different from that of pure DMF. Consequently, the measured chemical shifts were corrected for only the bulk diamagnetic susceptibility of DMF. The results of this study are also given in Table II.

The observed formation constants, together with those of Shih[17] for K^+ (log $K_{K^+\cdot 18C6}$ = 2.70 ± 0.04) Rounaghi[21] for Tl^+ (log $K_{Tl^+\cdot 18C6}$ = 3.35 ± 0.06), yield the selectivity series

$$La^{3+}, Ca^{2+} < Ni^{2+} < Na^+ < Mg^{2+} < K^+ < Sr^{2+} < Tl^+ < Pb^{2+} < Cs^+ < Ba^{2+}$$

Neglecting, for the moment, La^{3+}, Ca^{2+}, and Ni^{2+}, the trends indicate that, as the size of the cation increases, along a set of cations with the same charge, the formation constants increase, probably due to the decreasing solvation as the cation gets larger; as the charge increases for a given size of the cation, the formation constant increases, due to the increase of the ion–dipole interactions.

The formation constant for the La^{3+} complex seems to be quite low, most likely due to strong ion pairing with the nitrate ion, which does not preclude the formation of a $La^{3+}\cdot 18C6$ complex but can reduce the relative amount of complex formed so much that it becomes impossible to measure accurately the formation constant without the knowledge of the extent of ion pairing. The low value for the formation constant for Ni^{2+} is explainable in terms of the geometry Ni^{2+} prefers for its complexes, which is octahedral. Because 18C6 is poorly suited to this geometry, the formation constant is fairly small.

At this time we have no explanation for the low formation constant for Ca^{2+}. It is still interesting to note that this type of behavior for Ca^{2+} has been seen before in water[22] and in 70:30 methanol/water mixtures.[23]

Conclusions

The competitive NMR method described above can be used to extend the applicability of the NMR technique to cations whose formation constants cannot be measured directly by this technique. Furthermore, this new competitive method allows the determination of formation constants that are greater than 10^5, and in principle, it should be possible to measure *very* large formation constants by the repeated application of the competitive technique with each succeeding formation constant becoming larger than the former one. In addition, this method can be used to determine the formation constants for some paramagnetic cation complexes.

Of course any technique has limitations, and this competitive technique is no exception. The need to be able to dissolve two cations with a common anion in a given solvent places restrictions on the systems that may be investigated. In order to determine the sought formation constants, there must be a known value within approximately 4 or 5 orders of magnitude and one of the cations must be suitable to the NMR technique. Because the uncertainty of the determined formation constant will be greater (on a percentage basis) than the uncertainty of the previously known formation constant, repeated application of the competition method will result in uncertainties that, eventually, would become excessively large. Finally, the probe nucleus must be in a fast exchange on the NMR time scale. At this time it appears doubtful that this technique can be applied generally to cryptates where, very often, the exchange is slow at room temperature. Further studies of the advantages and the limitations of this technique are being continued in our laboratory.

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Cooperative Excited-State Behavior in Platinum(II) Magnus-Type Double-Salt Materials. Active and Inactive Photosensitizers for H_2 Production in Aqueous Suspension

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Diffuse-reflectance and emission behavior are used to characterize the lowest excited state of the following $[Pt^{II}]^{2+}[Pt^{II}]^{2-}$ double salts and in some cases their hydrates: $[Pt(NH_3)_4][PtCl_4]$ (MGS), $[Pt(bpy)_2][PtCl_4]$ (PB(Cl); bpy = 2,2′-bipyridine), $[Pt(bpy)(MHB)][PtCl_4]$ (PHB(Cl); MHB = 4-methyl-4′-heptyl-2,2′-bipyridine), $[Pt(bpy)_2][Pt(CN)_4]$ (PBC), and $[Pt(bpy)(MHB)][Pt(CN)_4]$ (PHBC). All of the salts containing the $PtCl_4^{2-}$ anion have lowest excited states of the ligand field type. In green MGS, where metal-metal interaction is significant, no emission occurs, but in yellow $PB(Cl)\cdot 2.5H_2O$ and PHB(Cl), where interaction is weak, emission characteristic of $PtCl_4^{2-}$ is observed. In orange $PBC\cdot 2H_2O$ and $PHBC\cdot 2.5H_2O$ and their red anhydrates, the lowest excited state is assigned as a delocalized $^3Pt(5d_{z^2}–6p_z)$ state. Both salts exhibit strong emission (in PBC powder at room temperature, the emission quantum yield is 0.002 ± 0.001 and the lifetime is 16.8 ± 2.5 ns), which overlaps well with an intense visible absorption band. PBC and PHBC powders are active as photosensitizers for the reduction of water in EDTA solutions. In the presence of Pt(0) catalyst, H_2 production is sustained at a constant rate to >1 turnover with respect to photosensitizer, with no evidence for photosensitizer degradation. In the absence of Pt(0), PBC produces H_2 at a constant rate that is less than 1% of the rate in the presence of Pt(0), but again, without degradation. MGS, PB(Cl), and PHB(Cl) are photoinert and completely inactive as photosensitizers in this reaction. These results are interpreted in terms of the cooperative excited-state structure of these materials.

