form a diastereoisomer with a resolving agent. Such a complex was resolved by the use of a chromatographic column packed with an asymmetric compound. The compounds usually employed are cellulose, lactose, and Sephadex.[11-13] The reported optical purities, however, were relatively low, in the range of 5–20%, in spite of modifications tried for improvement. For example, a column was modified with an optically active molecule[13] or an optically active ion was added in an eluting solvent.[14]

In contrast to the reports cited above, the present chromatography on a Δ-Ni(phen)$_3^{2+}$–montmorillonite column demonstrated remarkably high efficiency in resolving neutral Co(III) complexes. The percentage resolutions attained in resolving Co(acac)$_3$, 73 and 89% for the Λ and Δ isomers, respectively, were about 4 times better than the best value reported in the literature (19.6%).[13] The results are surprising, when one compares the short length of our column (1 cm) with that of the others (300–100 cm). Another advantage in the present method is that the resolution was performed by elution with pure solvents. Accordingly, one gets rid of the difficulty of removing undesired additives from an eluant.

Tris(1,10-phenanthroline)iron(II) and tris(2,2′-bipyridyl)copper(II) are suggested to be adsorbed over a clay surface with their C_3 axes perpendicular from electric dichroism[15] and ESR measurements,[16] respectively. Δ-Ni(phen)$_3^{2+}$ may also be adsorbed on the present clay column in the same manner. There are two possible sites at which a cobalt(III) complex interacts with Δ-Ni(phen)$_3^{2+}$ on the montmorillonite clay, which has a well-known layered structure.[17,18] According to a molecular model, at an adjacent site of the Ni(phen)$_3^{2+}$ a Λ isomer is more closely stacked with the Ni(II) complex than its counterpart, while at a site over the head of the Ni(II) complex a Δ isomer fits more closely. Then, it is likely that Co(acac)(gly)$_2$ was resolved at the former site and Co(acac)$_3$ was on the latter one.

Registry No. Co(acac)$_2$(gly), 17819-63-5; Co(acac)(gly)$_2$, 17872-14-9; *mer*-Co(gly)$_3$, 30364-77-3; Δ-Ni(phen)$_3^{2+}$, 23385-79-7; montmorillonite, 1318-93-0.

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Emission Quenching and Photochemistry of Aqueous Pt(CN)$_4^{2-}$

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In a preceding paper (*J. Am. Chem. Soc.* **1982**, *104*, 3596) the emission around 525 nm from concentrated aqueous solutions of Pt(CN)$_4^{2-}$ salts is found to be due to various oligomers, probably a tetramer and higher *n*-mers. We report here that this phosphorescence is efficiently quenched by O$_2$ and NO$_2^-$ and possibly by other excitation energy transfer quenchers. A number of reducible species are also good quenchers, and the effect is attributed to reduction by oligomer excited states. In the particular case of Co(NH$_3$)$_6^{3+}$, concomitant Co(II) production occurs with a quantum yield of 0.62 at room temperature. Although the oligomer excited states should be able to reduce water, no photoproduction of hydrogen is observed.

Introduction

We have reported on the photophysics of aqueous K$_2$Pt(CN)$_4$ and BaPt(CN)$_4$ solutions, along with a summary of the literature background, including that regarding the crystalline salts.[2] The compounds show emission both *in the solution and* in the solid state. In the latter case, the emission shows components attributable to intramolecular processes associated with the chainlike stacking of Pt(CN)$_4^{2-}$ units. In the case of concentrated solutions, we reported evidence that there is considerable association into dimer, trimer, and higher oligomers, each with a characteristic absorption and emission behavior, and some tentative excited-state assignments were made. Of particular interest here is the phosphorescence of aqueous Pt(CN)$_4^{2-}$ in 0.2–0.4 M solution. The emission is at 510–530 nm, with a lifetime in the range of 500–700 ns, both τ and $\lambda_{\max}$ increasing with increasing concentration. As a matter of brevity, we will refer to this emission as being at 525 nm. This emission band is attributed to phosphorescence from pentamer and higher *n*-mer units, possibly stacked in a manner similar to that in the crystalline state. BaPt(CN)$_4$ is more associated than is K$_2$Pt(CN)$_4$ or, conversely, a given degree of association occurs at a lower concentration. The typical emission maximum for phosphorescence is now at 490 nm.

