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Electronic Spectra of Octahedral Platinum(IV) Complexes

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Received February 13, 1970

Electronic spectra for a number of octahedral platinum(IV) complexes of the type PtL_6^m (L = Cl^-, Br^-, SCN^-, $SeCN^-$, N_3^-, CN^-, NO_2^-, NH_3, and 0.5en) are reported in nonaqueous media and in media which form rigid transparent glasses at liquid nitrogen temperature. In nearly every case spectral resolution is greatly improved at low temperature. Detailed assignments of the spectra are made. A spectrochemical ordering of ligands for platinum(IV) is presented and trends in ligand → metal charge-transfer energies are discussed.

Introduction

One of the chief difficulties in formulating detailed electronic structural models for complexes of the second- and third-row transition elements is the lack of reliable high-resolution spectral data to substantiate energy level schemes. The octahedral complexes of platinum(IV) are no exception. Even though electronic spectra have been reported[1-7] for a number of platinum complexes, the data are scattered and are mostly from aqueous solution measurements. Some of these aqueous measurements are subject to question because of the tendency of platinum(IV) complexes, particularly those with halide ligands, to undergo hydrolysis.[8-9] Solutions containing excess ligand have been used to repress hydrolysis, but these are unsatisfactory since ligand absorptions tend to obscure charge-transfer bands of the complex. Also amine and ethylenediamine (en) complexes act as acids in aqueous media[10,11] and their spectra depend on pH because of the presence of conjugate base complexes which have spectra that differ substantially from the fully protonated complexes.[1,12] Furthermore aqueous solutions of many platinum(IV) complexes are quite sensitive to light.[13,14] Ordinary laboratory lighting can cause substantial changes in the spectra resulting from photochemical reaction.

The present paper reports detailed spectral measurements for a variety of platinum(IV) complexes of the type PtL_6^m, where L = Cl^-, Br^-, SCN^-, $SeCN^-$, N_3^-, CN^-, NO_2^-, NH_3, and 0.5en. To avoid hydrolysis and to minimize photochemical reactions, spectral measurements were made in a variety of nonaqueous solvents, carefully protected from light. Where possible, measurements were also made in media which form rigid, transparent glasses when cooled to near liquid nitrogen temperature. Such measurements at low temperature have been quite successful in improving spectral resolution.[15,16] Aqueous solution measurements on $Pt(en)_3^{4+}$ and $Pt(NH_3)_6^{4+}$ were made using the perchlorate salts in dilute perchloric acid. Under these conditions measurements could be made to 52,000 cm^{-1} without complications due to anion absorption or conjugate base formation.

Experimental Section

Preparation of Compounds.—Starting material for the complexes was hydrogen hexachloroplatinate(IV), H_2PtCl_6,[17] which was prepared from platinum sponge. Tetra-*n*-butylammonium chloride (Eastern Chemical Co.) and bromide (Eastman Organic Chemicals) were used as supplied, without further purification. All other chemicals used were reagent grade. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Platinum analyses were also performed in our laboratory by ashing the complexes at red heat.

Tetra-*n*-butylammonium Hexachloroplatinate(IV), $[(n\text{-}C_4H_9)_4N]_2[PtCl_6]$.—A concentrated aqueous solution of H_2PtCl_6 was treated with a stoichiometric amount of tetra-*n*-butylammonium chloride. A precipitate formed immediately and was collected, washed with water and ether, and then dried under reduced pressure. *Anal.* Calcd for $[(n\text{-}C_4H_9)_4N]_2[PtCl_6]$: Pt, 21.85; C, 43.05; H, 8.13; Cl, 23.83. Found: Pt, 21.68, 22.01; C, 42.84; H, 7.96; Cl, 23.54.

Tetra-*n*-butylammonium Hexabromoplatinate(IV), $[(n\text{-}C_4H_9)_4N]_2[PtBr_6]$.—Excess concentrated hydrobromic acid was added to an aqueous solution of H_2PtCl_6. The solution was heated and then treated with a small amount of bromine and evaporated twice with hydrobromic acid to a small volume. The cooled, concentrated solution was stirred with a concentrated aqueous solution of tetra-*n*-butylammonium bromide, whereupon a precipitate formed immediately and was collected and dried as above. *Anal.* Calcd for $[(n\text{-}C_4H_9)_4N]_2[PtBr_6]$: Pt, 16.82; C, 32.15; H, 6.26; N, 2.42; Br, 41.35. Found: Pt, 16.67, 16.99; C, 33.29; H, 6.41; N, 2.55; Br, 41.15.

Tetra-*n*-butylammonium Hexathiocyanatoplatinate(IV), $[(n\text{-}C_4H_9)_4N]_2[Pt(SCN)_6]$.—Aqueous H_2PtCl_6 was neutralized with sodium hydroxide and then treated with an aqueous solution containing an excess of sodium thiocyanate. The solution was

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heated for 0.5 hr on a steam bath. After cooling the complex was precipitated with tetra-*n*-butylammonium chloride, collected, washed with water and ether, and dried under reduced pressure. *Anal.* Calcd for $[(n\text{-}C_4H_9)_4N]_2[Pt(SCN)_6]$: Pt, 18.97; C, 44.38; H, 7.06; S, 18.71. Found: Pt, 19.00, 18.88; C, 44.71; H, 7.20; S, 18.17.

Tetra-*n*-butylammonium Hexaazidoplatinate(IV), $[(n\text{-}C_4H_9)_4N]_2[Pt(N_3)_6]$.—This complex was prepared by the same procedure as used for the thiocyanate complex, except sodium azide was used instead of sodium thiocyanate. *Anal.* Calcd for $[(n\text{-}C_4H_9)_4N]_2[Pt(N_3)_6]$: Pt, 20.93; C, 41.23; H, 7.79; N, 30.05. Found: Pt, 20.92, 21.16; C, 41.39; H, 7.89; N, 30.28.

Tetra-*n*-butylammonium Hexaselenocyanatoplatinate(IV), $[(n\text{-}C_4H_9)_4N]_2[Pt(SeCN)_6]$.—A concentrated aqueous solution of H_2PtCl_6 was neutralized with sodium hydroxide and mixed with a solution containing an excess of potassium selenocyanate. Then a solution of tetra-*n*-butylammonium chloride was immediately added dropwise. The mixture was warmed for a few minutes and then the precipitate was collected and dried as before. *Anal.* Calcd for $[(n\text{-}C_4H_9)_4N]_2[Pt(SeCN)_6]$: Pt, 14.89; C, 34.85; H, 5.54; N, 8.56. Found: Pt, 15.22, 15.10, 15.17; C, 35.07; H, 5.26; N, 8.71.

Tetra-*n*-butylammonium Hexanitroplatinate(IV), $[(n\text{-}C_4H_9)_4N]_2[Pt(NO_2)_6]$.—This compound was prepared from potassium hexanitroplatinate(IV), $K_2Pt(NO_2)_6$, which was prepared by the literature method.[18] The potassium salt was dissolved in a minimum of water. A concentrated solution of tetra-*n*-butylammonium chloride was added. A pale yellow solid was collected, washed, and dried as before. *Anal.* Calcd for $[(n\text{-}C_4H_9)_4N]_2[Pt(NO_2)_6]$: Pt, 20.40; C, 40.19; H, 7.59; N, 11.72. Found: Pt, 20.41; C, 40.40; H, 7.39; N, 11.39.

Tetra-*n*-butylammonium Hexacyanoplatinate(IV), $[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_6]$.—This complex was prepared from the potassium salt. The potassium salt was prepared by the method reported by Babkov[19] with a few modifications: a sample of $K_2[Pt(CN)_5I]$ was prepared by treating a solution of $K_2[Pt(CN)_4]$ with a stoichiometric amount of ICN. A portion of $K_2[Pt(CN)_5I]$ was dissolved in water and solid KCN was added with stirring. After a few minutes, a white precipitate was formed. After one day, all of the precipitate was collected, dissolved in a minimum of water, and solid KCN was added again. This procedure was repeated each day for 3 or 4 days. After this time, the solid was collected and recrystallized twice from water. The tetra-*n*-butylammonium salt was then precipitated, collected, and dried. *Anal.* Calcd for $[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_6]$: Pt, 23.33; C, 54.58; H, 8.68; N, 13.40. Found: Pt, 23.41, 23.31, 23.39, 23.38; C, 54.39; H, 8.79; N, 13.46.