Introduction

The photosensitized reduction of water has been a subject of intensive research in the last several years,[1] due largely to the worldwide interest in solar energy conversion. Since the discovery of electron-transfer quenching of excited $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) in aqueous solution 12 years ago,[2] there has been

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considerable research in the area of inorganic complexes as redox photosensitizers, both in homogeneous solution[3] and at electrode[4] and microheterogeneous[5] interfaces. As part of our continuing investigation of photoinitiated water reduction by microheterogeneous systems in aqueous solution,[6] we have recently focused our attention on water-insoluble materials composed of linear-chain metal complexes, as possible photocatalysts. Because of the metal–metal interaction in these materials, cooperative phenomena[7] such as high-temperature superconductivity and semiconductivity have long been predicted. Of interest to us was the possibility that some of these materials might possess a conduction band or cooperative excited-state structure that would facilitate multielectron redox reactions such as the reduction of water at the solid–liquid interface. We wish to report here the first example of the application of Magnus-type $[Pt^{II}]^{2+}[Pt^{II}]^{2-}$ double salts as particulate photosensitizers for water reduction.

Experimental Section

Preparation of Complexes and Double Salts. High-purity K_2PtCl_4, $K_2Pt(CN)_4$, and $[Pt(NH_3)_4]Cl_2$ were used as received from Strem Chemicals. $[Pt(bpy)_2](ClO_4)_2$ was synthesized from K_2PtCl_4 via the isolated intermediate $Pt(bpy)Cl_2$ according to a published procedure[8] and washed repeatedly with toluene to remove excess ligand. The surfactant analogue $[Pt(bpy)(MHB)](ClO_4)_2$, where MHB = 4-methyl-4′-heptyl-2,2′-bipyridine,[9] was synthesized from $Pt(bpy)Cl_2$ by the same procedure[8] and was also washed repeatedly with toluene before use.

Double salts were prepared by mixing a dilute ($<10^{-3}$ M) aqueous solution of the appropriate cationic complex with a dilute aqueous solution containing an equal number of moles of the desired anionic complex. Following immediate precipitation of the double salt, the mixtures were centrifuged and decanted and the precipitate washed several times to remove soluble counterions. Solids were dried in air and, in some cases, desiccated further under vacuum to produce anhydrous powders. The materials listed below were characterized by elemental analysis and diffuse reflectance. A summary of the acronyms assigned to the complexes may be found in Table I.

$[Pt(NH_3)_4][PtCl_4]$ (Magnus' green salt, MGS): light green powder, λ_{max} = 600 nm. Anal. Calcd for the anhydrate: H, 2.02; N, 9.34; Cl, 23.68. Found: H, 2.14; N, 9.26; Cl, 24.22.

$[Pt(bpy)_2][PtCl_4]\cdot 2.5H_2O$ (PB(Cl)): yellow powder, $\lambda_{max} < 350$, $\lambda_{sh} \approx 400$ nm. Anal. Calcd for the 2.5 hydrate: C, 26.81; H, 2.14; N, 6.27; Cl, 15.18. Found: C, 26.78; H, 2.11; N, 6.25; Cl, 14.94.

