or four). In contrast, linear two coordination for isoelectronic Au(I) complexes is the preferred geometry. The electronic spectra for these complexes exhibit a number of intense bands in the UV−vis region, which were assigned to metal-to-ligand charge-transfer (MLCT) transitions with some metal 5d → 6p character. The lowest energy band for the Pt(0) complex is markedly red shifted by 1.4 μm^{-1} ($1\ \mu m^{-1} = 10^4\ cm^{-1}$) when compared to that for the Au(I) complex. A significant red shift is a characteristic feature of both MLCT and 5d → 6p transitions as the metal oxidation state is lowered from I to 0. Further, with the aid of magnetic circular dichroism (MCD) spectroscopy,[2] three prominent positive A terms were found for the Pt(0) complex and two positive A terms for the Au(I) complex, indicating the presence of degenerate Π_u excited states. The absorption and MCD spectra were interpreted in terms of transitions to dipole-allowed $\Sigma_u{}^+$ and Π_u excited spin−orbit states of metal 5d → $1\pi_u$ configurations,[1] where the $1\pi_u$ LUMO has metal 6p and ligand P_π character.

Even though assignments of the $Pt(P(t\text{-}Bu)_3)_2$ spectra were made which were analogous to those for $Au(P(t\text{-}Bu)_3)_2{}^+$, the spectral patterns are different and required the assumption of some unresolved transitions. Therefore, the present study was undertaken in order to provide some new high-quality absorption and MCD spectral measurements under higher resolution conditions at low temperatures. This paper reports both the absorption and MCD spectra for the $Pt(P(t\text{-}Bu)_3)_2$ complex at 295 and 80 K in a 2-methylpentane solvent. The 2-methylpentane solutions form transparent, strain-free glasses at 80 K, which preserves an isotropic environment about the complex.

Experimental Section

Bis(tri-*tert*-butylphosphine)platinum(0) was prepared by the literature method[3] and analyzed as previously described; room-temperature spectra in acetonitrile compared favorably with the earlier study. Electronic absorption spectra were measured by means of a Cary 5E spectrophotometer, and absorption and MCD spectra were determined simultaneously along the same light path by means of a spectrometer built in this laboratory and described earlier.[4] MCD spectra were obtained at a field of 8.0 T by means of a superconducting magnet system of split coil design (Oxford Instruments Spectromag 4000) equipped with a variable-temperature insert. The sample temperature was controlled to within ±0.1 K by passing cold He gas over the sample in a 1 cm path quartz cell. All of the spectra were corrected for a solvent blank at the same measurement temperature. Contraction of the 2-methylpentane solvent on cooling from 295 to 77 K was measured to be 22 ± 2%. There was no evidence of strain birefringence at temperatures of 80 K and above. Both the absorption and MCD spectra sharpened and changed in a self-consistent and reproducible fashion for scans between 150 and 80 K. However, upon cooling to ca. 40 K or below, serious problems were encountered. The MCD spectra exhibited spurious, nonreproducible changes with an inconsistent loss of MCD signal, and the glass routinely cracked, sometimes destroying the quartz cell. Although the absorption spectra continued to sharpen as the sample was cooled to 40 K and below, the MCD spectra were deemed unreliable below 80 K because of the strain induced by the thermal contraction of the glass.

Results and Discussion

Electronic absorption and MCD spectra at 295 and 80 K are presented in Figure 1. Spectral data are collected in Table 1, where the 80 K data are corrected for the solvent contraction.

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[1] Jaw, H.-R.; Mason, W. R. *Inorg. Chem.* **1989**, *28*, 4370.

[2] For a review of MCD spectroscopy, together with the standard (Stephens) definitions and conventions that are used here, see: Piepho, S. B.; Schatz, P. N. *Group Theory in Spectroscopy with Applications to Magnetic Circular Dichroism*; Wiley-Interscience: New York, 1983.

[3] Goel, R. G.; Ogini, W. O.; Srivastava, R. C. *J. Organomet. Chem.* **1981**, *214*, 405.