Hexaammineplatinum(IV) Chloride Hydrate, $[Pt(NH_3)_6]Cl_4 \cdot H_2O$.—The chloride salt was prepared from $[Pt(NH_3)_5Cl]Cl_3$[20] by treatment with liquid ammonia in a steel autoclave at room temperature for 24 hr.[21] After this time, the autoclave was opened and the ammonia evaporated. The yellow solid in the autoclave was treated with 5 *M* aqueous ammonia and the solution was filtered. The filtrate was heated to remove the ammonia and was then mixed with an equal volume of concentrated hydrochloric acid at ice bath temperature. The white solid was collected, washed with acetone and ether, and then dried. *Anal.* Calcd for $[Pt(NH_3)_6]Cl_4 \cdot H_2O$: Pt, 42.67. Found: Pt, 42.54, 42.87, 42.58.

The perchlorate salt was prepared by precipitation from a concentrated aqueous solution of the chloride salt with concentrated perchloric acid at ice bath temperature. The solid was collected and then dissolved in a minimum of acetone. Ether was then mixed with the acetone solution, precipitating the perchlorate. It was again collected and then dried. Analysis was difficult because of the tendency of the compound to explode on heating. Results indicate that the perchlorate salt is a hydrate with approximately two water molecules per formula weight. *Anal.* Calcd for $[Pt(NH_3)_6](ClO_4)_4 \cdot 2H_2O$: N:H, 1:3.67. Found: N:H, 1:3.50, 1:4.00.

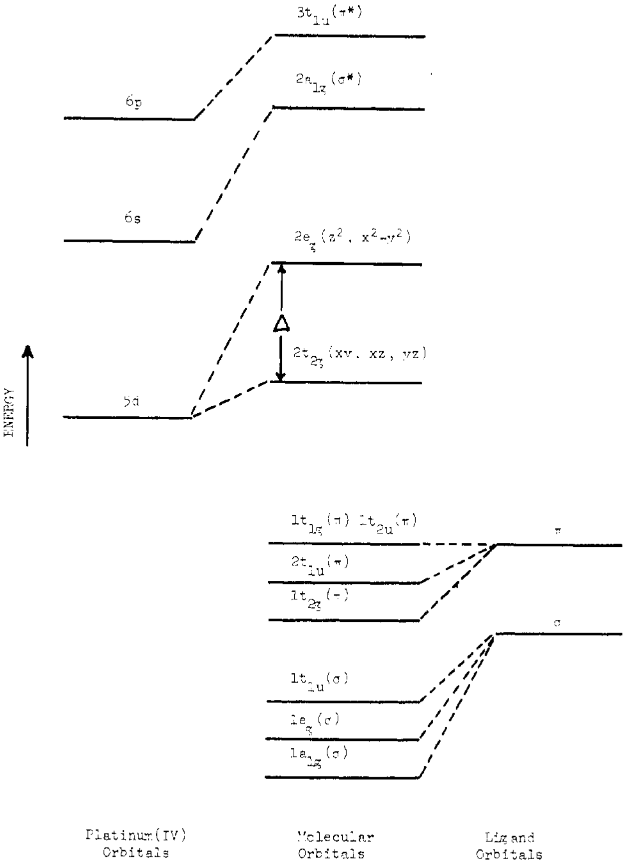

Figure 1.—Molecular orbital energy levels for octahedral halide and pseudohalide complexes.

Tris(ethylenediamine)platinum(IV) Chloride, $[Pt(en)_3]Cl_4$.—The published procedure[22] was used for this salt with excellent results. The salt was recrystallized from hydrochloric acid three times and finally dried at 110°. *Anal.* Calcd for $[Pt(en)_3]Cl_4$: Pt, 37.72; C, 13.93; H, 4.68; N, 16.25; Cl, 27.42. Found: Pt, 37.62; C, 13.71; H, 4.70; N, 16.14; Cl, 27.41.

The perchlorate salt was prepared by treating a solution of the chloride salt with a stoichiometric amount of $AgClO_4$ and separating the AgCl by filtration. The solution was concentrated and excess 72% $HClO_4$ was added at ice bath temperature. A white crystalline compound was formed on evaporating overnight. The product was collected and washed with ice cold ethanol and several portions of ether; the compound was dried 48 hr under reduced pressure at room temperature. *Anal.* Calcd for $[Pt(en)_3](ClO_4)_4$: Pt, 25.23; C, 9.32; H, 3.12; N, 10.87. Found: Pt, 25.09, 25.28; C, 9.13; H, 3.43; N, 10.91.

Spectral Measurements.—Spectro Grade solvents were used throughout except for 2-methyltetrahydrofuran, which was of reagent grade and was further purified by passing it over a column of activated alumina.

The measurements at liquid nitrogen temperature were made using a 2:1 mixture of 2-methyltetrahydrofuran and methanol ($2\text{-}CH_3THF\text{-}CH_3OH$). The solvent contraction and the near-ultraviolet cutoff point have been reported previously,[15] and the molar absorptivities of complexes at low temperature were corrected for the solvent contraction.

Spectral measurements were made on a Cary Model 14 spectrophotometer using 1.00-cm quartz cells. Low-temperature measurements were made with a liquid nitrogen dewar fitted with quartz windows.

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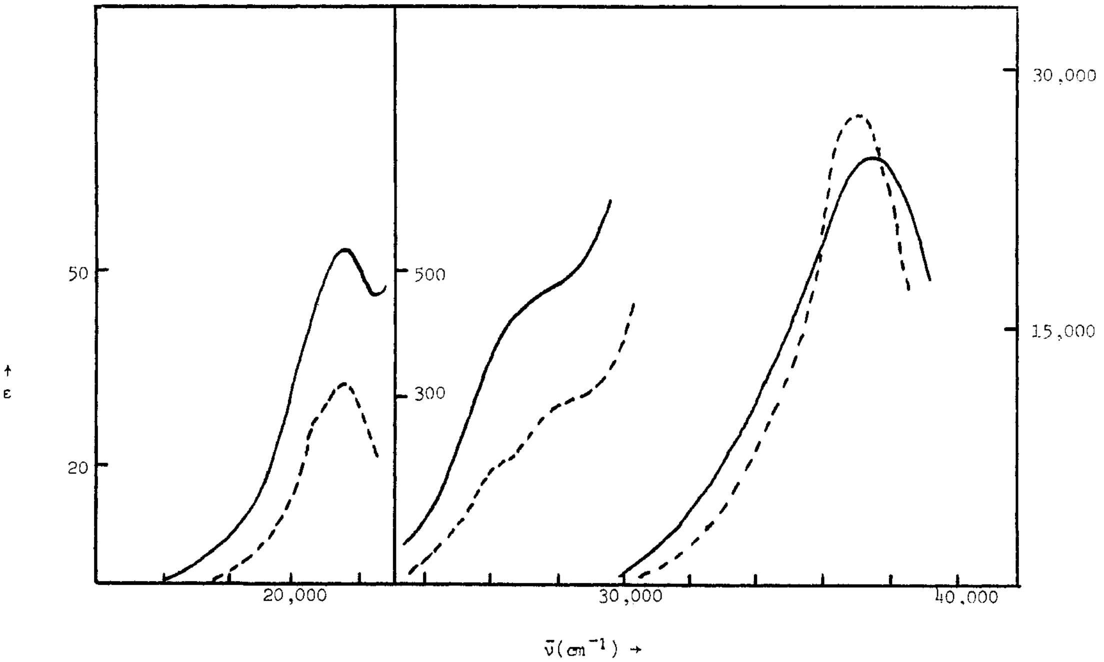

Figure 2.—Electronic spectra of $[(n\text{-}C_4H_9)_4N]_2[PtCl_6]$ in 2-CH_3THF-CH_3OH: ——, 300°K; - - -, 77°K.