$[Pt(bpy)(MHB)][PtCl_4]$ (PHB(Cl)): yellow powder, $\lambda_{max} < 350$ nm, $\lambda_{sh} \approx 400$ nm. Anal. Calcd for the anhydrate: C, 35.16; H, 3.37; N, 5.86; Cl, 14.82. Found: C, 34.74; H, 3.22; N, 5.95; Cl, 14.57.

$[Pt(bpy)_2][Pt(CN)_4]\cdot 2H_2O$ (PBC): deep orange powder, λ_{max} = 485 nm. Anal. Calcd for the dihydrate: C, 32.80; H, 2.30; N, 12.75. Found: C, 32.68; H, 2.75; N, 12.70. By using dilute monomer solutions, it was sometimes possible to obtain colloidal PBC, which was then separated from precipitate by centrifugation and which remained stable for several hours. The addition of nonionic stabilizing polymers failed to prevent eventual precipitation of the colloids.

$[Pt(bpy)(MHB)][Pt(CN)_4]\cdot 3H_2O$ (PHBC): deep orange powder, λ_{max} = 480 nm. Anal. Calcd for the trihydrate: C, 39.51; H, 3.62; N, 11.52. Found: C, 38.48; H, 3.48; N, 11.49.

Attempts to synthesize $[Pt(NH_3)_4][Pt(CN)_4]$ by precipitation resulted in a white material that was analyzed as $Pt(NH_3)_2(CN)_2(KCl)_2$ after repeated centrifugation and washing. This material was slightly water soluble, and emission data closely resembled the emission of anhydrous $K_2Pt(CN)_4$ (Strem, dried under vacuum until yellow).[11] We doubt that this is a true Pt(II) double salt but suspect it is a coprecipitate of both monomer salts caused by a simple salting-out effect.

Photophysical Measurements. Diffuse-reflectance spectra were measured on a Cary 17D spectrophotometer with a MgO integrating sphere attachment. Emission and excitation spectra were measured on a Spex Fluorolog spectrometer. Excitation spectra were internally corrected relative to a standard quantum counter, and emission spectra were corrected by the method of Parker and Rees.[12] The emission quantum yield of PBC powder was determined by the method of Wrighton et al.[13] Emission lifetimes and some emission spectra were determined by Carl Craig and Professor Richard Watts at the University of California, Santa Barbara, CA, using a laser apparatus described elsewhere.[14] The room-temperature lifetimes of hydrous and anhydrous PBC were measured with a Photochemical Research Associate Model 3000 single-photon-lifetime apparatus and deconvoluted by computer with the program supplied with the instrument.

Photochemical H_2 Production. Five-milliliter samples containing 2 g/L of double salt, 0.05 M EDTA (pH 4.7), and in some cases 10 mg/L Pt(0) sol[15] catalyst were sealed in 10-mL Wheaton serum vials, sonicated briefly to disperse the double-salt particles and to complete precipitation of Pt sol onto the particle surfaces, and degassed with argon. Up to eight samples, vigorously stirred, were photolyzed simultaneously in a thermostated merry-go-round apparatus.[16] The photolysis source was an Osram 150-W Xe lamp run at 140 W and fitted with a 420-nm cutoff filter to remove near-UV radiation. Typically, 1.1 W of light was delivered to the merry-go-round apparatus. H_2 was sampled periodically by syringe with use of a Varian 3700 gas chromatograph equipped with a molecular sieve column and argon carrier gas. After prolonged (≥ 48 h) irradiation, samples were centrifuged and the supernatant was evaporated. The supernatant residue was analyzed for degradation products of the double salt by atomic absorption (Pt) and infrared spectroscopy (ligands, Pt complexes).

Results and Discussion

The Pt(II) double salts in this study show remarkable differences in absorption and emission characteristics and in photosensitizing ability. These results are summarized in Table I. Using spectroscopic and photophysical data, it is possible to relate the differences in photochemical behavior of these materials to differences in electronic structure and to establish criteria for photosensitizing ability based upon cooperative excited-state behavior.

