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Photophysics of Aqueous $Pt(CN)_4^{2-}$

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Abstract: A detailed study of the non-Beer's law behavior of the absorption features of the UV spectrum of aqueous $K_2Pt(CN)_4$ and $BaPt(CN)_4$ allows a more definitive set of excited-state assignments than previously possible for the monomer. Concentration dependence, quenching, and lifetime studies of the several room-temperature emission features allow a distinction between fluorescences and phosphorescences and a probable assignment as to the oligomers responsible. Two excited-state absorptions and a long-lived chemical transient are found.

The tetracyanoplatinites, known for well over a hundred years, have been variously studied by quite a number of investigators. Our interest, however, was stimulated by recent work of Gliemann, Yersin, and co-workers,[1-9] who studied the low-temperature emission from various salts of $Pt(CN)_4^{2-}$. They concluded that the stacking that occurs in the crystal leads to a splitting of the platinum *z*-axis orbitals, the emission properties being sharply dependent on the Pt–Pt distance, *R*. Our interest was in whether stacking association might occur in solutions and, if so, in the consequent photophysical and photochemical behavior.

Emission from aqueous solutions of the Ba, Mg, and K salts is well-known,[10-15] the most recent work being that of Rossiello and Furlani[16] and Webb and Rossiello.[17] The matter of possible oligomer formation in solution has not been directly studied, however, nor have there been any clear assignments of the emission features. Day[18,19] did conclude that since the tetracyanoplatinites form insulating crystals in which the molecular units are clearly distinguishable, it seems a priori probable that the lowest crystal excited states are neutral Frenkel excitons formed from simple molecular transitions coupled by an intermolecular interaction potential. The simplest approximate treatment is by Davydov theory.[20] One predicts a shift to lower energy of the transition that is polarized along the Pt–Pt axis, or the *z* direction, proportional to R^{-3} (as observed).

The absorption spectrum of $Pt(CN)_4^{2-}$ has been analyzed theoretically by various authors,[21-33] but only one paper has specifically attempted a treatment of the dilute aqueous solution spectrum.[29] The spectrum is complex; there are four distinct but nonsymmetric features, which may be deconvoluted into six Gaussian components.

Experimental Section

Materials. The tetracyanoplatinate salts were prepared by a modification of a literature method.[34] To platinum(II) chloride (Alfa Inorganics) was added a 20% excess of potassium cyanide dissolved in a minimum of water. The resulting solution was filtered, and the filtrate was evaporated at 60–80 °C to about half the volume (12 cm^3 for 5 g of $PtCl_2$) and allowed to cool. The resulting crystals could be recrystallized from dilute aqueous potassium cyanide. $Ba[Pt(CN)_4]\cdot 4H_2O$ was prepared by adding a slight excess of barium chloride to a warm concentrated solution of the potassium salt of the complex, and filtering off any $Ba(OH)_2$ that formed. Crystals separated on cooling and were recrystallized from dilute aqueous barium chloride. Other chemicals used were of reagent grade.

Absorption Spectra. Routine spectroscopic measurements were made by means of either a Cary Model 14R or a Beckman Acta MVI recording spectrophotometer. In order to examine the concentration dependence of the more intense absorption bands, however, it was necessary to use a micrometer, variable path-length cell (Beckman Research and Industrial Instruments Co., Ltd., England, Model BC-14). Path-length settings would be read to 0.0005 cm directly and to 5×10^{-5} cm with the vernier. The scale was calibrated by means of measurements on standard potassium chromate solutions. The cell could be thermostated to ±1 °C.

Emission Spectra. Most of the measurements were made with the use of an Aminco Model 4-8400 excitation grating monochromator and Model 4-8401 emission grating monochromator. Excitation was by a 200-W Xe–Hg lamp, and the detector was a Hamamatsu R446 photomultiplier tube (PMT). Excitation spectra were run on a Perkin-Elmer Model MPF-3 spectrofluorimeter (R446 PMT)[35] or a Perkin-Elmer Model 650-10S instrument equipped with either a R454 or a R928 PMT. All emission spectra are uncorrected.

