is calculated making $F_3CNC^{+\cdot}$ some 25 kJ/mol more favorable. This is in accordance with the observation that the molecular peak in the mass spectrum is several times more intense for F_3CNC than for F_3CCN.[34]

As an additional result of the geometry-optimized ΔSCF(MNDO) calculations, one also can obtain an approximation for the adiabatic first ionization energies, i.e. the energy difference between the ground state of the neutral molecule and that of the radical cation in their equilibrium geometries. The results, 12.5 eV for F_3CNC and 13.9 eV for F_3CCN, can be checked by the onset of the respective first PE bands (Figures 1 and 2); the satisfactory agreement again lends credence to the reliability of the employed computational methods also for highly fluorinated compounds.

Acknowledgment. This project has been supported by the Land Hessen, the City of Berlin, the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie. The MNDO program has kindly been provided by M. J. S. Dewar. R.D. wishes to thank the Studienstiftung des Deutschen Volkes for a scholarship.

Registry No. $H_2C{=}CHN$, 64987-66-2; $H\overline{C{=}CHN}H$, 157-17-5; $H_2C{=}N^+{=}^-CH$, 89554-95-0; $H_2\overline{CCH{=}N}$, 157-16-4; $HC{\equiv}CNH_2$, 52324-04-6; $H_3CN{=}C$, 593-75-9; $H_2C{=}C{=}NH$, 17619-22-6; H_3CCN, 75-05-8; $FC{\equiv}CNF_2$, 89554-96-1; $F\overline{C{=}CFN}F$, 89554-97-2; $F_2C{=}CFN$, 89554-98-3; $F_2C{=}N^+{=}^-CF$, 89554-99-4; $F_2C{=}C{=}NF$, 89555-00-0; $F_2\overline{CFF{=}N}$, 89555-01-1; $F_3CN{=}C$, 19480-01-4; F_3CCN, 353-85-5.

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Contribution from the Istituto Chimico dell'Università and Centro di Studio sulla Fotochimica e Reattività degli Stati Eccitati dei Composti di Coordinazione del CNR, 44100 Ferrara, Italy

Cyano-Bridged Ruthenium(II)/Platinum(II) Complexes: Synthesis, Photophysical Properties, and Excited-State Redox Behavior

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Received July 14, 1983

Two addition compounds between the $Ru(bpy)_2(CN)_2$ chromophore and the $Pt(dien)^{2+}$ moiety, $[(CN)(bpy)_2RuCNPt(dien)]^{2+}$ and $[(dien)PtNC[Ru(bpy)_2]CNPt(dien)]^{4+}$, have been prepared and isolated as perchlorate salts. Spectroscopic data (IR, UV/vis, luminescence) clearly indicate that in both complexes the ruthenium and platinum metal ions are bonded via cyanide bridges. The complexes are luminescent in fluid solution, with emission wavelengths (in the 580–630-nm range) and lifetimes (in the 60–630-ns range) depending on the solvent. The half-wave redox potentials in DMF solutions have been measured and found to be always more positive than those of the parent $Ru(bpy)_2(CN)_2$ complex. Both cyano-bridged complexes behave as powerful excited-state reductants (half-wave potentials −1.16 and −1.45 V vs. SCE in DMF). The excited states of both complexes are quenched by methylviologen at diffusion-controlled rates by an electron-transfer mechanism. Laser flash photolysis indicates substantial yields of cage escape for these reactions. The properties of the new bimetallic complexes are compared with those of the parent $Ru(bpy)_2(CN)_2$ compound.

