

in the two independent molecules of I are best described as slightly distorted octahedra similar to those found in other $(\text{CO})_5\text{Mo}(\text{P-donor ligand})$ complexes.¹² The dihedral angles formed by the three equatorial planes of four donor atoms are 90.1 (1), 87.4 (1), and 89.8 (1) $^\circ$ in molecule A and 87.6 (1), 90.2 (1), and 89.3 (1) $^\circ$ in molecule B. As previously observed in other complexes of the type $(\text{CO})_5\text{M}(\text{P-donor ligand})$ and $(\text{CO})_4\text{M}(\text{P-donor ligand})_2$ (M = Cr, Mo),^{1,12} the lengths of the Mo-C bonds involving the CO ligands trans to the P-donor groups (1.998 (3) and 2.003 (3) Å in A and B, respectively) are significantly shorter than the average of those involving CO ligands cis to the P-donor groups (2.040 (3) and 2.038 (3) Å in molecules A and B, respectively).

The Mo(0) atom and the Cu(II) ion in I are separated by distances of 7.078 (1) and 7.079 (1) Å in molecules A and B. These distances are considerably longer than the 5.679 (1) Å Mo-Ni distance in II¹ and the 3.966 (1) Å Pt-Cu distance in *cis*-Cl₂Pt(Pacac)₂Cu (III; PacacH = [*o*-(diphenylphosphino)benzoyl]pinacolone).⁴ The differences in the metal-metal distances in these complexes is due to both (i) differences in the flexibility and the size of the bridging ligand (II vs. III) and (ii) differences in the degree of restraint on relative metal positions due to differences in the number of bridging ligands (I vs. II).

The structure of the title compound, in comparison with those of other heteropolymetallic complexes, suggests several features that appear to be related to the presence of a single salicylaldiminato-diphenylphosphino bridging ligand between the metal centers. These include (i) the stacking interactions between a phenyl ring of the phosphino ligand group and the polar or partially charged atoms at the heterometal center and (ii) the expansion of the distance separating the metal centers relative to that in the related heterobimetallic complex II, in which the centers are bridged through two salicylaldiminato-diphenylphosphino ligands. These features may be of significance to the catalytic properties of complexes similar to I and II, in which the molybdenum center

is replaced by catalytically active group 9 or 10 metals. The syntheses and structural analyses of complexes of the latter type are currently in progress.

Acknowledgment. We thank Mary Ann Jones for assistance in the drawings. This research was supported in part by grants from Research Corp. and the Graduate School of the University of Alabama at Birmingham and by the X-ray Crystallographic Core Facility of the Comprehensive Cancer Center at the University of Alabama at Birmingham (National Cancer Center Grant CA-13148). H.E. is a recipient of an NIH Research Career Development Award (Grant DE 00106).

Registry No. I, 102942-28-9; $(\text{CO})_5\text{MoPPPh}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$, 102942-29-0; $(\text{CO})_5\text{MoPPPh}_2\text{NHCH}_2\text{CH}_2\text{N}=\text{CH}-o\text{-C}_6\text{H}_4\text{OH}$, 102942-30-3; $(\text{CO})_5\text{MoPPPh}_2\text{Cl}$, 23581-74-0; $\text{PPPh}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$, 102942-27-8; *o*-salicylaldehyde, 90-02-8.

Supplementary Material Available: A listing of atomic positional and thermal parameters (6 pages). Ordering information is given on any current masthead page.

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Received February 21, 1986

Articles

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Magnetic Circular Dichroism Spectra for the Tetraammineplatinum(II) and Bis(ethylenediamine)platinum(II) Cations

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Received February 12, 1986

Electronic absorption and magnetic circular dichroism (MCD) spectra are reported for $[\text{Pt}(\text{NH}_3)_4](\text{ClO}_4)_2$ and for $[\text{Pt}(\text{en})_2](\text{ClO}_4)_2$ (en = ethylenediamine) in 0.100 M HClO_4 and in CH_3CN in the UV region from 2.8 to 5.2 μm^{-1} . The spectra for the two cations are remarkably similar. A weak feature, which has no counterpart in the absorption, is observed near 3.1 μm^{-1} in the MCD spectra for both cations. This feature, which has not been reported previously, and two other bands in the 3.0-4.3- μm^{-1} region are ascribed to ligand field (LF) transitions. A strong MCD minimum associated with the more intense absorption band near 4.5 μm^{-1} is shown by moment analysis to consist of a significant positive *A* term and a negative *B* term. The intense band in the region 4.9-5.1 μm^{-1} observed for both cations shows a strong positive *A* term in the MCD. In addition, a negative *B* term is resolved on the low-energy side of the strong positive *A* term for this band for $\text{Pt}(\text{NH}_3)_4^{2+}$ in 0.100 M HClO_4 . Both the band near 4.5 μm^{-1} and the intense band at 4.9-5.1 μm^{-1} are interpreted in terms of dipole-allowed $5d \rightarrow 6p$ transitions. This interpretation leads to new assignments of these bands and an ordering of the occupied $5d$ MO's of $a_{1g}(z^2) > b_{2g}(xy) \approx e_g(xy, yz)$. This ordering is discussed in the context of its similarity to that of $\text{Pt}(\text{CN})_4^{2-}$.