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(20) Authors dealing with solution association, particularly Gray,[45] have discussed this phenomenon in terms of molecular orbital theory without giving the resultant red-shifted transition a particular name, whereas the solid-state physicists have called[1,19,21] the observable, analogous solid-state transitions, Davydov transitions. We adopt this nomenclature, here and throughout the remainder of the text, solely for the sake of an expediently short handle, without specifically endorsing the mathematical applicability of the theory to solution chemistry. See ref 30–33 of our ref 1 or ref 4 of ref 21 for reviews of Davydov theory.

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(35) We wish to thank Professor H. B. Gray for the use of this equipment.

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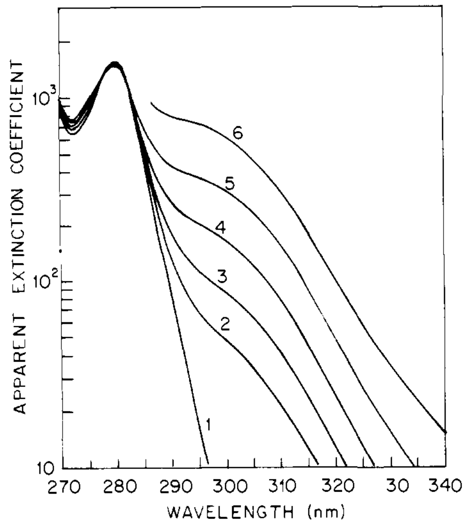

Figure 1. Apparent molar extinction coefficients for various concentrations of $K_2Pt(CN)_4$. Concentrations: 1, 8.96×10^{-3} M; 2, 0.152 M; 3, 0.218 M; 4, 0.311 M; 5, 0.445 M; 6, 0.635 M. Temperatures: 2, 3, and 5 are at 23 °C; 4 is at 25 °C; 1 and 6 are at room temperature, ca. 26 °C.

Time-Resolved Measurements. Emission lifetimes and time-resolved emission spectra were obtained by means of a Korad pulsed Nd-glass laser system previously described.[36,37] Typically, a 20-ns pulse of 353.3-nm wavelength was used for excitation and a 14-stage RCA 7265 PMT as detector. Suitable filters were used to screen out scattered light. Two sets of emission spectra were obtained with the use of an optical multichannel analyzer (OMA) detector (courtesy of EG and G PARC), which included a Model 1205A OMA, Model 1211 high-frequency pulse generator, and Model 1205B silicon-intensified vidicon (SIT). Transient absorption spectra were determined with the use of a monitoring beam at right angles to the excitation pulse, again as previously described.[37,38] A standard Polaroid film was used to verify the polarization of the emissions. The transmission of crossed Polaroid films varied with wavelength, but was a maximum of 0.4%.

Results

Absorption Spectra. The results of a series of measurements using the micrometer cell are shown in Figure 1. The features of interest are the lack of concentration dependence of the peak at 280 nm and the strongly non-Beer's law behavior of the long-wavelength tail, which grows to a strong shoulder in 0.635 M $K_2Pt(CN)_4$. The extinction coefficients in the figure are apparent ones, based on the Pt(II) formality, C. If the long-wavelength feature is due to a single oligomer formed according to the equilibrium

$$n\mathrm{Pt(CN)_4^{2-}} \overset{K}{\rightleftharpoons} [\mathrm{Pt(CN)_4^{2-}}]_n \tag{1}$$

then if most of the complex is monomer, the apparent extinction coefficient of the long-wavelength region should be given by $\epsilon_{app} = \epsilon_n K C^{n-1}$ where ϵ_n is the extinction coefficient of the oligomer. As shown in Figure 2, a satisfactory fit was obtained with $n - 1 = 2$ or $n = 3$, so that trimer formation is indicated.