[4] Mason, W. R. *Anal. Chem.* **1982**, *54*, 646. The spectrometer has been upgraded with some newer electronic components, including a modern DSP lock-in amplifier (Stanford Research Instruments SR850), but the optical components and measurement methodology have remained essentially the same.

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Table 1. Spectral Data for 2-Methylpentane Solutions at 295 and 80 K

295 K						80 K^a					
abs				MCD		abs				MCD	
band no.	$\bar{\nu}$ (μm^{-1})	λ (nm)	ϵ (M^{-1} cm^{-1})	$\bar{\nu}$ (μm^{-1})	$\Delta\epsilon_M$ [(M cm T)$^{-1}$]	band no.	$\bar{\nu}$ (μm^{-1})	λ (nm)	ϵ (M^{-1} cm^{-1})	$\bar{\nu}$ (μm^{-1})	$\Delta\epsilon_M$ [(M cm T)$^{-1}$]
				2.577	−5.46					2.584	−7.99
I	2.604	384.0	4 940	2.614	0	I	2.606	383.4	5 500	2.612	0
				2.650	+4.13					2.637	+6.24
				2.990	−1.20					3.010	−3.32
II	3.032	329.8	4 350	3.040	0	II	3.043	328.6	4 630	3.045	0
				3.069	+0.78					3.086	+3.11
				3.193	−16.86					3.191	−23.58
IIIa	3.213	311.2	16 800	3.277	0	IIIa	3.205	312.0	19 700	3.275	0
IIIb	3.327	300.6	9 800^b	3.367	+11.94	IIIb	3.313	301.8	10 000^b	3.367	+15.51
				3.554	−0.034^b					3.566	+0.955^b
				3.797	−7.41	IVa	3.762	265.8	5 900^b	3.751	−6.46
IV	3.968	252.0	20 200^b	4.006	−0.320^b	IVb	3.888	257.2	13 600	3.857	−7.79
						IVc	3.987	250.8	20 800	4.000	−1.12^b
V	4.146	241.2	28 500	4.177	+8.47	V	4.144	241.3	31 500	4.160	+9.70
VI	4.744	210.8	11 900^b	4.579	+0.741	VIa	4.643	215.4	8 500	4.496	+2.55
						VIb	4.921	203.2	9 300		

[a] Corrected for solvent contraction. [b] Shoulder.

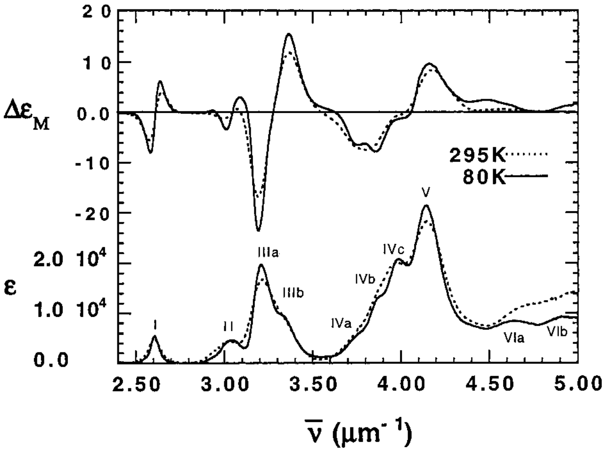

Figure 1. Absorption (lower curves) and 8.0 T MCD (upper curves) spectra for Pt(P(t-Bu)$_3$)$_2$ in 2-methylpentane solution at 295 and 80 K. The x-axis energy units are 1 μm^{-1} = 10^4 cm^{-1}. The 80 K spectra were corrected for 22% solvent contraction before being plotted.