Introduction

The electronic absorption spectrum of the D_{4h} square-planar $\text{Pt}(\text{NH}_3)_4^{2+}$ cation in aqueous solution consists of a weak broad band at 3.5 μm^{-1} (ϵ 44), a shoulder near 4.2 μm^{-1} (ϵ 155), and another shoulder near 4.5 μm^{-1} (ϵ 480).¹⁻⁴ These three bands

have been assigned as ligand field (LF) transitions on the basis of their low intensities.^{1,2} The temperature dependence of the first two bands in single crystals of $[\text{Pt}(\text{NH}_3)_4]\text{SO}_4$ has shown that they are vibronic and thus consistent with the LF assignment.³

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Further, the shoulder near $4.2 \mu\text{m}^{-1}$ exhibits in-plane polarized vibrational structure at 1.5 K, which strongly suggests the presence of $^1A_{2g}(b_{2g}(xy)b_{1g}(x^2 - y^2))$ LF state expected to be exclusively in-plane polarized.³ At higher energy an intense band is observed at $5.09 \mu\text{m}^{-1}$ (ϵ 10600).²⁻⁴ This band has been assigned as an allowed $5d \rightarrow 6p_z$ transition centered on the Pt(II) ion.^{1,2} This assignment was considered reasonable because the NH_3 ligand is a simple σ donor without occupied π orbitals, which could give rise to low-energy ligand to metal charge transfer (LMCT). In 1972 this laboratory reported the magnetic circular dichroism (MCD) spectrum for the $\text{Pt}(\text{NH}_3)_4^{2+}$ cation, measured with a 1-T field.⁴ Even though the signal to noise ratio was somewhat unfavorable above $4.5 \mu\text{m}^{-1}$, a strong positive A term was found for the intense band. This result is consistent with a transition to the $d \rightarrow p$ $^1E_u(e_g(xz, yz)^3 a_{2u}(z))$ state and thus was offered as support for the $5d \rightarrow 6p_z$ transition assignment, which had been advanced earlier.² It is of interest to note that the intense band for $\text{Pt}(\text{NH}_3)_4^{2+}$ is one of the few examples where an allowed $d \rightarrow p$ transition has been observed separately from other allowed intense transitions such as metal to ligand charge transfer (MLCT) or LMCT. This can be traced to the nonbonding nature of the $6p_z$ metal orbital, $a_{2u}(z)$, and the lack of ligand π orbitals in the complex.

A renewed interest in the $d \rightarrow p$ process in square-planar Pt(II) complexes was kindled recently when MCD evidence was presented for $5d \rightarrow 6p_z$ transitions for the PtCl_4^{2-} and PtBr_4^{2-} anions.⁵ The spectra of these ions however are complicated by the presence of LMCT from the halide ligands at energies that overlap the $d \rightarrow p$ transitions. The MCD for these halo complexes, like that for $\text{Pt}(\text{NH}_3)_4^{2+}$, was interpreted in terms of the $^1E_u(e_g(xz, yz)^3 a_{2u}(z))$ $d \rightarrow p$ excited state. A question is naturally raised in each of these cases as to the location of the $d \rightarrow p$ states associated with the other two excited configurations $b_{2g}(xy)a_{2u}(z)$ and $a_{1g}(z^2)a_{2u}(z)$. Furthermore, the strong spin-orbit coupling of $5d$ electrons of Pt(II) ($\xi_{5d} \sim 0.40 \mu\text{m}^{-1}$) would be expected to mix singlet and triplet states of all three $5d6p_z$ configurations, and transitions to formally spin-forbidden excited states should gain appreciable intensity. Thus, if the intense band at $5.09 \mu\text{m}^{-1}$ for $\text{Pt}(\text{NH}_3)_4^{2+}$ is assigned as a transition to a predominantly singlet state, then transition(s) to predominantly spin-forbidden state(s) should be found at lower energy. These questions, together with our general interest in the $d \rightarrow p$ process in square-planar complexes, have prompted a careful reexamination of the electronic absorption and MCD spectra for the $\text{Pt}(\text{NH}_3)_4^{2+}$ cation. Some new spectral measurements are reported here for $\text{Pt}(\text{NH}_3)_4^{2+}$ in 0.100 M HClO_4 and in acetonitrile obtained with a 7-T field and a greatly improved signal to noise ratio compared to that of our 1972 measurements. In addition, measurements have been extended to the related $\text{Pt}(\text{en})_2^{2+}$ ($\text{en} = \text{ethylenediamine}$) cation in 0.100 M HClO_4 and in acetonitrile. These new MCD spectra reveal detail that requires some reinterpretation of the spectral assignments, especially in the region of the $4.5\text{-}\mu\text{m}^{-1}$ absorption band.

Experimental Section

The tetraammineplatinum(II) perchlorate and bis(ethylenediamine)-platinum(II) perchlorate salts were prepared from corresponding chloride salts^{6,7} by a published procedure.^{2,4} Both salts gave satisfactory elemental analyses, and their electronic spectra were in agreement with earlier reports.^{2-4,8} Spectral grade acetonitrile was 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.⁹ The MCD spectra were measured at 7 T with a superconducting magnet system (Oxford Instruments SM2-7, fitted with a room-temperature bore). All spectra were corrected for solvent blank and were checked for Beer's law compliance.