It has been reported that dilute (10^{-2}–10^{-4} M) aqueous Pt(CN)$_4^{2-}$ shows no photochemistry to 254-nm irradiation.[3] The purpose of the present investigation was to determine whether excited states of the oligomers present at high concentrations are reactive either toward net photochemistry or with respect to potential emission quenchers. As to photochemistry, several possibilities were a priori plausible. A number of cyano complexes have been found to show photoelectron production,[4,5] and this was an attractive possibility here. Partially oxidized Pt(CN)$_4^{2-}$ is well-known in the solid state,[6,7] an important stoichiometry being K$_2$Pt(CN)$_4$·0.3Br,

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which corresponds to one Pt(IV) per six platinum units (the Br^- is not coordinated to any Pt). Some of the higher oligomers present in concentrated solution might thus be able to show oxidation via photoelectron ejection. Alternatively, cyano complexes also show photosubstitution, as do also Pt(II) square-planar complexes generally.[4] Thus photoaquation of aqueous $Pt(CN)_4^{2-}$ oligomers was another distinct possibility. Last, it has become clear that excited states of coordination compounds can be both good oxidizing and good reducing agents.[8-10] There was a possibility, then, of reactive as well as of electron-transfer quenching of oligomer excited states.

Experimental Section

Materials. The preparation of $K_2Pt(CN)_4$ and $BaPt(CN)_4$ was as previously described. Compounds used as potential quenchers were generally of reagent grade. $EuCl_3$ (Alfa Ventron) was recrystallized, however, to remove impurities, as was paraquat (*N,N'*-dimethyl-4,4'-bipyridinium iodide), prepared by the method of Meyer et al.[11] $Co(en)_3Cl_3$ (en denotes ethylenediamine) and $Co(NH_3)_6Cl_3$ were recrystallized from earlier preparations[12,13] and checked for spectral purity. $KAu(CN)_4$ and $K_2Ni(CN)_4$ were prepared by standard procedures in earlier work.[14] The EDTA (ethylenediaminetetraacetate) complexes of Fe(III), Eu(III), Th(IV), and Cu(II) were prepared as 1:1 adducts of Na_2EDTA and the corresponding metal chloride or nitrate. These EDTA complexes were not analyzed for stoichiometry as their use was for qualitative purposes only. Solutions of the $Fe^{III}EDTA$ complex were made basic before use since the $Pt(CN)_4^{2-}$ solutions are alkaline.

The mixed-valence compound $K_2Pt(CN)_4 \cdot 0.3Br$ was crystallized from aqueous $K_2Pt(CN)_4$ that had been oxidized by the indicated stoichiometric amount of Br_2.[15]

Procedures for the Quenching Experiments. The same laser equipment as before[2,12,16] was used and likewise the equipment for absorption and spectrofluorimetric emission spectra.[2]

For the conservation of platinum, most of the quenching experiments were made spectrofluorometrically, with the use of a 4-mm path length, 6-mm diameter round Pyrex cell of 0.5 cm^3 capacity, usually containing 0.4 M $K_2Pt(CN)_4$. Excitation was at 366 nm. If a single quencher concentration was used, this was around 0.01 M. When $BaPt(CN)_4$ was used, a lower concentration, around 0.1 M, sufficed to give behavior comparable to that of the 0.4 M potassium salt. Excitation was now at 313 nm, to obtain a sufficient absorbance, and a standard 1 × 1 cm quartz cell was used. In both series of experiments, solutions were deaerated just before use by prolonged argon bubbling.