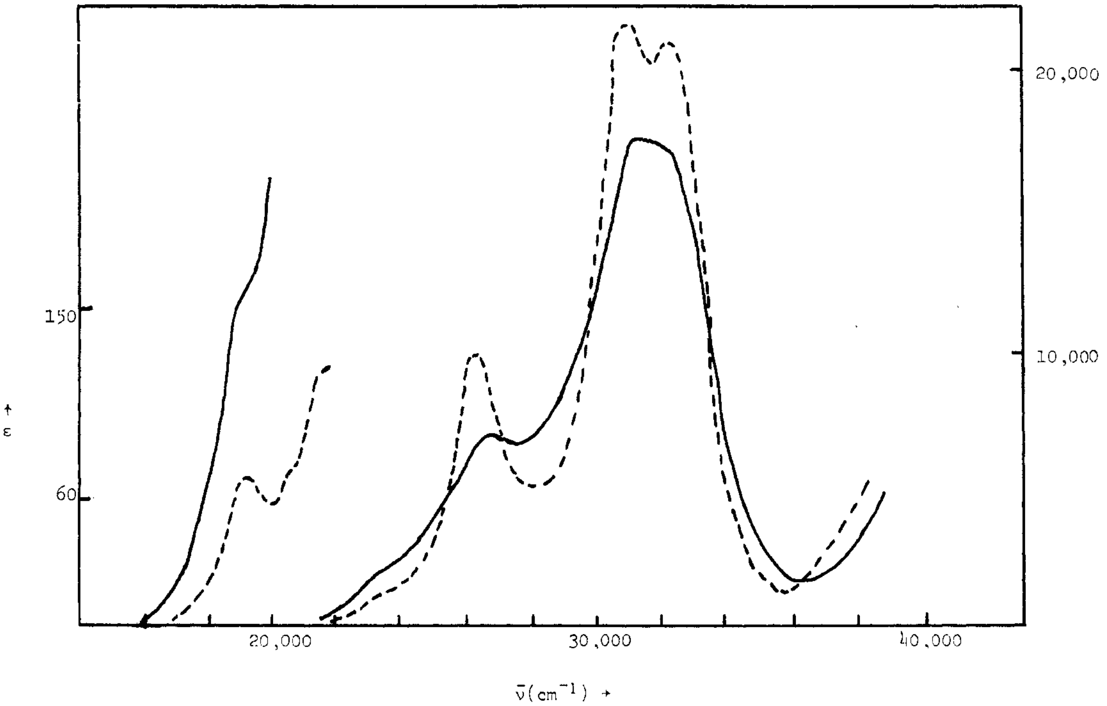

Figure 3.—Electronic spectra of $[(n\text{-}C_4H_9)_4N]_2[PtBr_6]$ in 2-CH_3THF-CH_3OH: ——, 300°K; - - -, 77°K.

Results and Discussion

Molecular Orbital Energy Levels.—A generalized molecular orbital energy level diagram suitable for a discussion of the electronic spectra of the platinum(IV) halide and pseudohalide complexes is given in Figure 1. The complexes in the present study all have low-spin d^6 electronic configurations and the highest filled level is $2t_{2g}(xy, xz, yz)$. Thus the ground state is diamagnetic and is designated $^1A_{1g}$.

Electronic Spectra of Platinum(IV) Halide Complexes.—Figures 2 and 3 present both the room-temperature and low-temperature spectra of $PtCl_6^{2-}$ and $PtBr_6^{2-}$ in a 2:1 mixture of 2-methyltetrahydrofuran and methanol (2-CH_3THF-CH_3OH). In both cases improved resolution is obtained at the lower temperature. The weaker low-energy bands decrease in intensity when cooled, which is characteristic of vibronically allowed d → d transitions. In contrast, the stronger, high-energy bands are observed to narrow in width and increase in maximum molar extinction—characteristic behavior of charge-transfer transitions. Quantitative spectral data for the halide complexes in a

TABLE I

ELECTRONIC SPECTRAL DATA AND ASSIGNMENTS FOR PLATINUM(IV) HALIDE COMPLEXES[a]

DMF	CH_3CN	CH_3OH	2-CH_3THF–CH_3OH		CH_2Cl_2	Assignment
			300°K	77°K		$^1A_{1g} \rightarrow$
			$[(n\text{-}C_4H_9)_4N]_2[PtCl_6]$			
21.50 (69)	21.60 (65)	21.70 (58)	21.50 (52)	20.70 (27)[b] 21.50 (32)	21.80 (74)	$\left.\begin{matrix}^3T_{1g}\\ ^3T_{2g}\end{matrix}\right\}$ or $T_{1g}(J)$
27.30 (530)[b]	27.70 (455)[b]	27.80 (470)[b]	27.90 (470)[b]	26.40 (200)[b]	27.40 (490)[b]	$^1T_{1g}$
				28.30 (294)		$^1T_{2g}$
	37.10 (28,800)	37.70 (27,500)	37.60 (24,100)	36.90 (28,800)	37.20 (30,500)	a, b $^1T_{1u}$
	49.50 (69,000)					c, $^1T_{1u}$
			$[(n\text{-}C_4H_9)_4N]_2[PtBr_6]$			
18.60 (150)[b]	19.00 (140)[b]	18.90 (140)[b]	19.00 (150)[b]	19.00 (69) 20.60 (72)	18.90 (148)[b]	$\left.\begin{matrix}^3T_{1g}\\ ^3T_{2g}\end{matrix}\right\}$ or $T_{1g}(J)$
22.60 (2350)[b]	22.70 (2000)[b]	22.90 (1890)[b]	22.50 (1500)[b]	22.50 (1000)[b]	22.60 (2150)[b]	$^1T_{1g}$
25.90 (7650)	26.10 (7700)	26.90 (8300)	26.50 (6900)	25.90 (8900)	26.30 (8300)	a $^1T_{2u}$
30.20 (21,550)	30.60 (20,400)	31.30 (23,700)	31.00 (16,900)	30.10 (22,000)	30.80 (24,000)	a $^1T_{1u}$
31.10 (20,700)	31.70 (19,900)	32.20 (23,600)	31.90 (16,800)	31.80 (20,200)	32.20 (22,500)	b $^1T_{1u}$
	43.70 (89,100)	43.90 (79,700)				c $^1T_{1u}$
	50.50 (40,900)					Bromide (?)

[a] $\bar{\nu} \times 10^{-3}$ cm^{-1} (ϵ, l. mol^{-1} cm^{-1}). [b] Shoulder (ϵ is for value of $\bar{\nu}$ given).

variety of solvents are given in Table I, together with detailed band assignments.

For a discussion of the spectral assignments, it may be pointed out that the first excited-state configuration for a d → d transition in a low-spin d^6 complex is $[2t_{2g}(xy, xz, yz)]^5[2e_g(z^2, x^2 - y^2)]^1$, which gives rise to spin-allowed $^1T_{1g}$ and $^1T_{2g}$ and spin-forbidden $^3T_{1g}$ and $^3T_{2g}$ excited states. Although excited-state configurations such as $[2t_{2g}(xy, xz, yz)]^4[2e_g(z^2, x^2 - y^2)]^2$ or $[2t_{2g}(xy, xz, yz)]^3[2e_g(z^2, x^2 - y^2)]^3$ may be visualized, transitions to states arising from these configurations are expected to be of too high energy to be observed. Furthermore, they should be weak since they formally represent two or more electron excitations. The one-electron excited states will be subject to configuration interaction with these higher configurations, but to a first approximation, the relative energies of the singlet and triplet states may be expressed as the diagonal elements of the full electrostatic matrix.[23] Thus the energies relative to the ground state, $^1A_{1g}$, may be given in terms of the d-orbital splitting, Δ, and the Racah parameters, B and C: $E(^3T_{1g}) = \Delta - 3C$, $E(^3T_{2g}) = \Delta + 8B - 3C$, $E(^1T_{1g}) = \Delta - C$, $E(^1T_{2g}) = \Delta + 16B - C$.