The apparent extinction coefficients at 366 nm for a 0.236 M solution obey a linear Arrhenius plot, with a slope corresponding to a ΔH for reaction 1 of −7.2 kcal mol⁻¹. Although the reaction was not studied in detail, increasing ionic strength led to increasing ϵ_{app}, interpreted as increasing association, as might be expected.

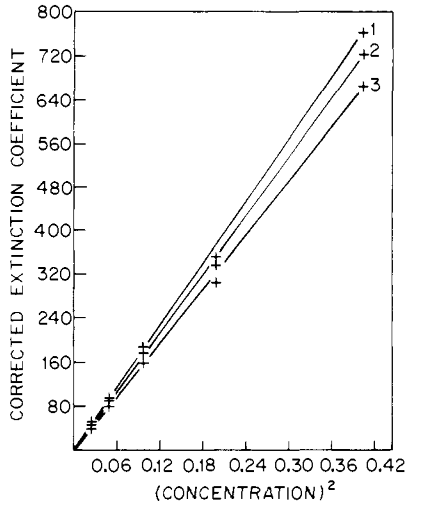

Figure 2. Relationship between apparent extinction coefficient (correction for a small estimated monomer contribution) and C^2, 25–27 °C. Wavelengths: 1, 295 nm; 2, 297.5 nm; 3, 300 nm.

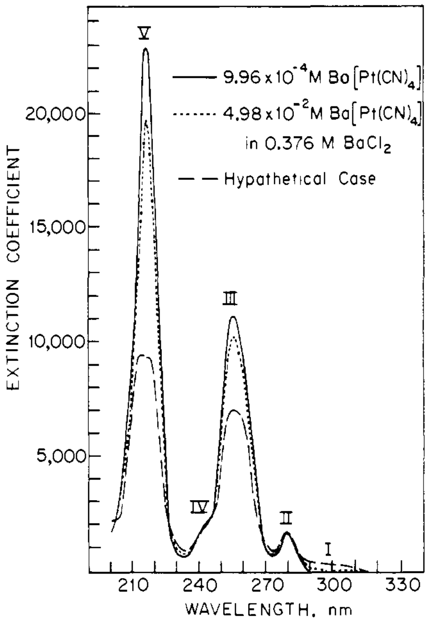

Figure 3. Disappearance of monomer charge-transfer bands with increasing concentration and ionic strength: (—) 9.96×10^{-4} M $BaPt(CN)_4$; (···) 4.98×10^{-2} M $BaPt(CN)_4$ in 0.376 M $BaCl_2$; (- - -) estimated dimer absorption spectrum.

It was of interest to look for non-Beer's law behavior in the rest of the absorption spectrum. The results are shown in Figure 3. $Ba[Pt(CN)_4]$ was used because qualitative indications were that K for association was larger with Ba^{2+} as the counterion that with K^+. It was thus possible to work with lower concentrations, a necessity to avoid reaching the limit of the micrometer cell. That is, the intensity of the 216 peak is so large that a Beer's law study would have been inaccurate if the potassium salt had been used. As may be seen in the figure, the intensity of both the 216-nm and 255-nm peaks is reduced at higher concentrations, while that of the 280-nm peak is unaffected. The fractional reductions in the former peaks are not the same, indicating that oligomer absorption does not go to zero or that more than one component is present, only one of which is concentration sensitive. The latter is the more likely possibility; Marsh and Miller[30] do conclude that both features should be split into pairs of Gaussian components. The actual data are as follows. For the dilute solution ϵ_{app} is 2.30×10^4 M⁻¹ cm⁻¹ at 216 nm and 1.19×10^4 M⁻¹ cm⁻¹ at 255 nm, while for the concentrated solution the values are 1.96×10^4 and 1.02×10^4, M⁻¹ cm⁻¹, respectively. The dashed curve in the figure indicates what the absorption spectrum might be for an oligomer-only solution.