Table I. Spectral Data

band no.	absorption			MCD	
	$\bar{\nu}$, μm^{-1}	λ , nm	ϵ , $\text{M}^{-1} \text{cm}^{-1}$	$\bar{\nu}$, μm^{-1}	$\Delta\epsilon_M$, $(\text{M cm T})^{-1}$
$[\text{Pt}(\text{NH}_3)_4](\text{ClO}_4)_2$ in 0.100 M HClO_4					
I	3.52	284	44	3.08	$+6.3 \times 10^{-4}$
II	4.20 ^a	238	155	4.13	$+5.7 \times 10^{-3}$
III	4.55 ^a	220	484	4.54	-0.35
IV	5.09	196	10600	4.91	-2.10
				5.04	-2.09
				5.16	0
				5.28	+2.81
$[\text{Pt}(\text{NH}_3)_4](\text{ClO}_4)_2$ in CH_3CN					
I	3.47	288	45	3.06	$+4.3 \times 10^{-4}$
II	4.30 ^a	233	186	4.48	-4.6×10^{-3}
III	4.59	218	530	4.13	$+7.0 \times 10^{-3}$
IV	5.04	198	11500	4.56	-0.48
				4.99	-4.35
				5.10	0
				5.21	+3.65
$[\text{Pt}(\text{en})_2](\text{ClO}_4)_2$ in 0.100 M HClO_4					
I	3.55	282	40	3.09	$+2.9 \times 10^{-4}$
II				3.57	-4.8×10^{-3}
III	4.47	224	443	4.13	$+6.5 \times 10^{-3}$
IV	4.93	203	8000	4.42	-0.32
				4.84	-3.52
				4.98	0
				5.10	+1.60
$[\text{Pt}(\text{en})_2](\text{ClO}_4)_2$ in CH_3CN					
I	3.53	283	44	3.10	$+4.7 \times 10^{-4}$
II	4.15 ^a	241	106	3.55	-5.4×10^{-3}
III	4.47	224	518	4.15	$+8.6 \times 10^{-3}$
IV	4.94	202	11400	4.42	-0.43
				4.87	-5.29
				4.99	0
				5.09	+3.94

^aShoulder. ^b A term.

Experimental MCD \bar{A}_1 and \bar{B}_0 parameters were determined from a moment analysis of the MCD spectra.¹⁰ The average energy about which the moments were determined, $\bar{\nu}_0$, was obtained by setting the first moment of the absorption to zero. \bar{A}_1 parameters were evaluated from $\int (\Delta\epsilon_M/\bar{\nu})(\bar{\nu} - \bar{\nu}_0) d\bar{\nu} = \langle \Delta\epsilon_M \rangle_1 = 152.5\bar{A}_1$, \bar{B}_0 parameters from $\int (\Delta\epsilon_M/\bar{\nu}) d\bar{\nu} = \langle \Delta\epsilon_M \rangle_0 = 152.5\bar{B}_0$, and the values of \bar{D}_0 (the dipole strength) from $\int (\epsilon/\bar{\nu}) d\bar{\nu} = \langle \epsilon \rangle_0 = 326.6\bar{D}_0$. The quantity $\Delta\epsilon_M$ is the differential molar absorptivity per unit magnetic field with units $(\text{M cm T})^{-1}$.

Results and Discussion

Absorption and MCD Spectra. Absorption and MCD spectra were obtained at room temperature for the $\text{Pt}(\text{NH}_3)_4^{2+}$ and $\text{Pt}(\text{en})_2^{2+}$ cations in 0.100 M HClO_4 and in acetonitrile. Figures 1 and 2 present the spectra of $\text{Pt}(\text{NH}_3)_4^{2+}$ in 0.100 M HClO_4 and $\text{Pt}(\text{en})_2^{2+}$ in CH_3CN , respectively; the spectra of both complexes in the other solvent were of comparable quality. Quantitative spectral data are collected in Table I. The spectra obeyed Beer's law to within experimental error, and there was no evidence for spectral changes due to solvolysis or decomposition over several days.

The spectra of each cation in the two solvents were quite similar apart from small shifts in band position and absorptivity. A comparison of the spectrum of $\text{Pt}(\text{NH}_3)_4^{2+}$ with that of $\text{Pt}(\text{en})_2^{2+}$ in the same solvent shows a strong similarity, which indicates that the lower symmetry of the $\text{Pt}(\text{en})_2^{2+}$ ion does not appreciably affect the electronic states involved. The PtN_4 donor atom symmetry common to both cations can therefore be reasonably approximated by D_{4h} , and subsequent discussion will be based on this assumption.