Photochemical H_2 Production. Of the double salts examined in a sacrificial water reduction system, only PBC and its analogue

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Table I. Photophysical Data for Pt(II) Double Salts

double salt	acronym	hydration no.	diffuse reflectance λ_{max}, nm	emission λ_{max}, nm ($\lambda_{excitation}$, nm)[a]	emission lifetime, μs[a]	excited-state assignt[b]
$[Pt(NH_3)_4][PtCl_4]$	MGS	0	600	none		lf ($PtCl_4^{2-}$)
$[Pt(bpy)_2][PtCl_4]$	PB(Cl)	2.5	*350, 400 sh	750 (400)[c]		lf ($PtCl_4^{2-}$)
	PB(Cl)[d]	0[e]	red	900 (356)[f]	13[f]	lf ($PtCl_4^{2-}$)
				771 (356)[f,g]	70.6[f,g]	
$[Pt(bpy)(MHB)][PtCl_4]$	PHB(Cl)	0	<350, 400 sh	745 (400)[c]		lf ($PtCl_4^{2-}$)
$[Pt(bpy)_2][Pt(CN)_4]$	PBC	2	485	570 (485)[c]	0.0168	Pt(d-p)
	PBC	0[e]	515	610 (515)[c]	0.0185	Pt(d-p)
$[Pt(bpy)(MHB)][Pt(CN)_4]$	PHBC	3	480	575 (480)[c]		Pt(d-p)
	PHBC	0[e]	495	620 (515)		Pt(d-p)

[a] Measurements at room temperature unless otherwise noted. [b] Legend: lf = ligand field; Pt(d-p) = Pt($5d_{z^2} \rightarrow 6p_z$). [c] Emission maximum checked to be independent of excitation wavelength. [d] Produced from violet precipitate; see text. [e] Produced by vacuum desiccation of hydrate. [f] Data provided by C. Craig and R. J. Watts. [g] Liquid-nitrogen temperature.

PHBC proved active as photosensitizers. In the presence of Pt(0) catalyst, both salts photosensitized the production of H_2 from water at a constant rate of ~100 nmol/h after a ~15-min induction period.[17] The rate of H_2 evolution remained constant for over 48 h, corresponding to turnover numbers of 1.2 for PBC and 1.1 for PHBC. Both turnover numbers, defined as (moles of H_2)/(moles of photosensitizer), represent lower limits as their calculations are based on the total amounts of bulk photosensitizer rather than active surface material. After 48 h of photolysis, no CN^-, bipyridine, Pt, or Pt complexes were detected in the supernatant, ruling out photodegradation of the surface. Photodegradation involving the production of insoluble species is unlikely as any buildup of degradative products on the surface of the particles would be expected to alter the rate of H_2 production via catalyst poisoning or surface passivation. No change was, however, observed in the rates of H_2 evolution. In the case of PBC, photolysis in the absence of Pt(0) catalyst produced H_2, but at a rate of less than 1 nmol/h. Again, no degradation products were detected after prolonged irradiation, although the photolysis was only continued to a turnover of a few percent with respect to PBC. The marked state enhancement of H_2 production in the presence of Pt(0) catalyst is typical for photoconversion systems.[1] The catalyst provides low-activation-energy pathways for intermediates leading to H_2 formation.

The double salts MGS, PB(Cl), and PHB(Cl) were completely photoinert to visible irradiation with or without Pt(0) catalyst. Neither H_2 nor photodegradation was evident after 48 h of irradiation.

Excited-State Characterization. Changes in monomer absorption spectra upon crystallization or double-salt formation, along with strong optical dichroism, have long been used as criteria for one-dimensional metal-metal interaction in linear-chain materials[7] and have been used to postulate such interaction in materials for which no crystal structure data are available.[18] In the case of Pt(II) haloamines, where the relatively weak ligand field exerted by Cl^- causes ligand field transitions to occur in the visible and near-UV regions, detailed single-crystal spectroscopy[19] has shown a pronounced effect of the Pt-Pt spacing upon d → d transitions in linear-chain materials. Much greater effects have been observed in the intense charge-transfer and d → p transitions of many linear-chain materials,[20] with red shifts of well over 10 000 cm^{-1} being typical for transitions polarized along the chain. The red shift of allowed transitions caused by metal-metal interaction has been well characterized in several spectroscopic studies of discrete square-planar dimers.[21] For many square-planar d^8 complexes,[22] increasing red shifts of allowed d^8 transitions occur upon oligomerization to dimers, trimers, tetramers, and extended-chain solids, providing direct evidence for delocalization of these excited states along the metal-metal chain.