Introduction

Metal polypyridine complexes have attracted in recent years an extraordinary deal of attention. This is partly due to the peculiar combination of redox potentials, chemical inertness, and excited-state lifetimes that makes them one of the most attractive class of sensitizers for photochemical water cleavage.[1-3] As a step toward the development of new photosensitizers, we are interested in studying the possibility and consequences of binding additional metallic centers to a metal polypyridine chromophore. Provided that the presence of the new metallic center does not destroy the useful redox and excited-state properties of the main chromophore, such polymetallic species could exhibit some very interesting photochemistry and thermal chemistry, particularly from the viewpoint of the competition between inter- and intramolecular electron-transfer pathways. Hopefully, suitably engineered molecules of this type could lead to highly efficient charge separation in the photochemical electron-transfer step of water-cleaving photochemical cycles. A very attractive metal polypyridine chromophore is from this point of view the dicyanobis(2,2′-bipyridine)ruthenium(II), $Ru(bpy)_2(CN)_2$, complex. This complex has a good combination of ground- and excited-state properties and behaves in many relevant aspects as its more famous congener tris(bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$. In addition, it offers two potential binding sites for other metals at the cyanide ligands.

Binuclear complexes containing cyanide-based bridging ligands have been extensively studied. The metal-containing moieties have been more frequently $Fe(CN)_5^{n-}$,[4,5] $Co(NH_3)_5^{3+}$,[5,6] $Co(CN)_5^{2-}$,[7] $Ru(NH_3)_5^{n+}$,[8-11] and $Ru(CN)_5^{3-}$[6,7,12,13] (n = 2,3), whereas the briding ligands include cyanide itself,[4,6-8,12,13] dicyanogen,[9] dinitriles,[10] dicyanamide,[11] and cyanopyridines.[5] Very recently, Kinnaird and Whitten[14] have reported on the formation of adducts between $Ru(bpy)_2(CN)_2$ and silver(I) ions while similar interactions with copper(II), nickel(II), and cobalt(III) ions had been previously invoked to explain some static quenching results.[15]

In a preliminary communication,[16] we described the formation in solution of neutral adducts between $Ru(bpy)_2(CN)_2$ and a number of platinum(II) olefin complexes. These adducts, while exhibiting interesting photophysical properties,

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were kinetically labile in coordinating solvents. We have now prepared and isolated as solid salts two stable cationic complexes containing the $Ru(bpy)_2(CN)_2$ and $Pt(dien)^{2+}$ (dien = diethylenetriamine) moieties in 1:1 and 1:2 ratios. We report here on the photophysical properties and on the excited-state redox behavior of these complexes.

Experimental Section

Materials. Ammonium hexachlororuthenate(IV) (Fluka), methylviologen (Ega Chemie), sodium cyanide, and 2,2′-bipyridine (Baker) were commercial products of reagent grade. Bromo(diethylenetriamine)platinum(II) bromide[17] and *cis*-dicyanobis(2-2′-bipyridine)ruthenium(II)[18] were prepared according to literature procedures.

Preparation of $[(CN)(bpy)_2RuCNPt(dien)](ClO_4)_2$. A 182-mg sample of [Pt(dien)Br]Br was dissolved in 25 mL of water, and 165 mg of $AgClO_4$ was added. The resulting precipitate of AgBr was filtered off and washed with five 5-mL portions of water. The aqueous solution containing $Pt(dien)(H_2O)^{2+}$ was mixed with 50 mL of a methanolic solution of $Ru(bpy)_2(CN)_2{\cdot}2H_2O$ (200 mg). The solution was heated at 60 °C with stirring for 2 h. The solution was reduced to 10 mL by evaporation under vacuum and added to 20 mL of acetone. The red-orange precipitate that formed was filtered, washed with acetone, and redissolved with water. This procedure was repeated two times, and the final red orange product was dried under vacuum. The purity of the complex was controlled by thin-layer chromatography on alumina plates with methanol (R_f 0.59; to be compared with 0.73 for $Ru(bpy)_2(CN)_2$). The complex is quite soluble in water and in most polar organic solvents. Attempts to obtain the complex in crystalline form were unsuccessful. Anal. Calcd for $[(CN)(bpy)_2RuCNPt(dien)](ClO_4)_2$: C, 32.47; H, 3.04; N, 13.11; Ru, 10.51; Pt, 20.28. Found: C, 32.13; H, 2.93; N, 12.82; Ru, 11.00; Pt, 19.30.