Emission Spectra. The emission shown by aqueous $Pt(CN)_4^{2-}$ is quite complex in its behavior. As illustrated in Figure 4, the spectrum is concentration dependent. The feature around 455–460 nm, labeled II, is barely evident with a 0.56 M solution, strengthens

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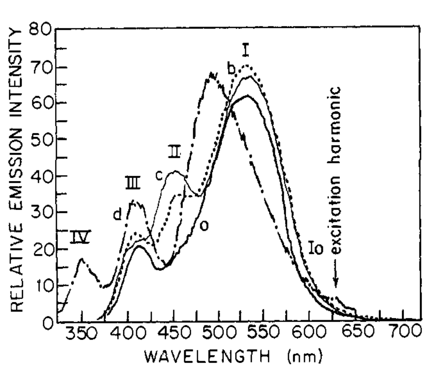

Figure 4. Emission spectra of aqueous $K_2Pt(CN)_4$ at 26 °C. (a) 0.56 M, 366-nm excitation; (b) 0.793 M, 366-nm excitation; (c) 0.793 M in 0.783 M KCl, 366-nm excitation; (d) 0.0996 M, 313-nm excitation, Ba^{2+} salt.

with 0.70 M solution, and becomes an actual maximum if the ionic strength is raised.[39] The emission is evidently associated with some oligomer. Feature IV, at 350 nm, is observed with 313-nm excitation; its concentration dependence was not studied because of absorption problems. Note that a 313-nm excitation, feature III, at 410 nm, is unchanged from 366-nm excitation, while feature II is essentially absent, presumably because of the low concentration used. Feature I is shifted to shorter wavelengths relative to its position with 366-nm excitation. Finally, there is an indication of a shoulder on the long-wavelength side of feature I, roughly in the 550-nm region.

Some of the above observations have been reported previously. Khvostikov[10] saw an emission at 525 nm with a resolved shoulder at 555 nm, and Rossiello and Furlani[16] found emissions at 410 and 552 nm. The two sets of authors thus cover our features Ia, I, and III. Features II and IV appear to be newly observed in this work.

In a more quantitative investigation of concentration dependence, we find that feature III at 410 nm (with 366-nm excitation) varies linearly with C^4, with zero intercept, over the range 0.392–0.560 M. This behavior contrasts with the conclusion of Rossiello and Furlani that the 410-nm emission is due to dimer formation. These authors, however, do not give their basis for this conclusion.[40] The peak maximum in the 480–530-nm region shifts with concentration (note Figure 13 of ref 38), unlike the case with the 410-nm peak. The peak intensity showed no simple power dependence of formal concentration, however; log–log plots were curved, of slope around 5.

As in the case of feature I of the absorption spectrum, the emission intensities were temperature dependent, decreasing with increasing temperature, as would be expected if they were due to one or another oligomer. The 410-nm emission (366-nm excitation) gave a slightly curved Arrhenius plot for data for the range of 2–25 °C (about 0.24 M solutions), of average slope corresponding to a heat of oligomer formation of -9.0 kcal mol^{-1}. The data for emission in the 500–530-nm region were also temperature dependent, again giving a slightly curved Arrhenius plot, of slope corresponding to a heat of oligomer formation of about -14 kcal mol^{-1}, or significantly larger.

Excitation spectra were also obtained. First, as evident in Figure 4, the emission spectra are excitation wavelength dependent.

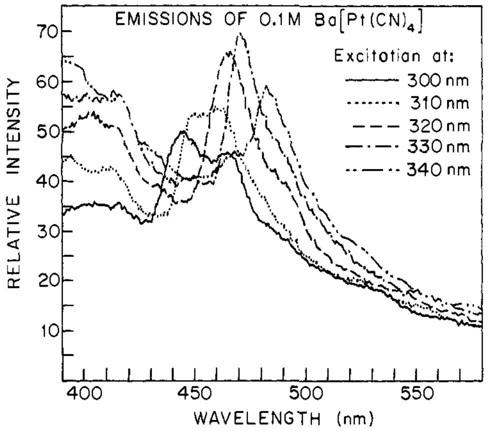

Figure 5. Excitation-wavelength dependence of the phosphorescence band, 0.1 M $BaPt(CN)_4$.