The intense bands observed in the spectra of the $PtCl_6^{2-}$ and $PtBr_6^{2-}$ ions are assigned to ligand to metal (L → M) change-transfer transitions since empty ligand orbitals are expected to be at energies too high to participate in bonding to any extent. Fully allowed transitions involve $^1T_{1u}$ states arising from the excited configurations $[1t_{1u}(\sigma)]^5[2e_g(z^2, x^2 - y^2)]^1$, $[2t_{1u}(\pi)]^5[2e_g(z^2, x^2 - y^2)]^1$, and $[1t_{2u}(\pi)]^5[2e_g(z^2, x^2 - y^2]^1$. It may be remarked that $^1T_{2u}$ states also arise from these configurations, but transitions to these states are orbitally forbidden in O_h symmetry and are expected to be much weaker.

$PtCl_6^{2-}$.—The two relatively weak bands observed at 21,500 and 27,900 cm^{-1} in 2-CH_3THF–CH_3OH at 300°K differ by nearly a factor of 10 in intensity. Consequently, they have been assigned to spin-forbidden and spin-allowed d → d transitions, respectively.[1] The marked decrease in intensity of these bands at low temperature is consistent with this assignment. The low-temperature spectrum also shows considerable improvement in resolution in the region of these bands. A shoulder at 20,700 cm^{-1} is resolved on the low-energy side of the 21,500-cm^{-1} band while shoulders are also found at 26,400 and 28,300 cm^{-1}. These bands may be assigned to the $^1A_{1g} \rightarrow {}^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$, and $^1T_{2g}$ transitions corresponding to $2t_{2g}(xy, xz, yz) \rightarrow 2e_g(z^2, x^2 - y^2)$. Such an assignment gives an unusually low value of the Racah B parameter (*ca.* 125 cm^{-1}), being only 17% of the free-ion value (720 cm^{-1}).[24] Alternatively, in view of the large spin–orbit coupling constant for Pt(IV), the weak bands at 20,700 and 21,500 cm^{-1} might be assigned to transitions to states $T_{1g}(J)$ arising from spin–orbit multiplet splitting of the $^3T_{1g}$ state. A similar suggestion has been offered[25] for the assignment of the two weak spin-forbidden bands in $IrCl_6^{3-}$. However this assignment is not entirely satisfactory either since the $^1T_{1g}$ and $^1T_{2g}$ assignments still predict a low value of B (*ca.* 125 cm^{-1}). Further study of these low-energy bands is clearly necessary to make confident detailed assignments.

Two intense charge-transfer bands are observed in the $PtCl_6^{2-}$ spectrum. In contrast to the temperature dependence of the lower energy bands, the band at 37,600 cm^{-1} sharpens and increases in maximum molar extinction. This behavior is characteristic of a fully allowed transition. The L → M assignment for this band is substantiated from the fact that the lowest energy charge-transfer in the isoelectronic iridium(III) complex, $IrCl_6^{3-}$, is observed[7] at 48,500 cm^{-1}. A red shift as the oxidation state of the central metal increases is typical of the L → M charge-transfer process. The detailed assignment of the 37,600-cm^{-1} band is $1t_{2u}(\pi)$, $2t_{1u}(\pi) \rightarrow 2e_g(z^2, x^2 - y^2)$ [$^1A_{1g} \rightarrow$ a, b $^1T_{1u}$] and thus

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(23) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, London, 1964.

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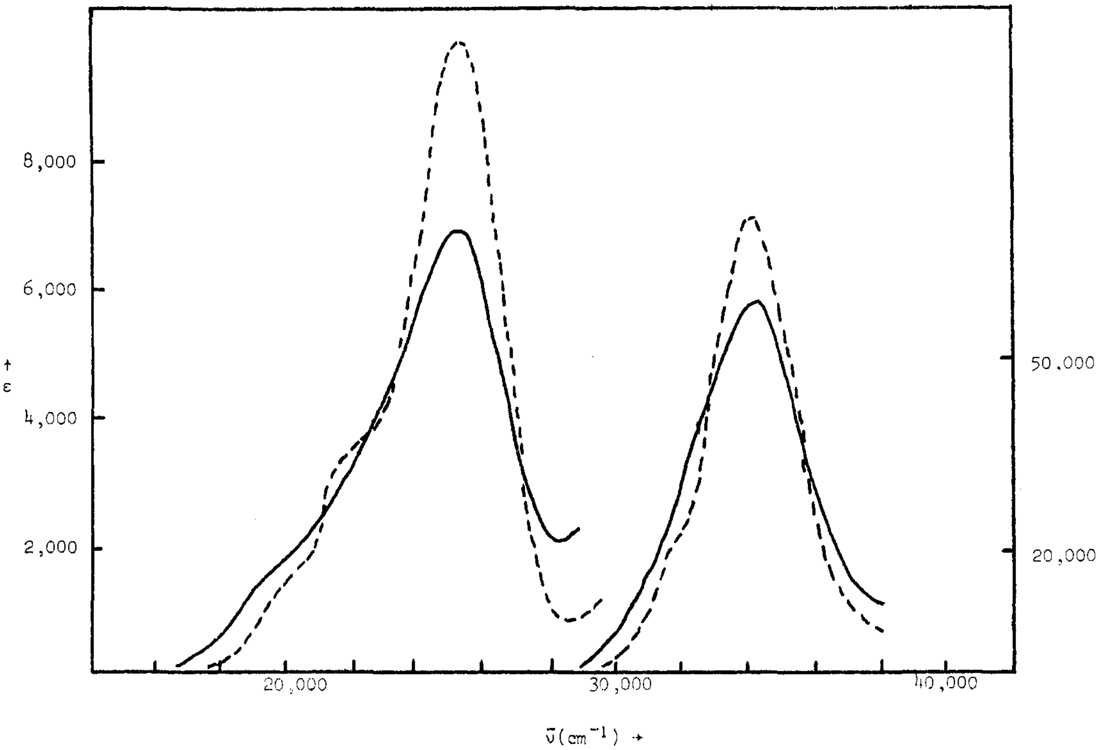

Figure 4.—Electronic spectra of $[(n\text{-}C_4H_9)_4N]_2[Pt(SeCN)_6]$ in 2-CH_3THF–CH_3OH: ——, 300°K, – – –, 77°K.

involves two ligand π orbitals. The second band observed at 49,500 cm^{-1} in acetonitrile solution is more intense than the first. This band must also be assigned to a L → M transition, but one involving ligand σ orbitals: $1t_{1u}(\sigma) \rightarrow 2e_g(z^2, x^2 - y^2)$ $[{}^1A_{1g} \rightarrow c\ {}^1T_{1u}]$.

$PtBr_6^{2-}$.—By analogy to the assignment for $PtCl_6^{2-}$ the weaker low-energy bands at 19,000, 20,600, and 22,500 cm^{-1} resolved in the low-temperature spectrum of $PtBr_6^{2-}$ are assigned to the ${}^3T_{1g}$, ${}^3T_{2g}$ (or $T_{1g}(J)$ spin-orbit states), and ${}^1T_{1g}$ excited states, respectively. The greater intensity of these bands compared to those observed for $PtCl_6^{2-}$ is likely due to increased ligand character in the $2t_{2g}(xy, xz, yz)$ orbital. The effect of this increased participation is increased charge-transfer "character" in the d → d transitions.