Preparation of $[(dien)PtNC[Ru(bpy)_2]CNPt(dien)](ClO_4)_4$. The same procedure used for the binuclear complex was followed, except that a 2:1 molar ratio between $Pt(dien)(H_2O)^{2+}$ and $Ru(bpy)_2(CN)_2$ was used. The purity of the complex was controlled by using alumina plates with methanol; the complex appeared as a yellow crescent starting from the base. Anal. Calcd for $[(dien)PtNC[Ru(bpy)_2]CNPt(dien)](ClO_4)_4$: C, 24.72; H, 2.35; Ni, 11.53; Ru, 6.93; Pt, 26.76. Found: C, 24.12; H, 2.91; N, 11.24; Ru, 7.95; Pt, 24.82.

Apparatus and Procedures. UV–vis spectra were recorded with a Varian Cary 219 spectrophotometer. The emission spectra were measured with a Perkin-Elmer MPF3 spectrofluorimeter equipped with a R 928 Hamamatsu tube. The emission lifetimes were measured with a J & K system 2000 ruby laser (frequency doubled; pulse half-width 25 ns) in a single-shot mode, with oscillographic recording. Infrared spectra were recorded with a Perkin-Elmer Model 283 spectrophotometer in Nujol mull. A Perkin-Elmer Model 608 atomic absorption spectrophotometer was used for the ruthenium and platinum analyses.

Potential sweep voltammetric curves were recorded by means of an Amel 448 three-electrode oscillographic polarograph. A saturated calomel electrode (SCE) was used as reference electrode, and all potentials are referred to it. The auxiliary electrode was a piece of platinum wire, and the indicator electrode was a dropping-mercury electrode (DME) or a platinum electrode with periodical renewal of the diffusion layer (PRPE). Before each experiment, the platinum electrode was conditioned according to previously described procedures.[19] Tetraethylammonium perchlorate (TEAP; 0.1 M) was used as supporting electrolyte, and 10^{-3} M DMF solutions of the complexes were examined. Half-wave potentials for the reversible couples were taken as the mean of the anodic and cathodic peaks.

Low-temperature emission spectra and lifetimes were measured in clear, glass-forming solvents (vide infra), by using an Oxford Instruments DN 704 cryostatic equipment with quartz windows and standard 1-cm spectrofluorimetric cuvettes.

All samples for laser lifetime determination in fluid solutions were freeze–pump–thaw degassed prior to the experiments (five cycles with a pressure of 10^{-6} torr).

Laser Flash Photolysis. The laser flash photolysis experiments were carried out by using an Applied Photophysics detection system coupled with a J & K 2000 ruby laser source, delivering 25-ns (half-width) pulses of 347-nm radiation. Each pulse consisted of ca. 2×10^{-8} einstein, which in the experimental conditions used corresponds to concentrations of absorbed photons in the reaction cell in the range 5×10^{-5}–10^{-4} M. The rate constants of the back-electron-transfer reactions of the primary products (vide infra) were straightforwardly measured by monitoring the second-order decay of the visible absorption of the reduced quencher. These experiments were performed in "optically diluted" (347-nm optical density lower than 0.5) solutions, in order to ensure a homogeneous distribution of primary products within the cell. The quantum yields of formation of primary redox products were obtained by measuring (i) the concentration of the reduced quencher immediately after the pulse (actually, ca. 100 ns after the pulse, as the subsequent decay occurs in a 100-fold longer time scale) and (ii) the concentration of absorbed laser photons, obtained by using an actinometric method based on benzophenone triplet absorption.[20] In doing this, both the complex and the benzophenone solutions had to be equal-absorbance, optically dense solutions (347-nm optical density higher than 2). This was necessary, since more dilute complex solutions would undergo partial bleaching during the laser pulse, leading to smaller than predicted laser light absorption. The quantum yields of primary product formation were converted into yields of cage escape by correcting for the extent of excited-state quenching and assuming, as is the case for $Ru(bpy)_2(CN)_2$,[26] that the quantum yield of formation of the lowest, emitting state is unity in all cases.