Photolyses. All photolyses were carried out with the use of a 200-W Xe–Hg medium-pressure lamp with an Illumination Industries CH 200 power supply and LH-3510 lamp housing. Wavelength selection was by means of a Janos 5-nm band-pass interference filter, or if a broad-band irradiation was needed, by means of Corning 7-54 and 5-57 glass filters (giving 375-nm irradiation). Infrared radiation was removed by means of a 5-cm water-filled cell, and the irradiated solutions could be thermostated by means of a jacketed cell holder. The cell used was generally a 1 × 1 cm fluorescence cell, and since aqueous $Pt(CN)_4^{2-}$ solutions are highly absorbing at the concentrations and irradiating wavelengths used, the solutions were stirred continuously by inert-gas bubbling.

Cyclic Voltammetry. The cyclic voltammograms were obtained with Princeton Applied Research Corp. equipment consisting of a Model 173 potentiostat-galvanostat and Model 175 universal programmer, and data were recorded by means of a Houston Instruments Omnigraphic 2000 recorder. The typical solution was 0.15 M in $Na_2Pt(CN)_4$ and 0.85 M in $NaClO_4$ (as supporting electrolyte), and the experiments were made with a stationary platinum electrode and at room temperature.

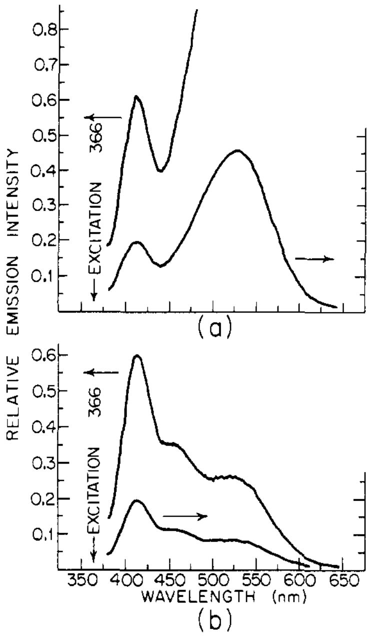

Figure 1. Emission spectrum of (a) 0.397 M $K_2Pt(CN)_4$ and (b) the same solution but with added 0.0200 M KNO_2. Excitation was at 366 nm in both cases.

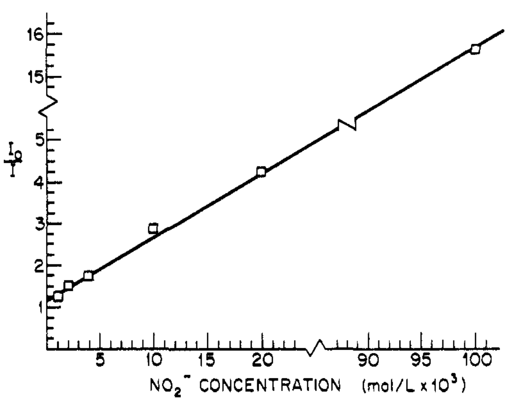

Figure 2. Stern–Volmer plot of NO_2^- ion quenching of the 525-nm phosphorescence of 0.397 M aqueous $K_2Pt(CN)_4$ (room temperature).

Results

Phosphorescence Quenching. The emission in the 450–600-nm region is relatively long-lived, as reported in the preceding paper.[2] We are concerned here with the effect of various potential quenchers on this emission. It was monitored spectrofluorimetrically in all but the case of O_2 quenching, and the quantitative degree of phosphorescence quenching was determined from the change, if any, in the intensity of the 525-nm emission maximum, which we have assigned as due to pentamer (plus higher oligomers).[2]

An immediate observation was that of oxygen quenching; all other quenching experiments were therefore performed with deaerated solutions. Figure 1 shows the quenching by NO_2^- ion. Note that the 410-nm fluorescence is unaffected and, further, that on nearly complete quenching of the 525-nm phosphorescence, a previously hidden fluorescence appears at 450 nm as a weak maximum (or strong shoulder); this is attributed to pentamer fluorescence.[2] The simple Stern–Volmer equation

$$\phi_e^0/\phi_e = 1 + K_{SV}(Q) \qquad (1)$$

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Table I. Quenching of Aqueous $[Pt(CN)_4]_n{}^{2n-}$ Phosphorescence