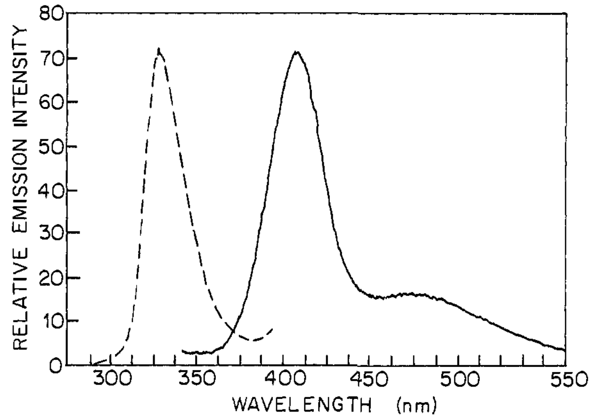

Figure 6. Excitation and emission spectra for 0.40 M $K_2Pt(CN)_4$ under conditions of complete phosphorescence quenching (0.01 M KNO_2): (---), excitation spectrum; (—), emission spectrum for 328-nm excitation.

Table I. Average Lifetime (±5%) at 510 nm of Aqueous, Argon-Deoxygenated Solutions of the Barium and Potassium Tetracyanoplatinites

salt	concn, M	temp, °C	lifetime, ns
K^+	0.44	20–22	660
K^+	0.40	20–22	642
K^+	0.37	20–22	642
K^+	0.34	20–22	623
K^+	0.29	20–22	595
K^+	0.26	20–22	531
Ba^{2+}	0.109	18	724
Ba^{2+}	0.099	20	539
Ba^{2+}	0.091	~20	447

Figure 5 illustrates this effect in more detail.[41] Clearly, several components are present. There is one at 445 nm, strongest with 300-nm excitation, another at about 465 nm, strongest with 320–330-nm excitation, and another in the region of 485–490 nm, strongest with 340-nm excitation. A weak feature is seen at around 525 nm.

Figure 6 shows a direct excitation spectrum taken under special conditions. The longer wavelength emissions have a relatively long lifetime (see further below) and, as to be detailed in another paper, are quenchable by dissolved oxygen and by NO_2^- ion. These emissions will be labeled as phosphorescences; the remaining ones will be called fluorescences. Figure 6 shows the excitation spectrum of the 410-nm feature (closer to 408 nm now) under complete phosphorescence quenching conditions. The excitation centers at 335 nm. The solid line in the figure shows the un-

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(39) It might be noted that literature reports have been that $Pt(CN)_4^{2-}$ solutions luminesce only at concentrations near saturation, with speculation that it was due to seed crystals at the onset of precipitation. We took great care that our solutions were not supersaturated, that is, that no microcrystalline material was present. As one approach, we confirmed that a 0.70 M solution should begin to show precipitate formation on cooling to 15 °C.[34] The solution was then warmed back to 26 °C, cooled to 19 °C, and filtered through a 0.025-μm Millipore filter before finally returning to 26 °C for the measurement.

(40) The difference in implied concentration dependence could have arisen if these authors worked under conditions of low optical density and in the region of our trimer absorption, but without realizing that in making an absorption correction, they were taking out part of the power dependence of the emission on the total or formal concentration.

(41) The considerable scatter evident in these data is due to the use of a 45° slant-faced spectrofluorimeter cell. This greatly reduced the self-absorption problem but led to increased scatter.