Table I. Spectroscopic and Redox Properties of the Complexes

	$Ru(bpy)_2(CN)_2$		I		II	
	H_2O	DMF	H_2O	DMF	H_2O	DMF
λ_{max}(abs), nm	428	505	416	460	408	426
λ_{max}(em),[a] nm	620	680	590	630	580	580
τ,[b] ns	250	205	140	630	60	90
$E_{1/2}(S/S^-)$,[c] V		−1.68		−1.62		−1.50
$E_{1/2}(S^+/S)$,[c] V		+0.73		+1.03		+0.86

[a] Room temperature. [b] Deaerated solution; room temperature. [c] Voltammetric potential vs. SCE; S stands for $Ru(bpy)_2(CN)_2$, I, or II.

Table II. Kinetic and Laser Photolysis Data for the Electron-Transfer Quenching of the Complexes by Methylviologen[a]

	$Ru(bpy)_2(CN)_2$	I	II
k_q, $M^{-1}\ s^{-1}$	3.5×10^9	2.2×10^9	7.4×10^8
k_{bet}, $M^{-1}\ s^{-1}$	4.7×10^9	5.3×10^9	4.8×10^9
Φ_{ce}	0.11	0.17	0.29

[a] Aqueous solution; ionic strength 0.3 M (Na_2SO_4).

Results

Stability in Solution. Solutions of $[(CN)(bpy)_2RuCNPt(dien)](ClO_4)_2$ (I) in DMF or water appear to be indefinitely stable in the dark. Aqueous solutions of $[(dien)PtNC[Ru(bpy)_2]CNPt(dien)](ClO_4)_4$ (II) undergo a limited amount of solvolysis, producing I and $Pt(dien)L^{2+}$ (L = H_2O, DMF). This can barely be seen by absorption spectral changes (vide infra) but can be very sensitively monitored by emission spectral changes (vide infra). With dilute solutions of II (ca. 10^{-4} M), the solvolytic equilibrium is established in a few hours, and the amount of I formed is of the order of 2–3% at room temperature.

Upon visible irradiation, I and II do not exhibit any additional photochemistry besides that of the parent $Ru(bpy)_2(CN)_2$ complex, which is slightly photosensitive in this region.[21]

All the quantitative results on I and II reported in Tables I–III and in Figures 1 and 3 refer to freshly prepared solutions handled in the dark.

Spectral Behavior. The visible spectra of I and II in DMF are reported and compared with that of $Ru(bpy)_2(CN)_2$ in

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Table III. Excited-State Redox Potentials (V)

complex, S	E-(S/*S)[a]	$E_{1/2}$-(S^+/S)[b]	$E_{1/2}$-(S/S^-)[b]	*$E_{1/2}$-(S^+/S*)[b]	*$E_{1/2}$-(*S/S^-)[b]
$Ru(bpy)_2(CN)_2$	2.05	0.73	−1.68	−1.32	0.37
I	2.19	1.03	−1.62	−1.16	0.57
II	2.31	0.86	−1.50	−1.45	0.81

[a] From 77 K emission spectra (Figure 3) in DMF/CH_2Cl_2 (9:1). [b] In DMF vs. SCE.

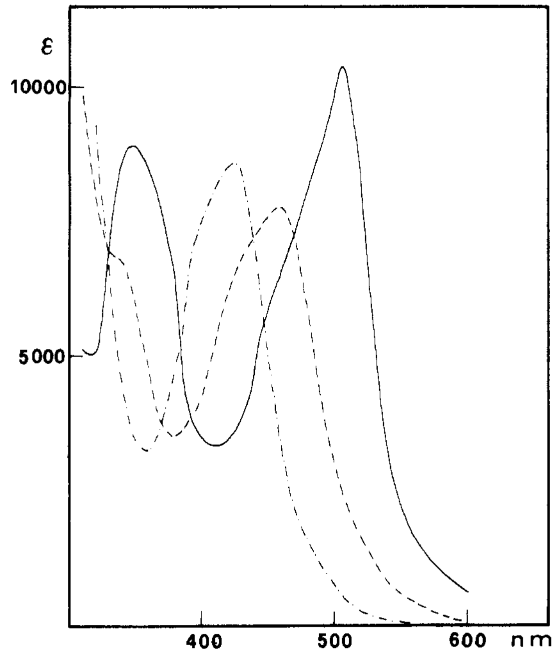

Figure 1. Absorption spectra of $Ru(bpy)_2(CN)_2$ (—), I (---), and II (-•-) in DMF solution.