In contrast to $PtCl_6^{2-}$ the pattern of the charge-transfer bands for $PtBr_6^{2-}$ is more complicated, both in number and in shape. Jørgensen[1] has previously assigned the bands at 27,000, 31,800, and 33,000 cm^{-1} as $L_\pi \rightarrow M$ and the bands at 44,200 cm^{-1} as $L_\sigma \rightarrow M$. The band at 50,500 cm^{-1} has also been noted previously,[2] but no definite assignment was made. The assignments are given in Table I. Specifically, the band at 26,000 cm^{-1} is assigned to the orbitally forbidden transition $1t_{2u}(\pi) \rightarrow 2e_g(z^2, x^2 - y^2)$ $[{}^1A_{1g} \rightarrow a\ {}^1T_{2u}]$ which may account for its lower molar extinction coefficient. The broad charge-transfer band at 30,000 and 33,000 cm^{-1} present in the room-temperature spectrum clearly resolves into maxima at low temperature. These bands are assigned to the overlapping transitions, $1t_{2u}(\pi) \rightarrow 2e_g(z^2, x^2 - y^2)$ $[{}^1A_{1g} \rightarrow a\ {}^1T_{1u}]$ and $2t_{1u}(\pi) \rightarrow 2e_g(z^2, x^2 - y^2)$ $[{}^1A_{1g} \rightarrow b\ {}^1T_{1u}]$, which are not resolved in $PtCl_6^{2-}$. The band at 43,700 cm^{-1} is logically assigned to $1t_{1u}(\sigma) \rightarrow 2e_g(z^2, x^2 - y^2)$ $[{}^1A_{1g} \rightarrow c\ {}^1T_{1u}]$. The molar extinction of this band (ϵ 89,000) is among the highest known for an octrahedral complex with simple ligands. Finally, the band observed at 50,500 cm^{-1} in acetonitrile solution has also been noted in aqueous solutions.[2] The molar extinction (ϵ 40,900) indicates an allowed transition. The assignment of this transition is not certain, but it is likely an intraligand (L → L) bromide transition from a bromide 4p → 4d or 5s, whichever is of lower energy.

Electronic Spectra of Pseudohalide Complexes.—Infrared evidence has been presented recently that indicates the modes of bonding in the $Pt(SCN)_6^{2-}$ and $Pt(SeCN)_6^{2-}$ are Pt–S and Pt–Se, respectively.[26] Though no structural data are avilable for these complexes, the ligands are presumably coordinated in an angular fashion with a Pt–X–CN angle <180°.[27] The azide ligand in $Pt(N_3)_6^{2-}$ is expected to be coordinated in a linear fashion.

Figure 4 presents the spectrum of the $Pt(SeCN)_6^{2-}$ ion in the 2-CH_3THF–CH_3OH solvent at 300 and 77°K. The results obtained in this case are typical of those obtained for $Pt(SCN)_6^{2-}$ and $Pt(N_3)_6^{2-}$. Since Pt(IV) orbitals are expected to be quite stable, it is likely that the $SeCN^-$, SCN^-, and N_3^- ligands participate primarily in L → M bonding. Consequently the energy level scheme used in the discussion of the halide complexes (Figure 1) will serve as a framework. In other words its will be assumed that empty ligand π^* orbitals participate in M → L bonding to a negligible ex-

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[26] A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965).

[27] S. E. Livingstone, *Quart. Rev. Chem. Soc.*, **19**, 398 (1965); J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).

TABLE II

ELECTRONIC SPECTRAL DATA AND ASSIGNMENTS FOR SOME PLATINUM(IV) PSEUDOHALIDE COMPLEXES[a]

DMF	CH_3CN	CH_3OH	2-CH_3THF-CH_3OH 300°K	2-CH_3THF-CH_3OH 77°K	CH_2Cl_2	Assignment $^1A_{1g} \rightarrow$
			$[(n\text{-}C_4H_9)_4N]_2[Pt(SCN)_6]$			
27.20 (7700)	27.40 (7600)	27.40 (7000)	27.30 (6600)	27.40 (8300)	27.20 (7700)	a $^1T_{2u}$
34.40 (65,400)	34.70 (71,500)	34.70 (70,500)	34.50 (48,300)	34.70 (51,300)	34.40 (68,700)	a, b $^1T_{1u}$
			$[(n\text{-}C_4H_9)_4N]_2[Pt(SeCN)_6]$			
18.00 (920)[b]	19.00 (1700)[b]	18.90 (1,500)[b]	18.50 (1250)[b]	19.60 (1480)[b]	18.90 (1600)[b]	$^1T_{1g}$
				21.70 (3400)[b]		$^1T_{2g}$
24.80 (7360)	25.00 (8600)	25.00 (7700)	24.80 (7000)	25.30 (10,000)	24.80 (8500)	a $^1T_{2u}$
				31.70 (25,900)		a $^1T_{1u}$
33.90 (71,600)	34.20 (92,000)	34.10 (85,200)	34.10 (60,700)	34.20 (70,500)	34.00 (86,800)	b $^1T_{1u}$
	48.80 (49,500)[b]					c $^1T_{1u}$
			$[(n\text{-}C_4H_9)_4N]_2[Pt(N_3)_6]$			
20.60 (280)[b]	20.60 (260)[b]	21.30 (300)[b]	21.10 (290)[b]	21.30 (250)[b]	20.60 (280)[b]	$^3T_{1g}$
31.50 (49,200)	32.80 (63,700)	33.00 (53,800)	33.00 (42,300)	32.90 (51,000)	32.60 (53,300)	a, b $^1T_{1u}$
	46.50 (44,220)	47.40 (44,000)				c $^1T_{1u}$
			$[(n\text{-}C_4H_9)_4N]_2[Pt[(CN)_6]$			
			No maxima or shoulders below 53,000 cm^{-1} in H_2O or CH_3CN			

[a] $\bar{\nu} \times 10^{-3}$ cm^{-1} (ϵ, l. mol^{-1} cm^{-1}). [b] Shoulder (ϵ is for value of $\bar{\nu}$ given).

tent. Table II gives spectral data for these complexes and $Pt(CN)_6^{2-}$.

$Pt(SCN)_6^{2-}$.—The spectrum of the $Pt(SCN)_6^{2-}$ ion contains only two bands at 300 and 77°K. Both narrow and increase in maximum molar extinction on cooling and may be assigned as charge-transfer processes. The $Pt(SCN)_6^{2-}$ complex is typical of a number of thiocyanato complexes in that it has intense bands in the 30,000–40,000 cm^{-1} energy region. Since bands in this region seem characteristic of several thiocyanato complexes, Jørgensen and others have suggested[7,28] the absorption is due to an intraligand process. It may be pointed out however that the free thiocyanate ligand does not absorb appreciably below 40,000 cm^{-1}. Furthermore, since the isoelectronic $Ir(SCN)_6^{3-}$ shows[6,29] no intense bands below 40,000 cm^{-1}, an L → M assignment seems attractive for the bands observed for $Pt(SCN)_6^{2-}$. An analogous red shift is observed[7,15,30] for the first intense band in the spectrum of $Au^{III}(SCN)_4^-$ relative to $Pt^{II}(SCN)_4^{2-}$. The molar extinction of the band at 27,400 cm^{-1} in $Pt(SCN)_6^{2-}$ is nearly a factor of 10 smaller than the band of 34,700 cm^{-1}. Therefore, the lower energy band is assigned as $1t_{2u}(\pi) \rightarrow 2e_g(z^2, x^2 - y^2)$ $[^1A_{1g} \rightarrow a\ ^1T_{2u}]$ while the higher energy band is assigned as $1t_{2u}(\pi)$, $2t_{1u}(\pi) \rightarrow 2e_g(z^2, x^2 - y^2)$ $[^1A_{1g} \rightarrow a, b\ ^1T_{1u}]$.