Except for a weak positive feature near $3.1 \mu\text{m}^{-1}$, the MCD spectra for $\text{Pt}(\text{NH}_3)_4^{2+}$ in the region of the LF bands below $4.3 \mu\text{m}^{-1}$ were substantially the same as reported earlier.⁴ The weak

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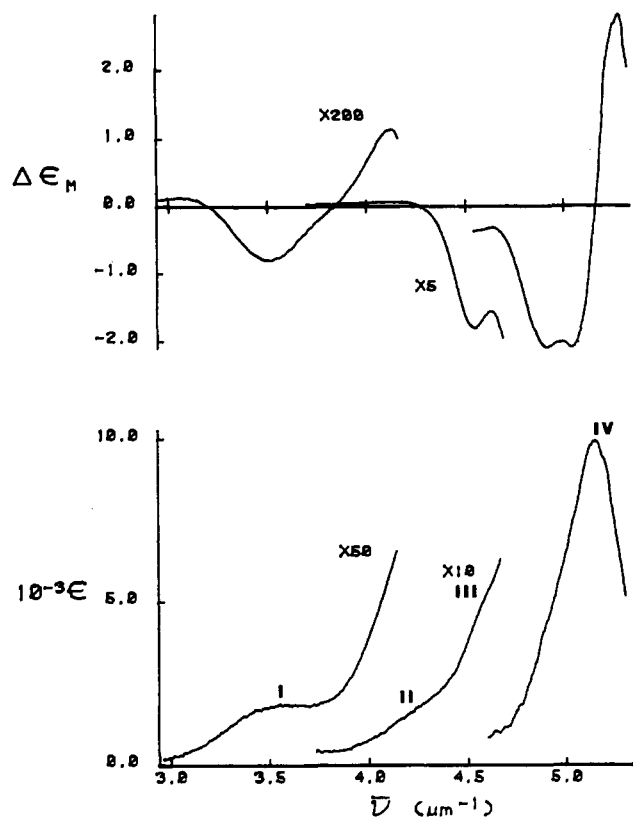


Figure 1. Electronic absorption (lower curves) and MCD (upper curves) spectra for $[\text{Pt}(\text{NH}_3)_4](\text{ClO}_4)_2$ in 0.100 M HClO_4 . The left absorption curve is multiplied by 50, and the center curve, by 10. The left MCD curve is multiplied by 200, and the center curve, by 5.

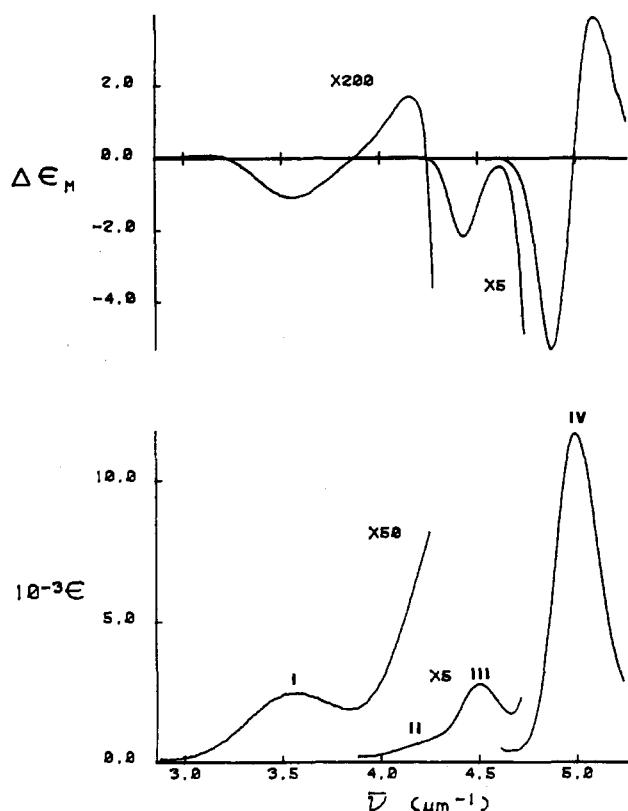


Figure 2. Electronic absorption (lower curves) and MCD (upper curves) spectra for $[\text{Pt}(\text{en})_2](\text{ClO}_4)_2$ in CH_3CN . The left absorption curve is multiplied by 50, and the center curve, by 5. The left MCD curve is multiplied by 200, and the center curve, by 5.

positive feature near $3.1 \mu\text{m}^{-1}$ is observed also for $\text{Pt}(\text{en})_2^{2+}$ in both solvents, and there is no corresponding absorption band

resolved lower in energy than band I for either cation. The MCD spectra thus reveal a new weak transition, which is most likely a spin-forbidden LF transition in view of its intensity. Apart from detecting this new transition, the MCD below $4.3 \mu\text{m}^{-1}$ is not able to provide more detailed information regarding electronic state assignment because the broad band I and poorly resolved band II do not permit precise MCD term assignments. It does seem clear that there are several weak transitions between 2.8 and $4.3 \mu\text{m}^{-1}$ that strongly overlap. The LF assignment for these transitions is certainly appropriate in view of the temperature dependence in the crystal spectra reported earlier.³