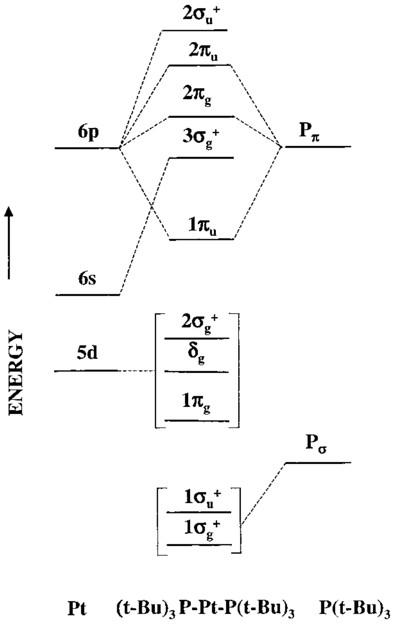

Figure 2. Molecular orbital energy levels for the linear two-coordinate Pt(P(t-Bu)$_3$)$_2$ complex.

The 295 K absorption and MCD spectra compare favorably with the spectra obtained earlier[1] for the Pt(P(t-Bu)$_3$)$_2$ complex in n-hexane at room temperature. As noted in the Experimental Section, special care was taken to ensure that the low-temperature glass which formed at 80 K did not suffer from strain birefringence which could interfere with the MCD measurements. The 80 K spectra show enhanced resolution, revealing bands IIIb, IVa, IVb, VIa, and VIb clearly, which were either poorly or not resolved at 295 K. The decrease in the bandwidth and overall sharpening of the spectra on cooling to low temperatures is consistent with dipole-allowed transitions.

Excited States and MCD Terms. A molecular orbital electronic structural model for Pt(P(t-Bu)$_3$)$_2$ was developed from earlier studies of 5d^{10} Au(I) complexes and was presented previously;[1] a simplified MO energy level diagram which will be useful here is shown in Figure 2. The lowest-energy excited configurations and states for the 5d → 6p/MLCT transitions are listed in Table 2 (z axis coincident with the molecular axis), where $2\sigma_g^+$, δ_g, and $1\pi_g$ are the occupied 5d Pt(0) orbitals 5d$_{z^2}$, 5d$_{x^2-y^2}$5d$_{xy}$, and 5d$_{xz}$5d$_{yz}$, respectively, and $1\pi_u$ is the Pt 6p$_x$6p$_y$/P(t-Bu)$_3$ π_u based LUMO. Electric dipole transitions are allowed from the totally symmetric 5d^{10} $^1\Sigma_g^+$ ground state to either Σ_u^+ (z polarized) or Π_u (xy polarized) states; the dipole forbidden states in Table 2 are enclosed in parentheses. The MCD $\bar{A}_1/\bar{D}_0$ parameter ratio[2] calculated (assuming pure atomic orbitals) for each degenerate Π_u spin−orbit state is also included in Table 2. The four Σ_u^+ and seven Π_u allowed spin−orbit states will be further intermixed because of a strong Pt(0) spin−orbit coupling interaction ($\zeta_{5d} \sim 0.3-0.4\ \mu$m^{-1}) giving rise to Σ_u^+(i) and Π_u(i) eigenvectors. A complete diagonalization of the spin−orbit secular determinants would be necessary to estimate energies and eigenvector coefficients. This has been done earlier for Au(I) complexes,[5] where the problem is substantially the same. These earlier calculations showed that an important result of the strong metal spin−orbit coupling was to spread the spin−

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(5) Chastain, S. K.; Mason, W. R. *Inorg. Chem.* **1982**, *21*, 3717. Savas, M. M.; Mason, W. R. *Inorg. Chem.* **1987**, *26*, 301.

Table 2. Excited Configurations and States

excited config[a]	no spin−orbit coupling	strong spin−orbit coupling[b]	calcd $\bar{A}_1/\bar{D}_0$
$(2\sigma_g^+)(1\pi_u)$	$a^1\Pi_u$	Π_u	+1
	$a^3\Pi_u$	Π_u	+1
		Σ_u^+	
		(Σ_u^-)	
		(Δ_u)	
$(\delta_g)^3(1\pi_u)$	$^1\Phi_u$	(Φ_u)	
	$^3\Phi_u$	(Φ_u)	
		(Γ_u)	
		(Δ_u)	
	$b^1\Pi_u$	Π_u	+1
	$b^3\Pi_u$	Π_u	+1
		Σ_u^+	
		(Σ_u^-)	
		(Δ_u)	
$(1\pi_g)^3(1\pi_u)$	$^1\Sigma_u^+$	Σ_u^+	
	$^3\Sigma_u^+$	(Σ_u^-)	
		Π_u	+2
	$^1\Sigma_u^-$	(Σ_u^-)	
	$^3\Sigma_u^-$	Σ_u^+	
		Π_u	+2
	$^1\Delta_u$	(Δ_u)	
	$^3\Delta_u$	(Δ_u)	
		(Φ_u)	
		Π_u	0