quencher (Q)	[Q]	[Pt]	anion	temp, °C	τ^0, ns	$k_q(\text{app})^a$
$K_2S_2O_8$	9.19×10^{-3}	0.40	K	24	642	2.2×10^8
KIO_3	9.14×10^{-3}	0.40	K	24	642	1.7×10^8 (1.4×10^8)
$K_2Ni(CN)_4$	4.6×10^{-2}	0.40	K	22.5	642	3.2×10^8 (1.3×10^8)
$Cu^{II}EDTA^b$	1.83×10^{-2}	0.40	K	24-25	642	3.9×10^8 (3.3×10^8)
$[Co^{III}(en)_3]Cl_3$	8.1×10^{-3}	0.40	K	24-25	642	1.3×10^9 (1.1×10^9)
$Eu^{III}Cl_3$	4.01×10^{-3}, 6.015×10^{-3}	0.0915	Ba	24	447	2.1×10^9
$KNO_2{}^c$		0.40	K	20.5	642	2.3×10^8
$KNO_2{}^d$		0.096	Ba	21	539	4.0×10^8 (3.1×10^8)
$Fe^{III}EDTA$ (basic)^b	$\approx 3.7 \times 10^{-3}$	0.40	K	24	642	1.7×10^9 (7.2×10^8)
$Fe^{III}EDTA^b$	$\approx 9.15 \times 10^{-4}$	0.0915	Ba	24	447	(1.8×10^9)
ferricyanide	8.33×10^{-3}	0.44	K	RT	660	(5.0×10^7)
paraquat	3.64×10^{-3}	0.40	K	25	642	$1.2 \times 10^9)$
paraquat^e		0.0991	Ba	23.5	539	(5.6×10^9)
oxygen	2.8×10^{-4}, 1.4×10^{-3}	0.33	K	RT	642	$3.0 \times 10^{9\,f}$
oxygen				29	642	1.7×10^9

[a] Numbers in parentheses are values corrected for absorption by the quencher. This was done by normalizing the fluorescence intensity of the quenched spectrum to that of the solution without quencher. [b] The actual structure of the EDTA complex was not determined. For cases *c*, *d*, and *e*, k_g's were determined from Stern–Volmer plots. [c] Six concentrations over the range 1×10^{-3} to 0.1 M. [d] Four concentrations over the range 1.4×10^{-2} to 5.5×10^{-2} M. [e] From points at 5.7×10^{-5} M and 1.14×10^{-4} M. [f] From lifetime quenching.

was obeyed (see Figure 2), where ϕ_e and $\phi_e{}^0$ denote emission yield in the presence and absence of quencher, respectively, taken to be proportional to the intensity of the phosphorescence maximum, and $K_{SV} = k_q\tau^0$, where k_q is the biomolecular quenching rate constant and τ^0 is the emission lifetime in the absence of quencher. From the slope in Figure 2 and the τ^0 value of 642 ns,[2] we find k_q to be 2.3×10^8 M^{-1} s^{-1}. This is smaller than the diffusion-limited value, perhaps because of the Coulomb barrier for encounters between $NO_2{}^-$ and highly negatively charged oligomers.

The relatively detailed study made with $NO_2{}^-$ ion was not considered necessary for the remaining survey of potential quenching. A reason is that the $Pt(CN)_4{}^{2-}$ solutions used were concentrated and contained a complex mixture of oligomers whose concentration might be affected by the addition of quencher species, particularly if the quencher were ionic, so that k_q would not in general have a simple meaning. The remaining results, with the exception of O_2 as quencher, are therefore reported in terms of $k_q(\text{app}) = [(I_e{}^0/I_e) - 1]/\tau^0(Q)$, with use of a single quencher concentration, I_e denoting intensity at the 525-nm emission maximum. Table I lists a number of compounds that showed easily measurable quenching with Q values in the range of 10^{-3}–10^{-2} M. The values of k_q(app) are around 10^8 M^{-1} s^{-1} for neutral and negatively charged species and around 10^9 M^{-1} s^{-1} for cationic species and for O_2. In the case of O_2, lifetime quenching, that is, τ^0/τ, was determined for two concentrations. The two lifetime-quenching points defined a line with the required 1.0 intercept, and the k_q value from these data is probably more reliable than the smaller value from the higher temperature determination of emission intensity quenching.