Table II. Assignment of Absorption and Emission Features

absorption	emission	wavelength, nm	wavenumber, $\times 10^3$ cm^{-1}	assignment	comments
V		216	46.2	monomer singlet-singlet abs	two components, one of d_{z^2} parentage
	(VI)	(233)	(42.9)	monomer fluorescence	extrapolated from crystal data on R^{-3} dependence
IV		243	41.1	monomer singlet-triplet abs	
III		255	39.2	monomer singlet-triplet abs	two components, one of d_{z^2} parentage
	(V)	(271)	(36.8)	monomer phosphorescence	extrapolated from crystal data on R^{-3} dependence
II		280	35.8	monomer singlet-triplet abs	(does not lead to emission)
I		295-300	33.7	trimer abs	from non-Beer's law behavior
Ia		335	29.8	tetramer abs	excitation peak of 410-nm emission
	IV	352	28.4	trimer fluorescence	5.3×10^3 cm^{-1} Stokes' shift
Ib		370	27.0	pentamer abs	
	III	410	24.4	tetramer fluorescence	5.4×10^3 cm^{-1} Stokes' shift
	II	445	22.5	trimer phosphorescence	excitation around 300 nm
	II	460	21.7	pentamer fluorescence	5.3×10^3 cm^{-1} Stokes' shift
	I	485	20.6	tetramer phosphorescence	excitation around 340 nm
	I, Ia	525-560		*n*-mer phosphorescence	
ESA		640	15.6	excited-state abs	
ESA		720	13.9	excited-state abs	

quenched portion of the emission; we regard the shoulder around 460 nm as real; that is, we consider it to be a fluorescence component and not due to incompletely quenched phosphorescence.

Emission Lifetimes and Time-Resolved Spectra. Table I summarizes the average measured phosphorescence lifetimes for a series of concentrations and for both the potassium and the barium salts. Note that in each case a single lifetime, τ, is observed. There is a clear concentration effect, the lifetime increasing with increasing concentration. There is no significant variation in τ with emission wavelength, however. Thus for the 0.26 M solution of the potassium salt, τ was 548 ns at 560 nm and 555 ns at 575 nm (353-nm excitation). This lack of wavelength dependence contrasts with the data of Tkachuk and Tolstoi,[13] which showed τ values in 77-K frozen solutions that ranged from 30 ns at 470 nm to 1.2 μs at 520 nm. However, our emissions labeled II and III in Figure 4 were prompt at room temperature (<9 ns). One or another of our observed emissions may correspond to their 30-ns emission at 77 K.

Time-resolved emission spectra are shown in Figure 14 of ref 38. One spectrum, collected during the first approximately 30 ns following the 353-nm excitation pulse (with 0.445 M $K_2Pt(CN)_4$), shows two peaks, corresponding to features II and III of Figures 4 and 6. A second spectrum, taken with a 200-ns delay, clearly shows only feature I as a broad emission centered at 520 nm with a possible short-wavelength shoulder.

Polarization. Some preliminary experiments were carried out to determine the polarization of the emissions, as given by

$$P = (I_z - I_{xy})/(I_z + I_{xy}) \qquad (2)$$

Here, z is the direction of polarization of the exciting pulse. The observed P for 0.0991 M $Ba[Pt(CN)_4]$ was 0.54 for 410-nm emission, 0.49 for 440-nm emissions, and 0.275 for phorescent emission at 512 nm. The general implication of the results (see ref 10,[42]) is that the fluorescence lifetime is shorter than the diffusional rotation time, while the phosphorescence lifetime, τ, is comparable to it, around 500–600 ns.

Excited-State Absorption. Several transient absorptions were observed. The first two have absorption maxima at 640 and 720 nm, as shown in Figure 7, and disappeared with the phosphorescence lifetime. The spectra were taken by sequential measurements at successive wavelengths. A third feature has a band maximum around 825 nm, and a 2-μs lifetime. This last was unaffected by dissolved oxygen sufficient to quench the phosphorescence. We suspect this absorption to be due to a chemical intermediate rather than to an excited state. If it is an intermediate, it is unstable and appears to return to starting complex since the PMT trace eventually returned to baseline. Thus any photochemistry in aqueous $K_2[Pt(CN)_4]$ solutions is reversible on this time scale (in the absence of redox quencher).