$Pt(SeCN)_6^{2-}$.—The low-temperature spectrum, Figure 4, reveals two weaker bands on the low-energy side of the intense band at 25,000 cm^{-1} which are assigned as d → d transitions, their high intensity being rationalized by their close proximity to charge-transfer system. At higher energy there is a total of four charge-transfer bands observed. The band at 25,000 cm^{-1} is the weakest of these, consequently this band is assigned as $1t_{2u}(\pi) \rightarrow 2e_g(z^2, x^2 - y^2)$ $[^1A_{1g} \rightarrow a\ ^1T_{2u}]$. At low temperature a shoulder is resolved on the side of the 34,200-cm^{-1} band. The assignment of this shoulder is not certain but might be due to $1t_{2u}(\pi) \rightarrow 2e_g(z^2, x^2 - y^2)$ $[^1A_{1g} \rightarrow a\ ^1T_{1u}]$, though splitting due to distortion of the octahedron resulting from the angular coordination of the $SeCN^-$ ligand cannot be ruled out. The maximum at 34,200 cm^{-1} which has an extremely high molar extinction ($\epsilon \sim$92,000 in acetonitrile) is assigned as $2t_{1u}(\pi) \rightarrow 2e_g(z^2, x^2 - y^2)$ $[^1A_{1g} \rightarrow b\ ^1T_{1u}]$. Finally a shoulder is also observed at 48,800 cm^{-1} in acetonitrile solution and is assigned as $1t_{1u}(\sigma) \rightarrow 2e_g(z^2, x^2 - y^2)$ $[^1A_{1g} \rightarrow c\ ^1T_{1u}]$.

It may be remarked here that both $Pt(SCN)_6^{2-}$ and $Pt(SeCN)_6^{2-}$ ions are quite sensitive to light. Solutions for the above measurements were prepared in the dark and carefully protected from the light during measurements. With such handling spectral curves were reproducible over periods of up to 1 hr. On exposure to light the intensities of the charge-transfer bands decrease and a new band appears in the spectrum of each complex, at 39,500 cm^{-1} for $Pt(SeCN)_6^{2-}$ and 41,700 cm^{-1} for $Pt(SCN)_6^{2-}$. The intensity of these new bands increases in proportion to the length of exposure to light and they are thus logically due to products of a photochemical process. Since $Pt(SeCN)_4^{2-}$ and $Pt(SCN)_4^{2-}$ have charge-transfer bands at 39,200 and 40,600 cm^{-1}, respectively, the photochemical reaction may be a reduction of Pt(IV) to Pt(II).

$Pt(N_3)_6^{2-}$.—The results obtained for $Pt(N_3)_6^{2-}$ agree substantially with those reported previously.[4] The weak shoulder at 21,000 cm^{-1} decreases in intensity slightly at low temperature and has been assigned as a spin-forbidden d → d transition, $^1A_{1g} \rightarrow {}^3T_{1g}$. This assignment was considered necessary because of the placement of the azide ligand in the spectrochemical series: $N_3^- \sim Cl^-$.[4] The spin-allowed bands are believed to be obscured by the charge-transfer system. The intense band at 33,000 cm^{-1} has been assigned[4] as the L → M transition $1t_{2u}(\pi)$, $2t_{1u}(\pi) \rightarrow 2e_g(z^2, x^2 -$

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[28] H. H. Schmidtke, "Physical Methods in Advanced Inorganic Chemistry," H. A. O. Hill and P. Day, Ed, Interscience, New York, N. Y., 1968, p 146.

[29] W. R. Mason and S. K. Arapkoske, unpublished results, 1969.

[30] W. R. Mason and H. B. Gray, unpublished data, 1967.

TABLE III

ELECTRONIC SPECTRA OF $[(n\text{-}C_4H_9)_4N]_2[Pt(NO_2)_6]$[a]

DMF	CH_3CN	CH_3OH	2-CH_3THF–CH_3OH 300°K	2-CH_3THF–CH_3OH 77°K	CH_2Cl_2	Assignment ${}^1A_{1g} \rightarrow$
30.30 (14,200)[b]	30.20 (14,000)[b]	29.90 (12,000)[b]	29.30 (11,900)[b]	30.30 (10,500)[b]	29.80 (14,800)[b]	a ${}^1T_{2u}$ or $n_0 \rightarrow 2e_g$
35.50 (35,300)	35.50 (41,000)	35.70 (34,500)	35.50 (32,900)	35.50 (40,700)	35.20 (41,800)	a, b ${}^1T_{1u}$
	49.60 (31,100)[b]					c ${}^1T_{1u}$ or $\pi \rightarrow \pi^*$ (NO_2^-)

[a] $\tilde{\nu} \times 10^{-3}$ cm^{-1} (ϵ, l. mol^{-1} cm^{-1}). [b] Shoulder (ϵ is for value of $\tilde{\nu}$ given).

y^2) [${}^1A_{1g} \rightarrow$ a, b ${}^1T_{1u}$]. Again the L → M character of this band is substantiated by a red shift[4] from $Ir(N_3)_6^{3-}$ to $Pt(N_3)_6^{2-}$. A second charge-transfer band is observed at 46,500 cm^{-1} in acetonitrile solution and is assigned as $1t_{1u}(\sigma) \rightarrow 2e_g(z^2, x^2 - y^2)$ [${}^1A_{1g} \rightarrow$ c ${}^1T_{1u}$].

$Pt(CN)_6^{2-}$.—No distinct maxima or shoulders were observed below 53,000 cm^{-1}. This result is not unexpected, however, since the isoelectronic $Ir(CN)_6^{3-}$ also contains[31] no bands below 50,000 cm^{-1}. The lowest energy transitions expected for d^6 cyano complexes are generally of the metal → ligand (M → L) type from occupied metal orbitals to higher energy $\pi^*(CN^-)$ levels.[31] A blue shift of absorption as oxidation state of the central metal increases is characteristic of transitions of this type of process. Some unrecrystallized samples of $K_2Pt(CN)_6$ showed weak absorption (ϵ ~2) at 39,000 cm^{-1}. However, $Pt(CN)_4^{2-}$ has intense absorption in this region and in view of the method of preparation of the $Pt(CN)_6^{2-}$ ion, this absorption is likely due to a platinum(II) impurity.

Electronic Spectra of Nitro and Ammine Complexes. $Pt(NO_2)_6^{2-}$.—Recently the preparation of $K_2Pt(NO_2)_6$ was reported,[18] but no spectral data were given. Figure 5 presents the spectrum of $[(n\text{-}C_4N_9)_4N]_2[Pt(NO_2)_6]$ in 2-CH_3THF–CH_3OH at 300°K and 77°K. Spectral data in a variety of solvents and band assignments have been included in Table III.

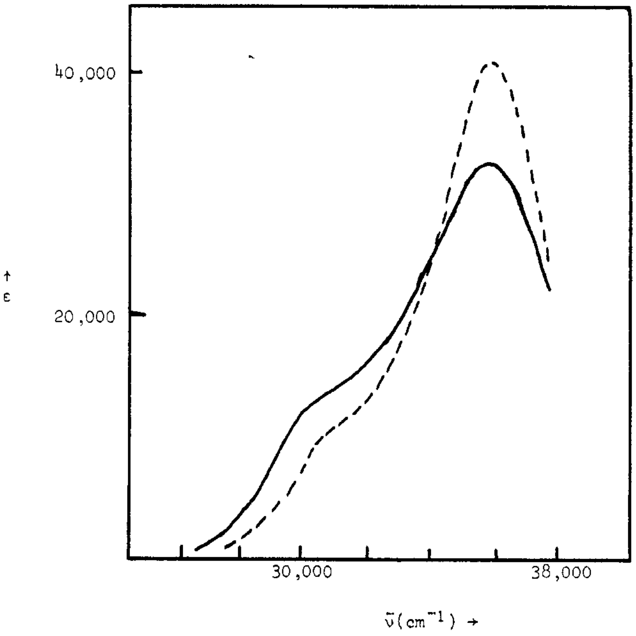

Figure 5.—Electronic spectra of $[(n\text{-}C_4H_9)_4N]_2[Pt(NO_2)_6]$ in 2-CH_3THF–CH_3OH: ——, 300°K; – – –, 77°K.

The electronic structures of octahedral nitro complexes have been discussed recently.[32] It has been pointed out that in addition to filled σ and π orbitals which participate in L → M bonding, the NO_2^- ligands also possess nonbonding orbitals located mainly on the oxygen atoms, n_0, and low-lying empty π^* orbitals. Thus the possibilities for charge transfer are more complicated than with simpler ligands. Specifically L → L, L → M, M → L, and nonbonding → metal ($L_n \rightarrow M$) type transitions may be visualized.