As an extension of the survey, a number of additional compounds were tested qualitatively as to whether or not significant quenching occurred with quencher concentrations around 0.01 M. Additional quenching species are the following, the number in parentheses being the approximate ratio of $I_e{}^0/I_e$ for the species to $I_e{}^0/I_e$ for $Co(en)_3{}^{3+}$ at about the same concentration: $Hg(CN)_2$ (17), $HgCl_2$ (17), $KAu(CN)_4$ (5), $[Co(NH_3)_6]Cl_3$ (1.2), *o*-phenanthroline (0.9), and 2,2′-bipyridine (0.5). There was noticeable quenching by the $Fe^{III}EDTA$ complex and by $K_3Fe(CN)_6$. Finally, paraquat quenching was determined for several concentrations, but the Stern–Volmer plot was curved, probably due to absorption of the exciting light by the quencher. The first two points, for around 10^{-4} M quencher, gave a line with the required intercept of unity and a slope corresponding to a k_q value of 8.9×10^9 M^{-1} s^{-1}. Such quencher absorption was often a complication, and this situation serves to reinforce the point that the above results are of value for qualitative but not for quantitative interpretation (with the exception of those for $NO_2{}^-$ and O_2, which should be free of complications).

Compounds showing no measurable quenching at concentrations around 0.01 M are $K_3Co(CN)_6$, $K_3Co(C_2O_4)_3$, KSCN, KNO_3, NH_4NO_3, $KAg(CN)_2$, Th(IV), EDTA, CH_3CN, $NaHSO_3$, $K_2S_2O_5$, NaN_3, NH_3VO_3, and N_2O. The acetate complex of $UO_2{}^{2+}$ gave indeterminate results because of its own emission and likewise for $[Ru(bpy)_3]Cl_2$, bpy denoting 2,2′-bipyridine. $[Ru(bpy)_3]Cl_3$ could not be studied since it was reduced by the $Pt(CN)_4{}^{2-}$ solution. KI, KCl, KCN, and $BaCl_2$ increased the emission intensity somewhat (10–20%) at high concentrations, probably because of increased oligomer concentration at increased ionic strength.

Photochemistry. Oligomers of $Pt(CN)_4{}^{2-}$ might show photoelectron production, and this possibility was tested by laser pulse irradiation of 0.4 M $K_2Pt(CN)_4$ using the 530-nm pulse from the Nd laser.[12,16] The hydrated electron absorbs at 690 nm,[4,18] and indeed, we observed a transient absorption at this wavelength. It was not quenched, however, on saturation of the solution with N_2O, a known $e_{aq}{}^-$ scavenger,[4] and the absorption proved to be merely the tail of an excited-state absorption whose maximum is at 640 nm.[2] We concluded that no detectable photoelectron production occurs. Either photoelectron production or photoreduction of solvent water should lead to H_2 formation and oxidized complex. No gas evolution nor any spectral changes occurred on irradiation leading to about 0.01 einstein L^{-1} of absorbed light quanta. (Spectral change, however, was not a sensitive indicator of photochem-

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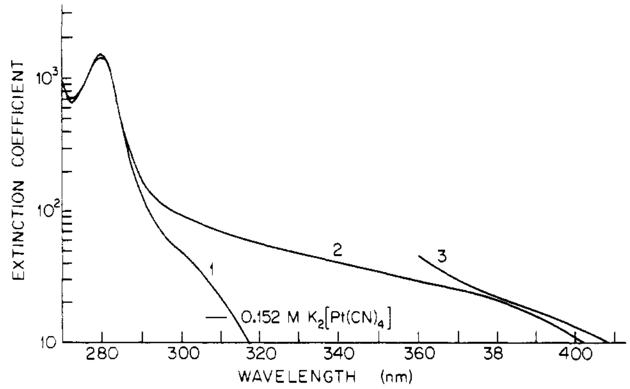