[a] Notation as in Figure 2, with filled orbitals omitted; ground state = $(1\pi_g)^4(\delta_g)^4(2\sigma_g^+)^2$, $^1\Sigma_g^+$. [b] Dipole-forbidden spin−orbit states are in parentheses.

orbit excited states over 1−1.5 μm^{-1} in energy if the zero-order singlet and triplet states were relatively close together. Such computations must certainly be considered qualitative, but they can serve as a useful guide for spectroscopic assignments (see ref 1 for details).

Spectral Assignments for Pt(P(*t*-Bu)$_3$)$_2$. The assignment of the intense band III at 3.2 mm^{-1} was made earlier[1] by analogy to a corresending intense band system in Au(P(*t*-Bu)$_3$)$_2^+$ at 4.8 μm^{-1}. The assignment was made to two close-lying transitions to the Π_u spin−orbit states originating from $a^1\Pi_u$ and $b^1\Pi_u$, on the basis of the observation of two closely-spaced positive A terms in the MCD spectrum. The absorption band for the Au(I) complex also showed the presence of two overlapping, but just resolved, bands (band III with a maximum at 4.78 μm^{-1} and band IV with a shoulder at 4.86 μm^{-1}). It was argued that, for the Pt(0) complex, the two transitions were unresolved (within their bandwidths) and that the single strong positive MCD A term observed was simply the sum of the two expected positive A terms. The present 80 K results shown in Figure 1 support this assignment; band III shows improved resolution, showing clearly two components: a maximum, band IIIa, assigned to $\Pi_u(a^1\Pi_u)$ and a high-energy shoulder, band IIIb, assigned to $\Pi_u(b^1\Pi_u)$. The strong positive MCD A term associated with band III is not resolved at 80 K, but when a moment analysis was performed over the whole band envelope (see ref 2, Chapter 7 for details), the experimental $\bar{A}_1/\bar{D}_0$ parameter ratio was found to be +2.50 ± 0.05, a value which is more than twice the calulated value for the A term for either of the Π_u states alone and more nearly what would be expected for their sum (+2.0; see Table 2). As was noted earlier,[1] the $a^1\Pi_u$ and $b^1\Pi_u$ states are expected to have nearly zero magnetic interaction between them (MCD B terms), which is a consequence of the nearly pure $5d_{z^2}$ character of the $2\sigma_g^+$ and the $5d_{xy}5d_{x^2-y^2}$ character of the δ_g orbitals, respectively. Therefore, there should be very little pseudo A term (B terms of opposite sign for close-lying states) contributions to the observed MCD for bands IIIa and IIIb, and the observed A term should be very nearly the sum of the A term contributions from the $\Pi_u(a^1\Pi_u)$ and $\Pi_u(b^1\Pi_u)$ states, apart from the smaller contributions from the admixture of the other five Π_u states to higher and lower energies. Given the approximations involved, it is satisfying that the $\bar{A}_1/\bar{D}_0$ found here is approximately the magnitude expected for the sum of the two states.[6]