MGS. MGS is the best characterized linear-chain double salt, since knowledge of its crystal structure[23] has allowed correlation of physical structure and spectroscopic properties. The Pt-Pt spacing along the chain is 3.24 Å, and the resulting metal-metal interaction causes a red shift of ~4000 cm^{-1} of a d → d transition of $PtCl_4^{2-}$ [24] to 600 nm (16 700 cm^{-1}) in the spectrum of MGS. In comparison with the d → d transition, an even greater red shift is observed for the Pt($d_{z^2} \rightarrow p_z$) transition,[20] which occurs at 280 nm (34 500 cm^{-1})[25] in MGS, 215 nm (46 300 cm^{-1})[26] in $PtCl_4^{2-}$, and 196 nm (50 950 cm^{-1})[27] in $Pt(NH_3)_4^{2+}$. The energy of the Pt($d_{z^2} \rightarrow p_z$) transition is quite sensitive to metal-metal interaction in Pt(II) crystals. In K_2PtCl_4 and other Pt-chain crystals where no appreciable interaction occurs[19] (4-4.1-Å Pt-Pt spacing), the energy of the d → p transition is essentially that of a monomer. In $[Pt(H_2P_2O_5)_4]^{4-}$ dimers, a Pt-Pt spacing of only 2.925 Å[28] results in a d → p transition energy of 368 nm (27 200 cm^{-1}).[21a] Thus, MGS may be thought of as an intermediate case in the range of possible metal-metal interactions.

We observe no emission from MGS, at either room temperature or 77 K, for excitation wavelengths in the range of 248-600 nm. Since the lowest excited states are perturbed ligand field states derived from $PtCl_4^{2-}$, weak long-lived emission corresponding to a spin- and Laporte-forbidden transition might be expected. K_2PtCl_4 exhibits such emission,[29] but $Pt(NH_3)_4^{2+}$ does not,

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(17) As a rough comparison, this rate is about 5% of the initial rate for H_2 production, under similar conditions, by the model photoconversion system containing 10^{-4} M $Ru(bpy)_3^{2+}$ sensitizer, 5×10^{-3} M methylviologen electron relay, 0.05 M EDTA sacrificial electron donor, and 10 mg/L Pt(0) sol catalyst. (For details of several comparable systems, see: Butler, C. D.; Houlding, V. H.; Frank, A. J. submitted for publication in *J. Phys. Chem.*) In the model system, the catalytic Pt sol is quickly deactivated unless stabilized against aggregation by protective polymers. Such protective polymers reduce the activity of the catalyst and often affect adversely the reproducibility of the rate of catalysis. In the case of PBC and PHBC, the quantum efficiency for H_2 production has not been determined as the molar concentration of particles and hence their absorption cross section are not readily measurable. Without quantum efficiency data, it is difficult to make meaningful comparisons between the PBC or the PHBC system and other photoconversion systems that generate H_2 from water.

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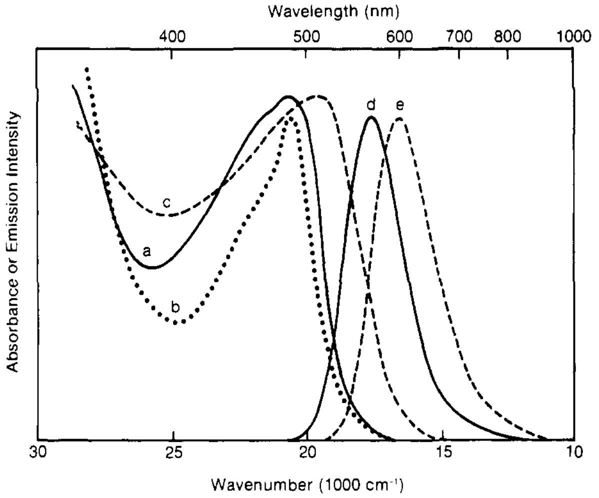

Figure 1. Absorption and emission spectra of PBC: (a) diffuse reflectance of PBC·2H_2O powder; (b) absorption of optically transparent colloidal PBC in water separated from the powder by centrifugation; (c) diffuse reflectance of anhydrous PBC powder; (d) corrected emission of PBC·2H_2O powder; (e) corrected emission of anhydrous PBC powder.

probably as a result of vibrational deactivation by N–H stretching modes. Quenching of $PtCl_4^{2-}$ emission in MGS might occur via a similar mechanism. The lack of emission upon excitation into the d → p absorption band shows that coupling between this excited state and the lower energy ligand field states is strong enough to preclude upper-excited-state emission, a result that is not surprising.