Figure 3. Spectroscopic evidence for partially oxidized tetracyanoplatinate photoproduct: curve 1, 0.152 M $K_2Pt(CN)_4$; curve 2, 0.0984 M $K_2[Pt(CN)_4Br_{0.3}]$; curve 3, difference spectrum between initial $K_2Pt(CN)_4$ plus 0.010 M $Co(NH_3)_6Cl_3$ and solution after photolysis (corrected for loss of $Co(NH_3)_6^{3+}$).

istry because of the necessarily high concentration of $Pt(CN)_4^{2-}$ used.)

Other possible types of excited-state processes are those of energy and electron transfer to some acceptor species. The decomposition of Co(III) ammine is known to be sensitized by organic triplet excited states.[18] With this in mind, a solution 0.4 M in $K_2Pt(CN)_4$ and 0.01 M in $Co(NH_3)_6^{3+}$ was irradiated at 313 nm, and indeed, there was a rapid disappearance of the cobalt complex. The absorbance of the latter at 313 nm is negligible nor is this complex very photosensitive.[4] Under the above conditions, some 90% of the oligomer emission was quenched. Quantitative measurements were not possible, however, because under the necessarily alkaline conditions, precipitation occurred, probably of a mixture of $Co(OH)_2$ and $CoPt(CN)_4$.

To avoid this complication, we repeated the experiments with added EDTA so that the Co(II) formed would remain in solution as the EDTA complex. With 0.009 M NaEDTA, sensitized reduction of $Co(NH_3)_6^{3+}$ to $Co(EDTA)^{2-}$ occurred with a quantum yield of 0.62. It appears that the oxidation product is oxidized $Pt(CN)_4^{2-}$ oligomer. Figure 3 shows the absorption spectrum of separately prepared $K_2Pt(CN)_4Br_{0.3}$, which is similar to that reported by Sallant and Jaklevic[15] and which corresponds to one Pt(IV) per six Pt units. The Co(II) yield of 0.62 thus corresponds to a Pt(IV) yield of 0.31. The above photolysis experiment gave a similar product spectrum, without the added EDTA and after removal of Co(II) product by filtration and correction for loss of $Co(NH_3)_6^{3+}$, as also shown in Figure 2. It was not possible to obtain the product spectrum at shorter wavelengths than shown in the figure because of the swamping absorption by unphotolyzed $Pt(CN)_4^{2-}$, nor was it possible to increase the degree of photolysis since the use of higher $Co(NH_3)_6^{3+}$ concentrations led to precipitation of the salt with $Pt(CN)_4^{2-}$.

Additional, qualitative observations were that irradiation of a solution with sufficient 2,2′-bipyridine concentration for nearly complete quenching of the $Pt(CN)_4^{2-}$ oligomer phosphorescence led to some photoreaction but in low quantum yield. Similarly, there was some photoreaction with added ferricyanide ion, resulting in Prussian blue type precipitation.

Cyclic Voltammetry. Dilute (10^{-4} M) solutions of $Na_2Pt(CN)_4$ show no oxidation wave up to voltages corresponding to oxidation of the platinum electrode (ca. 1.2 V vs. SCE).[19] While the unassociated complex does not easily oxidize, oligomers present in more concentrated solutions do. Figure 4 shows the voltammogram for 0.15 M $Na_2Pt(CN)_4$, which indicates that oxidation occurs from slightly below 0.4 V up to around 0.7 V vs. SHE. This observation is consistent with the report that single crystals of partially oxidized $Pt(CN)_4^{2-}$ can be grown at an electrode immersed in a concentrate solution if applied potential is of the order of 0.7 V. While quantitative interpretation of Figure 4 is not possible, it is clear that concentrated aqueous $Pt(CN)_4^{2-}$ is oxidizable at potentials far below that required for the monomer species.