At energies above $4.3 \mu\text{m}^{-1}$ some differences in the MCD of $\text{Pt}(\text{NH}_3)_4^{2+}$ in 0.100 M HClO_4 (Figure 1) were observed compared to our earlier report.⁴ Specifically, the negative minimum at $4.54 \mu\text{m}^{-1}$ associated with band III was better resolved, and a new negative feature was observed at $4.91 \mu\text{m}^{-1}$ on the low-energy side of the strong positive A term for band IV. The negative feature at $4.91 \mu\text{m}^{-1}$ is accompanied by a broadening of band IV on the low-energy side ($\bar{\nu}_{1/2} \sim 0.38 \mu\text{m}^{-1}$), but no corresponding absorption band is found. To make certain that the MCD was not an artifact, the spectra in this region were determined several times with different instrumental parameters and solution concentrations, all with the same result. The MCD spectrum for $\text{Pt}(\text{NH}_3)_4^{2+}$ in CH_3CN shows clearly the negative minimum for band III and the positive A term for band IV but no sign of the negative feature on the low-energy side of the positive A term. Absorption band IV in CH_3CN is significantly narrower ($\bar{\nu}_{1/2} \sim 0.26 \mu\text{m}^{-1}$) than that in 0.100 M HClO_4 , and it is likely that the state(s) responsible for the extra feature in the latter medium have moved closer (within bandwidths) to that for band IV. The width of absorption band IV for $\text{Pt}(\text{en})_2^{2+}$ parallels the behavior for $\text{Pt}(\text{NH}_3)_4^{2+}$: in 0.100 M HClO_4 band IV is broader ($\bar{\nu}_{1/2} \sim 0.38 \mu\text{m}^{-1}$) than in CH_3CN ($\bar{\nu}_{1/2} \sim 0.25 \mu\text{m}^{-1}$). However, the MCD for $\text{Pt}(\text{en})_2^{2+}$ in 0.100 M HClO_4 does not show the negative feature on the low-energy side of the A term for band IV, but the A term is unsymmetrical with the low-energy negative portion distinctly larger than observed for the A term for the cation in CH_3CN .

Band III presents another problem. For both cations this band has a higher absorptivity than the vibronic LF bands I or II, but the absorptivity is somewhat low for an electric-dipole-allowed transition. Earlier assignments^{1,2} of band III were to another LF transition, but the temperature dependence for this band in single crystals of $[\text{Pt}(\text{NH}_3)_4]\text{SO}_4$ was found to be different from that of the lower energy LF bands.³ Unfortunately a precise determination of band intensity was precluded by strong in-plane polarized absorption in the region of the maximum, but the band narrowed and revealed some vibrational structure at low temperature,³ which is typical behavior for an allowed transition. In the present study the data in Table I show that the MCD for band III is 50–100 times stronger than for the LF bands I and II in each case. This result, together with the difference in temperature dependence, suggests that the excited state for band III is not a vibronic LF state but rather a weak dipole-allowed state. A logical possibility for such a state is a spin-orbit $d \rightarrow p$ state of triplet parentage, and this possibility is considered in more detail below.

In an effort to obtain quantitative parameters from the MCD spectra, a careful moment analysis for band IV for both cations in each solvent was performed. Band III was also deemed sufficiently resolved for $\text{Pt}(\text{NH}_3)_4^{2+}$ in CH_3CN and for $\text{Pt}(\text{en})_2^{2+}$ in both solvents for an analysis. The ratios \bar{A}_1/\bar{D}_0 and \bar{B}_0/\bar{D}_0 calculated¹⁰ from the moments are collected in Table II. The treatment for band IV for $\text{Pt}(\text{NH}_3)_4^{2+}$ in 0.100 M HClO_4 included both the negative feature at $4.91 \mu\text{m}^{-1}$ and the positive A term of band IV, since contributions from each are believed to be present but unresolved in the other cases. The results include all states in the region of band IV and thus would include all A terms, B terms, and possibly pseudo A terms¹⁰ present. Table II shows that band IV is characterized by a strong positive A term ($\bar{A}_1/\bar{D}_0 \sim +0.8$ to $+1.2$) and a negative B term. A significant positive A term is also found for band III ($\bar{A}_1/\bar{D}_0 \sim +0.8$ for $\text{Pt}(\text{NH}_3)_4^{2+}$ in CH_3CN or $+0.5$ for $\text{Pt}(\text{en})_2^{2+}$ in 0.100 M HClO_4 or CH_3CN) and is accompanied also by a negative B term. The presence of

Table II. Absorption and MCD Band Parameters

band no.	$\bar{\nu}_{\max}$, μm^{-1}	$\bar{\nu}_{1/2}$, μm^{-1}	ϵ , $\text{M}^{-1} \text{cm}^{-1}$	$\bar{\nu}_0$, μm^{-1}	moment analysis		
					\bar{A}_1/\bar{D}_0	$10^4 \bar{B}_0/\bar{D}_0$, cm	\bar{D}_0 , D
IV	5.09	0.38	[Pt(NH ₃) ₄](ClO ₄) ₂ in 0.100 M HClO ₄ 10600	5.05	+0.75 ^b	-9.9 ^b	1.44
III	4.59	<i>c</i>	[Pt(NH ₃) ₄](ClO ₄) ₂ in CH ₃ CN 530	4.57	+0.77	-47	0.019
IV	5.04	0.26	11500	5.06	+0.80	-6.2	1.37
III	4.47	<i>c</i>	[Pt(en) ₂](ClO ₄) ₂ in 0.100 M HClO ₄ 443	4.42	+0.52	-45	0.011
IV	4.93	0.38	8000	4.94	+1.00	-3.8	1.23
III	4.47	~0.3	[Pt(en) ₂](ClO ₄) ₂ in CH ₃ CN 518	4.45	+0.51	-29	0.029
IV	4.94	0.25	11400	4.96	+1.17	-4.9	1.58