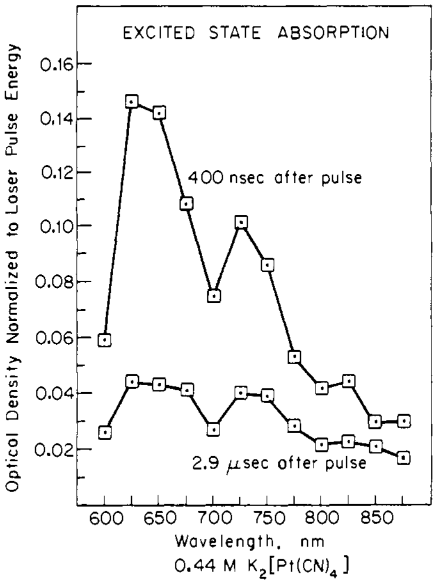

Figure 7. Excited-state and chemical-transient absorption spectra: (upper curve) 400 ns after pulse; (lower curve) 2.9 μs after pulse.

Discussion

Our qualitative conclusions are summmarized in the assignment table, Table II. The importance of the electronic structure of $Pt(CN)_4^{2-}$ monomer is attested by the existence of some 12 previous attempts at excited-state assignments[22,23] (see ref 30 in particular). Our contribution to the situation is in the information of Figure 3, which shows, for the first time, that the bands we label V and III do not obey Beer's law, but partially disappear with increasing concentration. Referring to March and Miller,[30] our bands V and III deconvolute into two Gaussian components each, and our observation is essentially that one of the components of each band disappears (or shifts to some hidden position) on oligomerization. Of the six low-lying spin–orbit allowed transitions, only two are of d_{z^2} parentage, ${}^1A_{1g} \rightarrow A_{2u}({}^1A_{2u})$ and ${}^1A_{1g} \rightarrow E_u({}^3A_{2u})$. These should be the concentration-sensitive transitions. The reason is that oligomerization should strongly perturbe orbitals of d_{z^2} parentage, through a Davydov shift to lower energy as Pt–Pt interaction occurs, while orbitals of other parentage should be relatively unaffected.

We can argue from the data of Yersin and Gliemann[3] that the $A_{2u}({}^1A_{2u})$ state lies at 45.5×10^3 cm^{-1} and the $E_u({}^3A_{2u})$ one, at 39.4×10^3 cm^{-1} above the ground state, in good correspondence with Figure 3. These authors find, in studying crystalline salts of $Pt(CN)_4^{2-}$, that the z-polarized absorption fits the equation $E = 45.5 - (8 \times 10^5)R^{-3}$ (R in Å), which, in the monomer limit of $R \rightarrow \infty$, extrapolates to just 45.5×10^3 cm^{-1}. Next, the fluorescence fits the equation $E = 42.9 - (8 \times 10^5)R^{-3}$, corre-

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Table III. Spectroscopic Assignments of the Absorption Bands

band Figure 3	designation ref 30	wavelength, nm	wavenumber, cm^{-1} × 10^3	transition, $^1A_{1g}$ to	polarization	parentage
V	6	213	46.8	$E_u(^1E_u)$	*xy*	$e_g(xz,yz)$
	5	216	46.2	$A_{2u}(^1A_{2u})$	*z*	$a_{1g}(z^2)$
IV	4	243	41.1	$E_u(^3B_{1u})$	both	$b_{2g}(xy)$
III	3	252	39.6	$E_u(^3A_{2u})$	*xy*	$a_{1g}(z^2)$
	2	258	38.7	$A_{2u}(^3E_u)$	*z*	$e_g(xz,yz)$
II	1	280	35.8	$E_u(^3E_u)$	*xy*	$e_g(xz,yz)$

sponding to a Stokes' shift of 2.6×10^3 cm^{-1}. The phosphorescence then fitted the equation $E = 36.8 - (6.3 \times 10^5)R^{-3}$, and if we add the same Stokes' shift, the monomer limit gives 39.4×10^3 cm^{-1} for the triplet absorption.