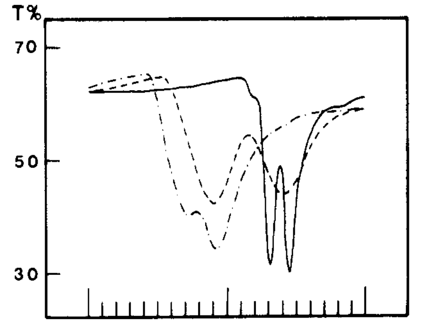

Figure 2. Infrared spectra of $Ru(bpy)_2(CN)_2$ (—), I (---), and II (-•-) in the CN stretching region (Nujol mull).

Figure 1. The evident feature is that increasing the number of platinum moieties bound to $Ru(bpy)_2(CN)_2$ causes a progressive blue shift of the prominent visible absorption band. A similar trend is observed in aqueous solutions (Table I) although here the bands are always at higher energy and the shifts between the complexes are smaller than in DMF.

The IR spectra of the two complexes (Figure 2) exhibit a substantial increase in the CN stretching frequencies, with respect to the parent $Ru(bpy)_2(CN)_2$.

Emission. Both I and II luminesce in fluid solution at room temperature, with relative (uncorrected) intensities of about 3 and 1, respectively, relative to $Ru(bpy)_2(CN)_2$. Emission spectra of $Ru(bpy)_2(CN)_2$, I, and II in DMF solutions are reported in Figure 3. They exhibit parallel shifts with respect to absorption. Again, the spectra in aqueous solution are blue shifted and with smaller relative shifts than in DMF (Table I). Low-temperature (77 K) spectra in absolute ethanol, 1:1 water/ethylene glycol, and 9:1 DMF/CH_2Cl_2 glasses are shown in Figure 4. They show the same trend as the room-temperature spectra, with a more structured band shape with a prominent vibrational progression of ca. 1400 cm^{-1}.

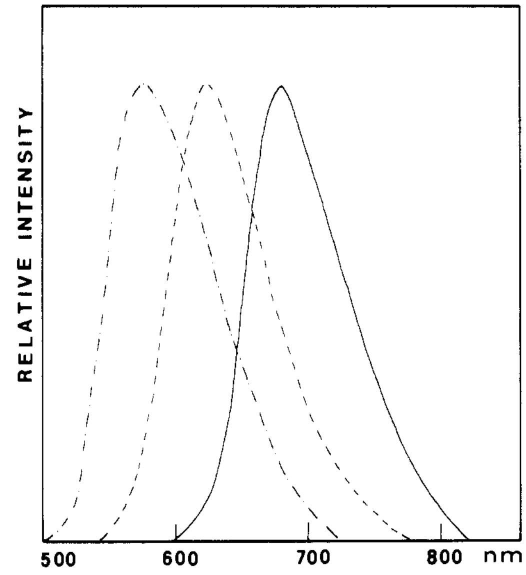

Figure 3. Emission spectra of $Ru(bpy)_2(CN)_2$ (—), I (---), and II (-•-) in DMF solution at room temperature.