The spectra obtained for $Pt(NO_2)_6^{2-}$ ion contain three intense bands between 30,000 and 50,000 cm^{-1} while the $Ir(NO_2)_6^{3-}$ complex shows[33] only a single band with comparable intensity near 50,000 cm^{-1}. Thus the typical red shift in absorption suggests L → M or $L_n \rightarrow$ M charge transfer. The shoulder at 30,000 cm^{-1} may correspond to the orbitally forbidden $1t_{2u}(\pi) \rightarrow 2e_g(z^2, x^2 - y^2)$ [${}^1A_{1g} \rightarrow {}^1T_{2u}$], but the band differs from the usual behavior and appears to *decrease* in intensity on cooling. The $L_n \rightarrow$ M transition $n_0 \rightarrow 2e_g(z^2, x^2 - y^2)$ is also forbidden in cubic symmetry and may be an alternative assignment. The maximum at 35,500 cm^{-1} shows the more typical temperature behavior and accordingly is assigned as $1t_{2u}(\pi)$, $2t_{1u}(\pi) \rightarrow 2e_g(z^2, x^2 - y^2)$ [${}^1A_{1g} \rightarrow$ a, b ${}^1T_{1u}$]. The intense band at 49,600 cm^{-1} in acetonitrile may be assigned as $1t_{1u}(\sigma) \rightarrow 2e_g(z^2, x^2 - y^2)$ [${}^1A_{1g} \rightarrow$ c ${}^1T_{1u}$]. However, the free NO_2^- ligand shows[34] an intense $\pi \rightarrow \pi^*$ absorption band near 48,000 cm^{-1}. Nearly all $M(NO_2)_6^n$ complexes that have been reported have an intense band between 48,000 and 50,000 cm^{-1}. Thus absorption in this region may be due to an intraligand process. Consequently the assignment of the band at 49,600 cm^{-1} in $Pt(NO_2)_6^{2-}$ to an intraligand band or a combination of the L → M transition and an intraligand process cannot be ruled out. A careful examination of spectral data for a variety of nitro complexes is in progress in hope of clarifying this point.

$Pt(NH_3)_6^{4+}$ and $Pt(en)_3^{4+}$.—The spectra of cationic ammine and ethylenediamine complexes are at best poorly defined. A band between 33,000 and 38,000 cm^{-1} has been reported[1,7] for $Pt(NH_3)_6^{4+}$. However the main product in the preparation of $[Pt(NH_3)_6]Cl_4$ is $[Pt(NH_3)_5Cl]Cl_3$ which has a distinct absorption band at 35,300 cm^{-1} in H_2O.[1,7] Thus the reported absorption may be due to small amounts of the pentaammine in the hexaammine samples. In the present study measurements were made on acetonitrile and dilute perchloric

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(31) J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 4260 (1968).

(32) K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, **6**, 562 (1967).

(33) D. L. Swihart, S. K. Arapkoske, and W. R. Mason, unpublished results, 1969.

(34) S. J. Strickler and M. Kasha, *J. Amer. Chem. Soc.*, **85**, 2899 (1963), and references cited therein.

acid solutions of $[Pt(NH_3)_6](ClO_4)_4$. Though the absorption increases at energies above 30,000 cm^{-1}, no distinctive shoulders or maxima were identified at energies less than 52,000 cm^{-1}. The perchlorate salt was found to dissolve in the 2-CH_3THF–CH_3OH solvent mixture, which permitted a low-temperature measurement. However no indication of a distinct band was found at energies lower than 37,000 cm^{-1}.

The absorption spectra and circular dichroism (CD) spectra of $(-)Pt(en)_3{}^{4+}$ have been reported recently,[12] and spectral bands were identified at 38,500 and 41,700 cm^{-1}. However both the absorption and CD spectra were found to be considerably dependent on the nature of the counterion and its concentration in solution, due to outer-sphere complexation. Measurements made in the present study on dilute perchloric acid solutions of $[Pt(en)_3]Cl_4$ showed a very poorly resolved shoulder at approximately 44,500 cm^{-1} (ϵ 2900) and a slight tailing between 35,000 and 40,000 cm^{-1} suggesting another weaker band at approximately 38,000 cm^{-1} (ϵ 250). Measurements on acetonitrile and dilute perchloric acid solutions of $[Pt(en)_3](ClO_4)_4$ however were even more poorly resolved and showed no distinct maxima or shoulders lower than 53,000 cm^{-1}. In view of the evidence[12] for outer-sphere chloride association with the $Pt(en)_3{}^{4+}$ cation, the faint shoulders for the chloride salt should be viewed with some caution. The weaker low-energy band has been assigned[12] as ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and the higher energy band as ${}^1A_{1g} \rightarrow {}^1T_{2g}$. At the very least these assignments are unacceptable since the lowest energy spin-allowed transition in $Ir(en)_3{}^{3+}$, which is distinctly resolved, is at 40,200 cm^{-1} in aqueous solution.[25] The corresponding band in the platinum(IV) complex should come at higher energy. Thus the lower energy band, if a genuine feature, is probably best assigned as ${}^1A_{1g} \rightarrow {}^3T_{1g}$ and the band near 44,000 cm^{-1} as ${}^1A_{1g} \rightarrow {}^1T_{1g}$.

Spectrochemical Series for Platinum(IV).—The ordering of ligands according to their effects on d-orbital splitting, Δ, is generally made from d → d transition energies. The extensive overlap of charge-transfer and ligand-field absorption in the spectra of platinum(IV) complexes makes accurate values of Δ and interelectronic repulsion parameters difficult to obtain. However in those cases where d → d bands can be identified an estimate of Δ may be made by assuming reasonable values of interelectronic repulsion. Table IV presents these estimates of Δ for each complex, along with the lowest energy L → M charge-transfer band, ${}^1A_{1g} \rightarrow$ a ${}^1T_{1u}$, ${}^1T_{2u}$. The charge-transfer energies parallel the stability of the highest filled ligand orbitals, and for the halide, pseudohalide, and ammine complexes increase in the same order as Δ. Thus the relative position of the L → M charge-transfer may be used to estimate spectrochemical strength of donor ligands in the absence of observable d → d bands. From Table IV the spectrochemical ordering of ligands for platinum(IV) may be given as $SeCN^- < Br^- < SCN^- < N_3{}^- < Cl^- < NH_3$, en $< NO_2{}^-$, CN^-. As is well known, the Δ parameter and therefore spectrochemical ordering depend on both σ and π bonding. The low positions for $SeCN^-$ and Br^- are likely due to strong L → M π bonding while the higher position of NH_3 and en results from strong σ donation. As noted earlier the rather high intensities of the ligand-field bands in $Pt(SeCN)_6{}^{2-}$ and $PtBr_6{}^{2-}$ are consistent with considerable ligand–metal orbital mixing producing enhanced ligand character in the $2t_{2g}(xy, xz, yz)$ orbital. Finally, though no explicit data are available, the customarily high position in the series is inferred for CN^- and $NO_2{}^-$. These ligands may participate in M → L bonding which will stabilize the $2t_{2g}(xy, xz, yz)$ relative to $2e_g(z^2, x^2 - y^2)$. It may be noted however that the lower energy L → M charge transfer for the nitro complex (35,500 cm^{-1}) compared to that of the cyano complex (>52,000 cm^{-1}) may be a consequence of weaker σ bonding in the nitro complex resulting from a comparatively more stable $2e_g(z^2, x^2 - y^2)$ level.