With the above assignments pinned, we can make the remaining ones for the monomer, as listed in Table III. These are consistent with the available data, including the CD,[33] MCD,[24,26] and polarization[32] results.

The assignments involving oligomers are necessarily qualitative as to state designation. First, we will take as acceptable that if a given feature depends on the *n*th power of concentration, then the corresponding *n*-mer is implicated. This stipulation neglects the possibly significant perturbation of ionic strength and ion-association effects at the relatively high concentrations involved. These effects, qualitatively, are in the direction of producing more association than that corresponding to *n*; that is, the apparent *n* value will be too large. However, comparison of curves b and c of Figure 4 suggests that while ionic strength has an effect, it is not so large as to change the nearest integral value of *n*. This conclusion also applies to absorption feature I.

First, we see no absorption attributable to dimer. Judging from the findings with rhodium phosphine, arsine, carbonyl, or isocyanide complexes, dimer Davydov shifts are of the order of 6.5×10^3 cm^{-1}.[43,44] If this were the case here, dimer absorption would be hidden under our bands III and II. The first oligomer we identify is the trimer, assigned from the concentration dependence of the intensity of band I. The dependence of ϵ_{app} on C^2 holds essentially over the whole band, so that the relative broadness of this band appears not to be due to absorption contributions by higher oligomers. Possibly the broadness reflects conformational looseness in the trimer. We assign the 353-nm fluorescence, feature IV of Figure 4, as trimer fluorescence, taking as reasonable the consequent Stokes' shift of 5.3×10^3 cm^{-1}. It was not possible to verify the concentration dependence of the intensity of this emission because of self-absorption problems.

The 409-nm emission, unquenchable and hence also a fluorescence, has a concentration dependence of intensity, indicating the source to be a tetramer. Its excitation peak is around 330–340 nm (Figure 5), and applying the same Stokes' shift as found above, we place the tetramer absorption at 340 nm. The next fluorescence peak is around 460 nm, as seen in Figure 6. We take this to be pentamer fluorescence and, again applying the same Stokes' shift, estimate the pentamer absorption to be at 370 nm. Yet another fluorescence is indicated in Figure 6, at around 530 nm. At this point, the species is best designated as some *n*-mer.

Turning to the long-lived, quenchable emission, we find that Figure 5 indicates a component around 445 nm; the excitation is around 300 nm, suggesting that the emission is trimer phosphorescence. The 485-nm peak, Figure 4d, should be assigned as tetramer phosphorescence, but the concentration dependence of intensity in this wavelength region suggests a higher *n*-mer, and identification has at this point become uncertain.

While we can tentatively identify various phosphorescences, it should be recalled that they show a single exponential decay over the wavelength region involved. Very likely, excitation energy transfer processes couple the various oligomers. The observed lifetime is thus a complex function of the various concentrations and energy-transfer rate constants. Consistent with this supposition is the observation that the lifetime is concentration dependent (Table I).

The two excited-state absorption features involve transition energies large enough that we are probably dealing with other than LUMO states. Actual assignment seems not possible.

A final consideration is the following. The literature gives a lower limit for the Davydov shift at the point of precipitation of d^8 square-planar complexes as about 16×10^3 cm^{-1}. The combination of Stokes' shift and singlet–triplet splitting in our case runs between 8.6 and 11.1×10^3 cm^{-1}. There could thus be a total of some 27×10^3 cm^{-1} between the monomer singlet–singlet absorption and the phosphorescence at the oligomerization or precipitation limit. The energy difference between the 560-nm phosphorescence and the 216-nm absorption is 28.3×10^3 cm^{-1}, in reasonable agreement with the estimate.

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Registry No. $K_2Pt(CN)_4$, 562-76-5; $BaPt(CN)_4$, 562-81-2.

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