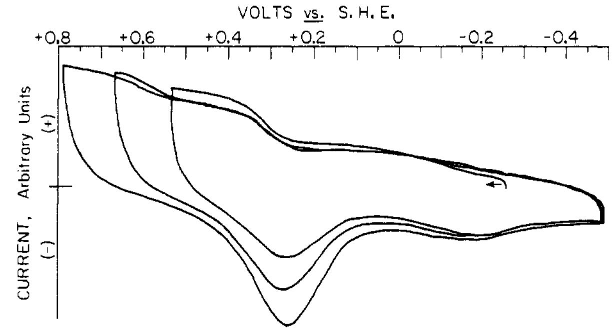

Figure 4. Three cycles of a cyclic voltammogram of a 0.15 M $Na_2Pt(CN)_4$, 0.85 M $NaClO_4$ solution.

Pulsed Infrared Laser Induced Visible Fluorescence (LIE). An earlier investigation reported that molecular emission could be induced in crystalline materials by means of the 1060-nm pulse of the Nd laser.[20] The effect could be due either to the mechanical shock wave of the pulse or to transient high electric fields and is seemingly related to triboluminescence. We find that both $BaPt(CN)_4{\cdot}4H_2O$ and $K_2Pt(CN)_4{\cdot}3H_2O$ show the LIE effect. The LIE spectrum of the barium salt is somewhat narrower than that of the photoexcited emission, while that of the potassium salt is quite similar except for added tailing to the red. The decay of the LIE with the barium salt is nonexponential, the apparent half-life increasing from 200 to 400 ns as the decay proceeded. This time scale could correspond to the rate of crack propagation in a crystal.[21] Finally, there was no effect when an 0.8 M solution of the potassium salt was used.

Discussion

In an appraisal of the pattern of quenchers and nonquenchers, it is to be kept in mind that the phosphorescence involved is from one or more $[Pt(CN)_4]_n^{-2n}$ species where n is *greater than* 4 and perhaps centers around 5 or 6. The total new charge on such oligomers is certainly reduced from $-2n$ by ion association, greater in the case of the barium salt than that of the potassium salt. (Even though a single emission lifetime is observed, there can be more than one emitting oligomer provided that the species are in rapid energy-transfer equilibrium.) Very likely, the phosphorescence is from a triplet state or states of energy around 55 kcal mol^{-1} or 2 V, judging from the emission wavelength (and to the extent that spin designations are valid with a heavy-metal complex). One might therefore expect energy-transfer quenching by species of triplet energy state lower than this value.

Two cases that fit the above criterion are NO_2^- and O_2. Treinin and Hayon[22] found the first triplet excited state of NO_2^- to be 53 ± 2 kcal mol^{-1} above the ground state, by means of a k_q vs. donor triplet energy titration. Note the likely charge effect on k_q in our system, in that $BaPt(CN)_4$ is more efficiently quenched than is $K_2Pt(CN)_4$ in aqueous solution. Association occurs at lower concentration with Ba^{2+} as

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counterion, as compared to K^+,[2] presumably assisted by ion-pairing. The net charge of oligomers present would thereby be reduced relative to the case with K^+ ion, which in turn would reduce the Coulomb barrier to encounters with NO_2^-.

Again, it seems likely that O_2 acts as an energy-transfer quencher, excited singlet state oxygen being produced; the energy requirement to form $^1\Delta_g$ O_2 is only 22 kcal mol^{-1}.[23] Note that k_q for O_2 is considerably larger than for NO_2^-, consistent with the lack of Coulomb barrier to encounters.