Bands I and II at 2.6 and 3.04 μm^{-1}, weaker and lower in energy than band III, also show strong positive MCD A terms. These bands were logically assigned as transitions to the Π_u states of triplet origin from $a^3\Pi_u$ and $b^3\Pi_u$, respectively.[1] At 80 K, band I has a larger $\bar{A}_1/\bar{D}_0$ value (+1.8 ± 0.1) than band II (+1.0 ± 0.1) and probably signals the involvement of pseudo A terms. Earlier spin−orbit calculations[5] for Au(I) complexes showed that the lower energy $\Pi_u(a^3\Pi_u)$ is expected to have a significant positive pseudo A term contribution from the close-lying (unresolved) Π_u and Σ_u^+ spin−orbit states from $a^3\Pi_u[(2\sigma_g^+)(1\pi_u)]$, whereas the higher energy $\Pi_u(b^3\Pi_u)$ is likely to have a negative pseudo A term contribution from the Π_u and Σ_u^+ spin−orbit states from $b^3\Pi_u[(\delta_g)^3(1\pi_u)]$. These expectations seem to be in accord with the results here for bands I and II, but it must be acknowledged that B term, and therefore pseudo A term, computations are difficult because contributions from all of the allowed states both to higher and lower energies must be taken into account.

Band IV shows what appears to be a vibrational structure on the low-energy side at 80 K. The shoulders IVa and IVb together with the maximum IVc show a separation of about 1100 cm^{-1} (possibly resulting from ν_{P-C}). These features are not connected to band V because the energy separation between band IVc and band V is significantly larger at about 1600 cm^{-1}. Therefore, the conclusion that there are at least two transitions, IV and V, in this region seems justified. Furthermore, the MCD spectrum shows features that mirror the vibrational structure for band IV, but in that for band V, a single broad maximum is observed, which presents the appearance of a positive B term. The assignment of band V to the transition to $\Sigma_u^+(^1\Sigma_u^+)$, the only allowed state of predominantly singlet origin from the $(1\pi_g)^3(1\pi_u)$ excited configuration, seems reasonable on the basis of the intensity and the MCD B term observed. A precise interpretation of band IV is more difficult, but its position to a lower energy and its lower intensity suggest that the features are due to a transition to a state (or states) with triplet character from the $(1\pi_g)^3(1\pi_u)$ configuration, for example, $\Pi_u(^3\Sigma_u^+)$, $\Pi_u(^3\Sigma_u^-)$, and $\Sigma_u^+(^3\Sigma_u^-)$. The MCD spectrum is not really well enough resolved at 80 K to decide among these possibilities.

Finally, Figure 1 shows a broad absorption at 295 K near 4.7 μm^{-1}, which is resolved into two weaker bands, VIa and VIb, at 80 K. The MCD spectrum in this region is not very helpful, showing only a weak broad positive feature. A broad high-energy band system was also observed earlier in acetonitrile and in *n*-hexane spectra,[1] where the MCD was unusually weak.

Concluding Remarks

The results obtained here serve to reinforce and strengthen the earlier assignments[1] by resolution of spectral features previously unresolved. The conclusions to be drawn from the interpretation of the spectra are (1) the 5d → 6p/MLCT character

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(6) A reviewer questioned the possibility that band IIIb might be a vibrational component built on an electronic transition, giving rise to band IIIa. While this possibility cannot be ruled out entirely, it would still require two (or more) closely spaced electronic states (unresolved transitions) for band IIIa in order to satisfactorily explain the large experimental $\bar{A}_1/\bar{D}_0$ which was determined over the entire band III.

of the transitions and (2) the closeness of the energy of the occupied Pt(0) 5d orbitals. Thus, the transitions to the states from $(2\sigma_g^+)(1\pi_u)$ and $(\delta_g)^3(1\pi_u)$ are very close in energy, with those from $(1\pi_g)^3(1\pi_u)$ somewhat higher in energy, indicating that, assuming the differences in interelectronic repulsions are small, the occupied one-electron orbital energy ordering is $2\sigma_g^+ \sim \delta_g > 1\pi_g$. The range of energies covered by the excited states is likely due to the Pt(0) spin−orbit interaction. The overall participation of these occupied orbitals in metal−ligand bonding must be minimal because of the closeness in energy of $2\sigma_g^+$ and $1\pi_g$ orbitals to the strictly nonbonding (by symmetry) δ_g orbital.

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