PB(Cl) and PHB(Cl). In these yellow double salts of Pt bipyridines with $PtCl_4^{2-}$, the diffuse-reflectance spectra are different from that which would be produced by the simple superposition of the spectra of the pale yellow cations and pale pink anion. However, no appreciable red shift of $PtCl_4^{2-}$ d → d transitions can be seen. Upon excitation in the range of 250–550 nm, PHB(Cl) at room temperature and PB(Cl) at 77 K exhibit extremely weak emission at ca. 750 nm (12 500 cm^{-1}), which is the d → d emission[30] maximum of K_2PtCl_4 at room temperature; perchlorate salts of Pt(bpy)$_2^{2+}$ and Pt(bpy)(MHB)$^{2+}$ were nonemissive at room temperature. From these observations, it can be reasonably inferred that little or no metal–metal interaction is present in these materials. Desiccation or heating did not produce a red color in either salt, contrary to previous reports for PB(Cl).[8] It is important to note that we once observed a brilliant violet precipitate in preparing PB(Cl), which became red upon drying. Elemental analysis was consistent with formulation of the red material as anhydrous PB(Cl). This phenomenon could not be repeated, but it is clear evidence for the existence of more than one crystalline form of PB(Cl). The absorption and emission characteristics of this material are listed in Table I. From the long emission lifetime, large Stokes shift, and very low intensity, we assign the emitting states as ligand field.

PBC and PHBC. The absorption and emission characteristics of these double salts of Pt(bpy)$_2^{2+}$ and Pt(bpy)(MHB)$^{2+}$ with Pt(CN)$_4^{2-}$ present a marked contrast to those of the double salts discussed above. The dehydrated forms are orange, due to an intense asymmetric absorption band at 485 nm (20 600 cm^{-1}) in PBC and 480 nm (20 800 cm^{-1}) in PHBC. Each salt exhibits a strong emission band at room temperature, which overlaps well with the absorption band (see Table I, Figure 1). Intense visible absorption has been previously reported[18b] for double salts of Pt(bpy)$_2^{2+}$ and Pt(*o*-phen)$_2^{2+}$ (*o*-phen = *o*-phenanthroline) with various Pt(II) anions. Considering the strong ligand fields of the constituent monomers of PBC and PHBC, it is unlikely that the emission is from a ligand field state, and analysis of the emission parameters of PBC rules out this assignment entirely. We measured an emission quantum yield of 0.002 ± 0.001 for PBC at room temperature. Lifetime measurements yielded a value of $\tau = 16.8 \pm 2.5$ ns at 20 °C, allowing a calculation of the radiative lifetime $k_r = \phi/\tau \approx 1.2 \times 10^5$ s^{-1}. A very small emission component with a lifetime $\leq$1 ns was also observed but could not be satisfactorily resolved due to its low intensity. We assign, respectively, the short- and long-lived emissions to the spin-allowed and spin-forbidden components of an allowed transition, most likely Pt($p_z \rightarrow d_{z^2}$).[20,21] The large magnitude of k_r rules out the possibility that the spin-forbidden emission is also Laporte forbidden, i.e., ligand field in origin.

Upon dehydration of PBC to its anhydrous form, a red shift of the d → p transition occurs, from 485 nm (20 600 cm^{-1}) to 515 nm (19 400 cm^{-1}), paralleled by a shift in the room-temperature emission maximum from 570 nm (17 540 cm^{-1}) to 610 nm (16 400 cm^{-1}) (Figure 1). This red shift is consistent with a decrease of the metal–metal distance in the material upon removal of water. Interestingly, the emission lifetime of the red anhydrous PBC is 18.5 ± 0.5 ns at room temperature, essentially unchanged from that of the hydrated material. The lifetime of anhydrous PBC increases to 696.5 ± 0.5 ns at 77 K, further evidence that the emission is phosphorescence. It is worthy of note that laser interrogation of PBC caused in situ dehydration of the material to the red form and sometimes produced a red shift of emission to as low as 650 nm (15 400 cm^{-1}). The cause of the additional red shift is not known, but it may be due to local melting of the crystal, causing further compression along the metal–metal axis.