^a Width at half-height estimated from experimental spectra. ^b Both *A* term and lower energy negative MCD included; see text. ^c Insufficient data.

a positive *A* term for band III is not very obvious from a casual examination of the spectra (for examples Figure 2) where the MCD gives the appearance of a negative *B* term, but a careful comparison of the positions of the absorption maximum and the MCD minimum shows the minimum to be consistently 0.03–0.05 μm^{-1} lower in energy. Further, the existence of an *A* term implies a degenerate state which in *D*_{4h} symmetry would be an in-plane polarized E state and thus be in agreement with the strong in-plane polarized absorption found for [Pt(NH₃)₄]SO₄ in the region of band III.³

Excited States and MCD Terms. The LF and d → p excited configurations that give rise to the electronic states of the PtN₄ cations arise from excitations from the occupied 5d MO's a_{1g}(z²), e_g(xz,yz), or b_{2g}(xy) to either the empty σ* 5d_{x²-y²}, b_{1g}(x²-y²) (LF configurations) or the nonbonding 6p_z, a_{2u}(z) (d → p configurations), respectively. These excited configurations, together with their individual excited states, are given in Table III. The electronic ground state corresponds to a_{1g}(z²)²e_g(xz,yz)⁴b_{2g}(xy)² for these diamagnetic cations and is totally symmetric ¹A_{1g}. The energy ordering of the occupied 5d MO's is not known for certain but was assumed in earlier studies¹⁻⁴ to be the same for PtCl₄²⁻, viz. b_{2g}(xy) ≥ e_g(xz,yz) > a_{1g}(z²). There seems to be no good justification for this ordering for the PtN₄ cations. In fact, from a crystal field viewpoint the a_{1g}(z²) orbital is expected to be weakly σ antibonding while the b_{2g}(xy) and e_g(xz,yz) orbitals of π symmetry are expected to be virtually nonbonding. It is likely, however, that the energy spread of these occupied orbitals is small since the bonding participation of the 5d_{z²} orbital is believed to be relatively low in such widely differing complexes as PtCl₄²⁻ and Pt(CN)₄²⁻.¹¹

Since the MCD spectra can provide little additional information regarding details in the LF spectra, the discussion that follows will be directed toward interpretation of bands III and IV. Selection rules for *D*_{4h} restrict dipole-allowed transitions to A_{2u} (z-polarized normal to the molecular plane) and to E_u (xy-polarized in the molecular plane) excited states. Therefore, the forbidden A_{1u}, B_{1u}, and B_{2u} d → p states in Table III are not considered because transitions to them are expected to be too weak to be observed. The allowed d → p A_{2u} states of Table III can give rise only to *B* terms in the MCD while the E_u states of Table III can exhibit both *A* and *B* terms (MCD *C* terms of course will be absent because the ground state is diamagnetic). The A_{2u} and E_u d → p states have exactly the same symmetries as the MLCT states of Pt(CN)₄²⁻ and related *D*_{4h} complexes containing π-acceptor ligands.¹¹⁻¹³ In these complexes the symmetries of the occupied 5d MO's are the same as for the PtN₄ cations, and the lowest energy unoccupied MO (LUMO) is also the same a_{2u} symmetry. The only difference in the two cases is the precise

Table III. Excited States for LF and d → p Transitions

excited config ^a	no spin-orbit coupling	spin-orbit states
LF States		
a _{1g} (z ²)b _{1g} (x ² -y ²)	¹ B _{1g} ³ B _{1g}	B _{1g} E _g , B _{2g}
e _g (xz,yz) ³ b _{1g} (x ² -y ²)	¹ E _g ³ E _g	E _g E _g , A _{1g} , A _{2g} , B _{1g} , B _{2g}
b _{2g} (xy)b _{1g} (x ² -y ²)	¹ A _{2g} ³ A _{2g}	A _{2g} A _{1g} , E _g
d → p States		
a _{1g} (z ²)a _{2u} (z)	¹ A _{2u} ³ A _{2u}	A _{2u} A _{1u} , E _u
e _g (xz,yz) ³ a _{2u} (z)	¹ E _u ³ E _u	E _u E _u , A _{1u} , A _{2u} , B _{1u} , B _{2u}
b _{2g} (xy)a _{2u} (z)	¹ B _{1u} ³ B _{1u}	B _{1u} B _{2u} , E _u

^a Ground-state configuration = a_{1g}(z²)²e_g(xz,yz)⁴b_{2g}(xy)²; filled orbitals omitted in excited configurations.