TABLE IV

ENERGIES OF Δ AND L → M CHARGE TRANSFER FOR $PtL_6{}^m$

L	$10^{-3}\Delta$,[a] cm^{-1}	$10^{-3}E$[L → M (${}^1A_{1g} \rightarrow$ a ${}^1T_{1u}$, ${}^1T_{2u}$)], cm^{-1}
$SeCN^-$	21.6	24.8
Br^-	24.5	26.5
SCN^-	. . .[c]	27.2
$N_3{}^-$	27.3[b]	32.5
Cl^-	28.4	37.2
NH_3	>40	>52.0
0.5en	~46.5[d]	>52.0
$NO_2{}^-$	. . .[c]	35.5
CN^-	. . .[c]	>52.0

[a] $\Delta = E[({}^1T_{1g})(2CH_3THF\text{–}CH_3OH \text{ at } 77°K)] + C$; $C \simeq 2000$ cm^{-1}. [b] $\Delta = E({}^3T_{1g}) + 3C$. [c] Insufficient data. [d] Aqueous measurements on $[Pt(en)_3]Cl_4$.

Ligand → Metal Charge-Transfer Energies.—Table V presents $L_\pi \rightarrow M$ [${}^1A_{1g} \rightarrow$ b ${}^1T_{1u}$] and $L_\sigma \rightarrow M$ [${}^1A_{1g} \rightarrow$ c ${}^1T_{1u}$] charge-transfer energies for the octahedral halide and pseudohalide complexes of platinum(IV). The $L_\pi \rightarrow M$ [${}^1A_{1g} \rightarrow {}^1A_{2u}$, ${}^1E_u$] charge-transfer energies of the corresponding square-planar platinum(II) complexes[16] are also included in Table V for com-

TABLE V

CHARGE-TRANSFER ENERGIES FOR SOME PLATINUM HALIDE AND PSEUDOHALIDE COMPLEXES[a]

Octahedral $PtL_6{}^{2-}$

Complex	$L_\pi \rightarrow M$ ${}^1A_{1g} \rightarrow$ b ${}^1T_{1u}$	$L_\sigma \rightarrow M$ ${}^1A_{1g} \rightarrow$ c ${}^1T_{1u}$	$\Delta_{\sigma-\pi}$
$PtBr_6{}^{2-}$	31,700	43,700	12,000
$PtCl_6{}^{2-}$	37,100	49,500	12,400
$Pt(N_3)_6{}^{2-}$	32,800	46,500	13,700
$Pt(SeCN)_6{}^{2-}$	34,200	48,800	14,600
$Pt(SCN)_6{}^{2-}$	34,700	>50,000	>15,000
$Pt(NO_2)_6{}^{2-}$	35,500	49,600[b]	14,100

Square-Planar $PtL_4{}^{2-}$

Complex	$L_\pi \rightarrow M$ ${}^1A_{1g} \rightarrow {}^1A_{2u}$, a ${}^1E_u$	Complex	$L_\pi \rightarrow M$ ${}^1A_{1g} \rightarrow {}^1A_{2u}$, a ${}^1E_u$
$PtBr_4{}^{2-}$	36,000[c]	$Pt(SeCN)_4{}^{2-}$	39,200[e]
$PtCl_4{}^{2-}$	44,100[c]	$Pt(SCN)_4{}^{2-}$	41,150[f]
$Pt(N_3)_4{}^{2-}$	40,500[d]	$Pt(NO_2)_4{}^{2-}$	47,000[g]

[a] Energies in cm^{-1}; solvent is CH_3CN at ~300°K. [b] Assignment uncertain. [c] Data from ref 16. [d] Data from ref 4. [e] Data from ref 6. [f] W. R. Mason, unpublished results, 1967. [g] W. R. Mason and S. K. Arapkoske, unpublished results, 1969.

parison. In all cases the $L_\pi \rightarrow M$ charge-transfer transition is of lower energy for the platinum(IV) complex than for the platinum(II) complex. This trend is expected since the platinum(IV) orbitals are more stable than those of the lower valent platinum(II). The ordering of ligands according to increasing $L_\pi \rightarrow M$ energy is slightly different for platinum(II) and platinum(IV). The ordering for platinum(II) is given as $Br^- < SeCN^- \sim N_3^- \sim SCN^- < Cl^- < NO_2^-$, while that for platinum(IV) is $Br^- < N_3^- < SeCN^- \sim SCN^- < NO_2^- < Cl^-$. The differing position of N_3^- and NO_2^- may be partly due to solvent differences for platinum(II) measurements and assignments of the charge-transfer processes in the nitro complexes. It is clear however the energy variation as a function of ligand is *greater* for platinum(II) than for platinum(IV), being some 11,000 cm^{-1} between Br^- and NO_2^- for platinum(II) but only 5400 cm^{-1} between Br^- and Cl^- for platinum(IV). The lower sensitivity of the $L_\pi \rightarrow M$ energies to the nature of the ligand may be an indication of comparatively lower π bonding in the octahedral complexes or a greater involvement of the metal acceptor level, $2e_g(z^2, x^2 - y^2)$, in σ bonding. The metal orbitals of platinum(IV) are expected to be more contracted in the octahedral complexes leading to less favorable overlap than in the case of the square complexes. On the other hand the greater metal charge in the octahedral complexes should facilitate strong σ interaction.

The two-band charge-transfer system with separation $\Delta\sigma-\pi$ of 10,000–16,000 cm^{-1} has been noted previously[16] as being a characteristic feature of both square-planar and octahedral halide complexes. It is seen in Table V that comparable separations of the $L_\pi \rightarrow M$ and $L_\sigma \rightarrow M$ charge-transfer bands are found for pseudohalide ligands as well. It is interesting that the polyatomic ligands show slightly larger $\Delta\sigma-\pi$ differences than the halide ligands. Since the changes in $\Delta\sigma-\pi$ are small, they may be due to differences in interelectronic repulsions on the ligands. Electronic repulsion is expected to be somewhat lower on the polyatomic ligands than on the halide ligands.

Another feature which may be noted from the charge-transfer data of Table V is that the $L_\pi \rightarrow M$ band in $Pt(SeCN)_6^{2-}$ compared to that in $Pt(SCN)_6^{2-}$ is shifted only 500 cm^{-1} to lower energy. The corresponding shift from $PtBr_6^{2-}$ to $PtCl_6^{2-}$ is 5400 cm^{-1}. It is unlikely that differences in electronic repulsions alone can account for the differences in these energy shifts. In view of the ligand orbital stability, $SeCN^- < SCN$ and $Br^- < Cl^-$, the small shift for the former ligands may be taken as indicating comparatively greater π-donor ability of $SeCN^-$ compared to SCN^- than of Br^- compared to Cl^- in platinum(IV) complexes.

Acknowledgment.—The authors wish to acknowledge the Council of Academic Deans' Fund of Northern Illinois University for support of this work.

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The Acid-Base Equilibria, Kinetics of Copper Ion Incorporation, and Acid-Catalyzed Zinc Ion Displacement from the Water-Soluble Porphyrin $\alpha,\beta,\gamma,\delta$-Tetra(4-N-methylpyridyl)porphine

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Received January 26, 1970

The preparation and properties of $\alpha,\beta,\gamma,\delta$-tetra(4-N-methylpyridyl)porphine are described. This porphyrin is water soluble from below pH 0 to above pH 14. Acid-base titrations show only the diacid-free base equilibrium ($pK_{3,4} = 2.2 \pm 0.2$) in the acid range, and the free base-monocation equilibrium ($pK_3 = 12.9 \pm 0.2$) in the basic region. The rate law for the dissociation of the Zn(II) chelate is first order in zinc porphyrin and second order in both hydrogen ion and chloride ion concentration. The kinetics of Cu(II) insertion into the free base porphyrin are reported. The properties of this porphyrin are notably different from most other porphyrins in terms of the electrostatic effect of the four positively charged N-methyl groups on the *meso* positions of the porphyrin.

Introduction

One of the major limitations in investigating the reactions of metalloporphyrin complexes is their lack of solubility over all pH ranges in aqueous solution. Most naturally occurring porphyrins have carboxylic acid functions which limit their solubility to basic regions, and interesting ligand substitution reactions have been studied with such Fe(III) and Co(III) derivatives.[2] Recently a number of acid solution soluble porphyrin complexes have been prepared and their properties examined. With *meso*-tetrapyridylporphine,[3] the acid-base equilibria,[4] metal ion electron-

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