A second possible quenching mechanism is by electron transfer. The cyclic voltammetry results indicate that the oligomers present in concentrated solution are oxidizable beginning at around 0.4 V vs. SHE, which in turn implies that the excited-state oligomers should be good reducing agents, by as much as 1.6 V vs. SHE. Reducible species are therefore potential quenchers. The remaining quenchers seem to fall in this second category. The redox mechanism certainly seems to apply to the case of Co(III) ammines. Not only is Co(II) produced, but the absorption spectrum of the photolyzed solution suggests the presence of oxidized $Pt(CN)_4^{2-}$ (see Results). Such ammine complexes are known, of course, to be reduced by excited-state $Ru(bpy)_3^{2+}$, whose reducing potential is about 0.8 V.[24,25] The quenching by paraquat also finds a parallel with $[Ru(bpy)_3^{2+}]^*$,[26,27] and that by 2,2′- and 4,4′-bipyridine is likely also redox in mechanism since these are reducible species.[28,29] Other likely redox quenchers are $Cu^{II}EDTA$, $Hg(CN)_2$, $Hg(Cl)_2$, $Fe^{III}EDTA$, and $Fe(CN)_6^{3-}$, since these are all relatively easily reduced.

The observation that Eu(III) quenches while $Eu^{III}EDTA$ does not (there was, however, an indication of weak quenching in this last case) may be mainly a reflection of the charge difference. However, the mechanism could, in this case, be one of the energy transfer; this process is known to occur in the crystalline state.[30]

A redox quenching mechanism seems indicated for $S_2O_8^{2-}$, $Au(CN)_4^-$, and IO_3^-, but these species could also undergo a *two*-electron reduction. Two-electron oxidation is certainly a possibility with the $Pt(CN)_4^{2-}$ oligomers. The red shift of both absorption and emission features on oligomerization, often called the Davydov shift,[2] is understood in terms of overlap of Pt(II) d_{z^2} orbitals, the z axis being that of the oligomer chain. In effect, there is partial delocalization giving rise to molecular orbitals extending the length of the oligomer. Oxidation becomes a removal of one more electrons from the HOMO of this set, and excitation, a promotion from the HOMO to the LUMO. A two-electron loss should be energetically favored, just as a single Pt(IV) unit is in a more stable oxidation state than is Pt(III), relative to Pt(II). A two-electron loss could be concerted, but given the dwell time of an encounter with a two-electron reductant, the process could also be sequential. There is thus at least a possibility that the above quenchers undergo a two-electron process during a reactive encounter.

In an observation of the nonquenching or very poorly quenching species, the ions SCN^-, NO_3^-, Cl^-, I^-, N_3^-, and SO_3^{2-} are poor quenchers of low-lying organic triplet states.[22] They are also poor oxidizing agents. $Co(CN)_6^{3-}$ has a low-lying triplet excited state[31] and very likely $Co(C_2O_4)_3^{3-}$ as well. Both are reducible, the latter complex especially so. The lack of quenching in these cases may therefore merely be due to a high Coulomb barrier between like and multicharged ions. $Th^{IV}EDTA$ has no low-lying states suited for energy transfer and is not readily reducible. The VO_3^- ion again should not be an energy-transfer quencher, but it is a potentially good oxidizing agent,[32] but in terms of a two-electron change. This last observation suggests that sequential rather than concerted two-electron redox quenching is favored kinetically, with the first step difficult in the case of VO_3^-. The lack of quenching by CH_3CN can be attributed to the lack of low-lying states and poor oxidizing ability.

In summary, triplet-state oligomers of aqueous $Pt(CN)_4^{2-}$ appear to undergo excitation energy transfer if the acceptor has a triplet (or spin-forbidden) excited state below about 2 V in energy. Alternatively, oligomers can undergo electron-transfer processes if the quencher is a good one-electron oxidant and, in some cases, if it is merely a good two-electron oxidant.

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Registry No. $Pt(CN)_4^{2-}$, 15004-88-3; $K_2S_2O_8$, 7727-21-1; KIO_3, 7758-05-6; $K_2Ni(CN)_4$, 14220-17-8; $Cu^{II}EDTA$, 12276-01-6; $[Co^{III}(en)_3]Cl_3$, 13408-73-6; $Eu^{III}Cl_3$, 10025-76-0; KNO_2, 7758-09-0; $Fe^{III}EDTA$, 15275-07-7; $Fe(CN)_6^{3-}$, 13408-62-3; paraquat, 4685-14-7; oxygen, 7782-44-7.

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