nature of the a_{2u} orbital. For Pt(CN)₄²⁻ and related complexes this orbital is visualized as having ligand π character, together with metal 6p_z character, whereas for the PtN₄ cations the a_{2u}(z) orbital is entirely 6p_z. Since spin-orbit coupling arises from the occupied 5d MO's and the calculation of MCD terms is insensitive to the nature of the a_{2u} orbital, the same type of spin-orbit treatment and MCD term calculation used previously^{11,12} for the MLCT states of Pt(CN)₄²⁻ can be applied here to the d → p states of the PtN₄ cations. To briefly summarize, each of the four E_u states and each of the two A_{2u} states will be intermixed by spin-orbit interaction giving the |E_u(i)⟩ and |A_{2u}(i)⟩ spin-orbit states in eq 1 and 2, respectively, where the a_i-f_i are mixing

$$|E_u(i)\rangle = a_i|{}^3B_{1u}\rangle + b_i|{}^3E_u\rangle + c_i|{}^1E_u\rangle + d_i|{}^3A_{2u}\rangle \quad (1)$$

$$|A_{2u}(i)\rangle = e_i|{}^3E_u\rangle + b_i|{}^1A_{2u}\rangle \quad (2)$$

coefficients among the zero-order singlet and triplet d → p states. These coefficients may be determined by diagonalizing the spin-orbit secular determinants given previously.^{11,12} The subsequent calculation of MCD *A* terms for the E_u(i) states proceeds by making the standard approximation that the MO's involved are pure 5d or 6p atomic orbitals on Pt and retaining only one-centered integrals. The \bar{A}_1/\bar{D}_0 ratio is given by the reduced matrix element of the magnetic moment operator $\mu = -\mu_B(L + 2S)$ (μ_B = Bohr magneton), eq 3,¹⁰ which reduces to eq 4 for the E_u(i)

$$\bar{A}_1/\bar{D}_0 = i/(2^{1/2}\mu_B)\langle E_u(i)||\mu^{A_{2u}}||E_u(i)\rangle \quad (3)$$

$$\bar{A}_1/\bar{D}_0 = (-2|a_i|^2 + |b_i|^2 + |c_i|^2 + 2|d_i|^2)|c_i|^2 \quad (4)$$

states of eq 1.¹⁰⁻¹³ The MCD *B* terms depend upon the reduced

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matrix elements $\langle A_{2u}(i) || \mu^E || E_u(i) \rangle$ and $\langle E_u(i) || \mu^{A_{2u}} || E_u(j) \rangle$ but are more difficult to calculate in a general way because they involve a summation of terms from all A_{2u} and E_u states of the molecule. The terms are weighted by an inverse energy difference between states, and therefore the summation is sensitive to the energy ordering of each individual state relative to all others.¹³

Assignment of Bands III and IV. The assignment of band III of the PtN_4 cations to a $d \rightarrow p$ spin-orbit state of predominantly triplet character is reasonable from both energetic and intensity considerations. The positive MCD A term present for band III implies an E_u state. There are three E_u states of triplet origin, $E_u(^3A_{2u})$, $E_u(^3E_u)$, and $E_u(^3B_{1u})$, but the last one can be eliminated because a spin-orbit state with a large $^3B_{1u}$ component ($|a_i|^2 \sim 1$) will have a negative \bar{A}_1/\bar{D}_0 from eq 4. Some rough spin-orbit calculations similar to those reported for $Pt(CN)_4^{2-}$ and related complexes¹¹⁻¹³ indicate that the $E_u(^3E_u)$ spin-orbit state is also unlikely for band III because, in every instance where 3E_u was set as the lowest energy triplet state, the $A_{2u}(^3E_u)$ state was calculated to be lower in energy than the $E_u(^3E_u)$ state and to have substantial singlet character, which should make a transition to this state easily observed in both absorption and MCD spectra. The most logical choice for assignment of band III is therefore to the $E_u(^3A_{2u})$ state. It is interesting to note that the $E_u(^3A_{2u})$ MLCT state is also the lowest energy spin-orbit state observed for $Pt(CN)_4^{2-}$ and other related complexes with π -acceptor type ligands.¹¹⁻¹³ In these cases, assuming contributions to B terms were limited only to close-lying states within the MLCT configurations, the B term for the lowest energy $E_u(^3A_{2u})$ state was predicted to be negative.¹³ An analogous prediction can be made here if the B term contributions arise only from the $d \rightarrow p$ A_{2u} and E_u states of Table III; the negative B term is in agreement with the experimental spectra.

The MCD in the region of band IV for $Pt(NH_3)_4^{2+}$ in 0.100 M $HClO_4$ (Figure 1) is most easily interpreted by assuming a negative B term on the low-energy side of a positive A term (or pseudo A term). This pattern would be consistent with an A_{2u} state slightly lower in energy than an E_u state. With band III assigned as the transition to the $E_u(^3A_{2u})$ state, a logical assignment of the negative B term would be to the $A_{2u}(^1A_{2u})$ state, while the positive A term is likely $E_u(^3E_u)$. A significant contribution to the A term from the $E_u(^3B_{1u})$ state is unacceptable because the wrong A term sign would be predicted, and the $E_u(^1E_u)$ state can be eliminated because of the absence of other lower energy features assignable to the spin-orbit states of 3E_u , which must be lower in energy than 1E_u . It should be emphasized that the E_u and A_{2u} states are strongly mixed, as indicated by eq 1 and 2. The designation used here to indicate their parentage is simply an effort to trace the origin of the predominant component. Thus the $E_u(^3E_u)$ state is expected to have a significant $E_u(^1E_u)$ component, which together with the $A_{2u}(^1A_{2u})$ would account for the high intensity of band IV.