One possibility is that the intense transition in PBC and PHBC is due to discrete dimers within the crystal lattice,[29] and not to an extended-chain structure. Certainly, strong metal–metal interaction in d^8 dimers is known to cause extreme red shifts of metal axis-polarized d → p transitions.[21] Several points argue in favor of an extended-chain structure, however. First, an extremely short Pt–Pt distance would be necessary to produce the observed energy of the d → p transition in PBC and PHBC, if only dimers were involved. Second, dehydration of the lattice produced a large red shift of emission and absorption in PBC, a typical observation of hydrated-chain structures. Finally, it was observed in elegant work by Isci and Mason[31] that some [Pt(CNR)$_4$][Pt(CN)$_4$] double salts formed ion pairs in aqueous solution with intense absorption features in the near-UV region. These bands were red shifted considerably with respect to monomer absorption due to dimerization. In the solid, the transitions were further red shifted into the visible region at energies comparable to those of PBC and PHBC. Therefore, in the absence of crystal structure data, we favor the description of PBC and PHBC as linear-chain materials.

Concluding Remarks

Photosensitization of the reduction of water by the Pt(II) double salts studied here is dependent upon the type of excited state involved in the redox process. We have shown that the chain-axis delocalized ^{3}Pt(d → p) states of PBC and PHBC are photoactive whereas the ligand field states of other materials are not, even when they are long lived (as in the case of PB(Cl)) or when significant metal–metal interaction is present (as in the case of MGS). These results support the conclusion of others[19] that ligand field states in linear-chain material are not appreciably delocalized by metal–metal interactions.

Two electronic structural effects are probably responsible in large part for the observed photosensitizing ability of PBC and PHBC upon visible irradiation. First, cooperative interaction by the Pt atoms along the chain lower the energy of the d → p excited states into the visible region of the spectrum and may also cause significant mobility of excitation energy in the form of an exciton or even an uncorrelated electron-hole pair. Second, strong ligand fields in the constituent monomer ions serve to raise the energy of the ligand field states above that of the d → p states. Our emission results show that deactivation of directly excited d → p states by lower energy ligand field states is a fairly efficient process, and this conversion process competes strongly with redox photosensitization from upper excited states of d → p type. By

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an increase in the energy of ligand field states, this nonproductive deactivation channel is removed and the efficiency of photosensitization is greatly increased.

Using these two criteria, it should be possible to design many Magnus-type materials that will be photoactive. Whether photoactivity is merely a result of light absorbed by surface chromophores or whether cooperative electronic structure allows transfer of excitons (or perhaps conduction-band electrons) from the bulk to the surface is a question of central importance to the study of these materials. From a theoretical viewpoint[32] it is very likely that some variation of an exciton model applies to the d → p states of d^8 linear-chain materials, and therefore bulk excitation is mobile. This study demonstrates that excitation can be harvested at the solid-liquid interface in redox processes. We are currently attempting to grow large single crystals of PBC in order to study the photoconductivity and other electrical properties of this material.

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Registry No. $[Pt(NH_3)_4][PtCl_4]$, 13820-46-7; $[Pt(bpy)_2][PtCl_4]$, 54822-44-5; $[Pt(bpy)(MHB)][PtCl_4]$, 98064-84-7; $[Pt(bpy)_2][Pt(CN_4)]$, 54806-40-5; $[Pt(bpy)(MHB)][Pt(CN)_4]$, 98064-85-8; H_2O, 7732-18-5; H_2, 1333-74-0; Pt, 7440-06-4.

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Synthesis and Spectroscopic Properties of Ethynylsulfur Pentafluoride ($SF_5C{\equiv}CH$)

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Ethynylsulfur pentafluoride, $SF_5C{\equiv}CH$, has been prepared by the dehydrobromination of $SF_5CH{=}CFBr$ (49%). It also can be obtained in a four-step process by the addition of SF_5Br to acetylene, followed by bromination of the resulting olefin, $SF_5CH{=}CHBr$, to form $SF_5CHBrCHBr_2$, which may be dehydrobrominated with K_2CO_3 to give $SF_5CBr{=}CHBr$. The latter, when treated with Zn, gives $SF_5C{\equiv}CH$ in an overall yield of 9%.

Introduction

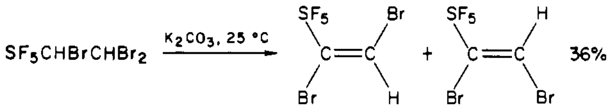
It is known that the introduction of SF_5 groups into molecular systems can bring about significant changes in their physical, chemical, and biological properties. These properties are manifested by various applications, such as solvents for polymers, as perfluorinated blood substitutes, as surface-active agents, as fumigants, and as thermally and chemically stable systems.[1] The synthesis and chemistry of these compounds are the subjects of ongoing studies. One compound of particular interest is ethynylsulfur pentafluoride ($SF_5C{\equiv}CH$) which has been used as the starting reagent for a number of novel and interesting derivatives that include saturated ethers, vinyl ethers, pyrazoles, cyclic alkenes, and alkyl-substituted phenylsulfur pentafluorides.[2] In addition, $SF_5C{\equiv}CH$ is found to be useful in preparing a number of SF_5-containing alkenes and alkynes.[2,3]

Results and Discussion

The original synthesis of $SF_5C{\equiv}CH$ involves four steps, starting with pentafluorosulfur chloride (SF_5Cl) and acetylene.[2] The overall yield for this sequence is only 11%. Since SF_5Br has been under study in our laboratories, an attempt was made to prepare $SF_5C{\equiv}CH$ in higher yields by the following sequence of reactions.

$$SF_5Br + HC{\equiv}CH \xrightarrow{57\ ^\circ C} SF_5CH{=}CHBr \quad 80\% \qquad (1)$$

$$SF_5CH{=}CHBr \xrightarrow{Br_2,\ h\nu} SF_5CHBrCHBr_2 \quad 46\% \qquad (2)$$



$$SF_5CHBrCHBr_2 \xrightarrow{K_2CO_3,\ 25\ ^\circ C} (SF_5)(Br)C{=}C(Br)(H) + (SF_5)(Br)C{=}C(H)(Br) \quad 36\% \qquad (3)$$

$$SF_5CBr{=}CHBr \xrightarrow{Zn,\ diglyme} SF_5C{\equiv}CH \quad 68\% \qquad (4)$$

Because of the unexpected low yields of reactions 2 and 3, the overall yield was only 9%. It is thought that the yields for reactions 2 and 3 could be improved, but it was found, unexpectedly, that direct dehydrobromination of $SF_5CH{=}CHBr$ gave the acetylene in yields of ~50%.

$$SF_5CH{=}CHBr \xrightarrow[\text{pet. ether}]{KOH} SF_5C{\equiv}CH \qquad (5)$$

Attempts to dehydrohalogenate $SF_5CH{=}CHCl$ were found to be ineffective and gave a yield of only 1-2% of the desired SF_5 alkyne. The compounds synthesized in reactions 1-3 are new and have been characterized by elemental and spectral analyses.

The common feature of these new compounds and $SF_5C{\equiv}CH$ is the presence of the SF_5 group. For the compounds reported in this paper, absorption bands in the 845-928-cm^{-1} region are assigned to S—F stretching vibrations. The S—F deformation modes are found near or at 600 cm^{-1}.[4] The infrared spectra of $SF_5CH{=}CHBr$ and $SF_5C{\equiv}CH$ contain the characteristic absorption band of the olefinic C=C or acetylenic C≡C stretching vibration at 1611 or 2118 cm^{-1}, respectively. For $SF_5CH{=}C(Br)SF_5$, $SF_5CH{=}C(CF_3)Br$, and $CF_3C{\equiv}CH$, the C=C/C≡C absorption bands are found at 1610, 1630, and 2165 cm^{-1}, respectively.[3,5,6] The C—H stretching vibrations for $SF_5CH{=}C$-

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