If the $A_{2u}(^1A_{2u})-E_u(^3E_u)$ assignment for band IV is correct, then the MCD must consist of both an A term for the $E_u(^3E_u)$ state (predicted to be positive) and a positive B term for the $E_u(^3E_u)$ state resulting from the magnetic interaction with the lower energy $A_{2u}(^1A_{2u})$ state. For $Pt(NH_3)_4^{2+}$ in CH_3CN and $Pt(en)_2^{2+}$ in either 0.100 M $HClO_4$ or CH_3CN , where the negative B term corresponding to $A_{2u}(^1A_{2u})$ is unresolved, the MCD for band IV

will contain a substantial pseudo A term contribution, which is also predicted to be positive if the $A_{2u}(^1A_{2u})-E_u(^3E_u)$ interaction dominates all others.¹¹⁻¹³ This combination of an A term and a pseudo A term due to close lying A_{2u} and E_u states is also found^{11,12} for the intense MLCT band at $3.85 \mu m^{-1}$ for $Pt(CN)_4^{2-}$. In fact, the absorption and MCD spectra for the $d \rightarrow p$ bands III and IV of the PtN_4 cations are remarkably similar to those observed for the two lowest energy MLCT bands in $Pt(CN)_4^{2-}$, except that the MLCT in the latter is red shifted by $\sim 1.0 \mu m^{-1}$ compared to the $d \rightarrow p$ in the former. This red shift of the MLCT is in accord with expectation since the a_{2u} LUMO has a contribution from the empty $CN^- \pi^*$ orbitals, which would stabilize it compared to the nonbonding $a_{2u}(z)$ orbital in the PtN_4 cations.

In view of the extensive mixing in the spin-orbit states given by eq 1 and 2 and the lack of information as to the energy of the higher lying $E_u(^1E_u)$, $A_{2u}(^3E_u)$, and $E_u(^3B_{1u})$ $d \rightarrow p$ states, a quantitative estimation of \bar{A}_1/\bar{D}_0 using eq 4 is not really feasible for either of the PtN_4 cations. The observed \bar{A}_1/\bar{D}_0 values for band III from the moment analysis may be considered reasonable when the facts that the excited state is not a pure $^3A_{2u}$ state ($|d_i|^2 < 1$) and that the singlet character is low ($|c_i|^2 \ll 1$) are considered. A similar statement may be made about the observed \bar{A}_1/\bar{D}_0 values for band IV, where both positive A and positive pseudo A terms contribute.

Conclusions. The new MCD data presented are consistent with the new assignments for bands III and IV of the PtN_4 cations. The placement of the $E_u(^3A_{2u})$ and $A_{2u}(^1A_{2u})$ states both of the $a_{1g}(z^2)a_{2u}(z)$ excited configuration as the lowest energy $d \rightarrow p$ states implies that the ordering of the occupied 5d MO's on Pt is likely $a_{1g}(z^2) > b_{2g}(xy) \approx e_g(xz,yz)$, assuming that differences in electronic repulsion between the $d \rightarrow p$ states are small. A rough estimate from some spin-orbit calculations¹¹⁻¹³ as before places the $a_{1g}(z^2)$ orbital only $0.3-0.5 \mu m^{-1}$ higher than $b_{2g}(xy)$ and $e_g(xz,yz)$, but the absence of the energies for the higher $d \rightarrow p$ states causes this estimate to lack precision. The relative energy of the $a_{1g}(z^2)$ MO for the PtN_4 cations is thus the same as for $Pt(CN)_4^{2-}$ and different from that ascribed to $PtCl_4^{2-}$ ($b_{2g}(xy) > e_g(xz,yz) > a_{1g}(z^2)$). The similarity of the relative ordering of the orbital energies between $Pt(CN)_4^{2-}$ and the PtN_4 cations, which is reflected in a remarkable similarity of the MCD for the MLCT and $d \rightarrow p$ transitions, is perhaps not surprising since the CN^- ligand and the N-donor ligands are both strong σ donors for Pt(II). The π -acceptor ability is thought to play a secondary role in bonding in $Pt(CN)_4^{2-}$, and the complex owes most of its stability to strong σ interaction.

Unfortunately little additional detail could be added to the interpretation of the LF spectra from the present results. However, if the $b_{2g}(xy)$ and $e_g(xz,yz)$ orbitals are nonbonding and very close in energy and the $a_{1g}(z^2)$ orbital is only slightly higher in energy, then the spread of LF states would be due mainly to differences in electronic repulsions and spin-orbit splitting. When reasonable values of these factors are assumed,¹ the energy spread is likely to be no more than $\sim 1.2 \mu m^{-1}$. If the new MCD band found near $3.1 \mu m^{-1}$ is the lowest energy LF state, then the range of the LF spectra would extend to $\sim 4.3 \mu m^{-1}$. The observed LF spectra are in accord with this expectation.

Registry No. $Pt(NH_3)_4^{2+}$, 16455-68-8; $Pt(en)_2^{2+}$, 19184-30-6.