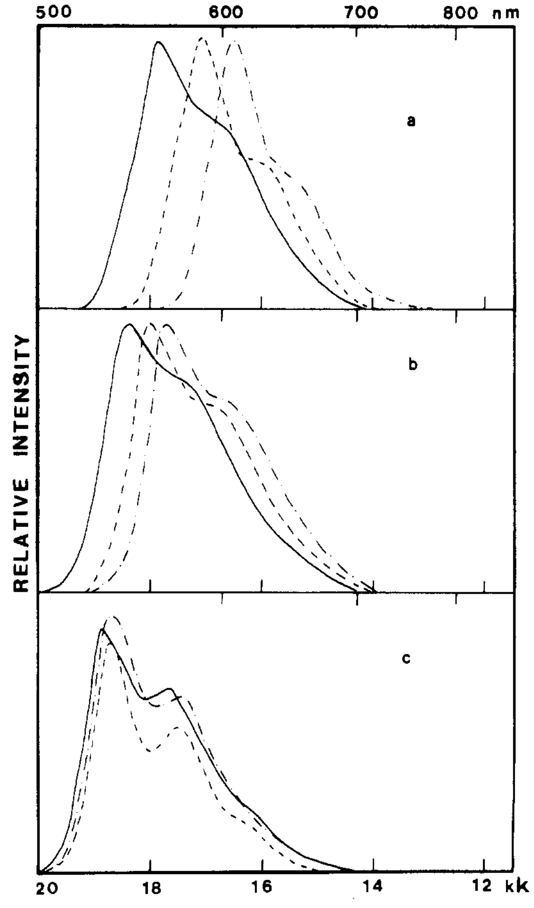

Figure 4. Low-temperature (77 K) emission spectra of $Ru(bpy)_2(CN)_2$ (a), I (b), and II (c), in different matrices: 1:1 H_2O/ethylene glycol (—), absolute ethanol (---), and 9:1 DMF/CH_2Cl_2 (-•-).

Excited-state lifetimes, measured by emission decay techniques, are reported in Table I for room temperature, deaerated aqueous and DMF solutions. As for $Ru(bpy)_2(CN)_2$,[22] the

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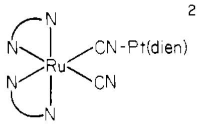
lifetimes are quenched by oxygen at a diffusion-controlled rate.

Redox Behavior. Cyclic voltammetry of $Ru(bpy)_2(CN)_2$, I, and II in DMF solutions showed a single, apparently reversible (scan speed 1 V/s), oxidation step in the anodic region up to 1.6 V (Table I). In the cathodic region, complex patterns involving at least two appreciably reversible (scan speed 1 V/s) reduction steps were observed. The potentials corresponding to the first reduction step are reported in Table I. Oxidation and reduction potentials for $Ru(bpy)_2(CN)_2$ are in fair agreement with those reported by Roffia and Ciano.[23]

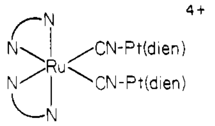
Electron-Transfer Quenching. In aqueous solutions, the emission intensity and lifetimes of $Ru(bpy)_2(CN)_2$, I, and II were quenched by the presence of the methylviologen dication (MV^{2+}). Coincident linear Stern–Volmer plots were obtained from intensity and lifetime quenching for each complex. The bimolecular quenching constant vlues, k_q, are reported in Table II. Laser flash photolysis showed that the quenching was accompanied by transient formation of the characteristic absorption of the reduced methylviologen monocation (λ_{max} 605 nm). Cage escape yields were obtained as limit quantum yields for formation of MV^+ in conditions of complete excited-state quenching, by measuring the concentration of absorbed photons/pulse with a relative actinometric method based on benzophenone triplet absorption (see Experimental Section). The quantum yield values, Φ_{ce}, are reported in Table II. After the laser flash, the MV^+ transient absorption disappeared by clean second-order kinetics. The rate constants for this thermal reaction, k_{bet}, are reported in Table II.

Discussion

Spectral data indicate very clearly that I and II are bi- and trimetallic complexes in which one and two $Pt(dien)^{2+}$ moieties are attached to $Ru(bpy)_2(CN)_2$ via cyanide bridges. In fact, the progressive blue shift in both absorption and emission spectra (Figures 1 and 3) with increasing numbers of $Pt(dien)^{2+}$ units is understandable in terms of the electron-withdrawing effect of these units on the $Ru(bpy)_2(CN)_2$ chromophore and of the d–π^* nature of the relevant transition.[24] The effect is entirely consistent with those observed in a number of closely related systems in which protons,[25,26] boron halides,[27] transition-metal ions,[14,15] and other platinum(II) complexes[16] act as Lewis acids.



I



II

The IR spectra in the CN stretching region (Figure 2) give substantial support to the structures proposed for compounds I and II. In fact, the general increase in CN stretching frequencies observed on going from $Ru(bpy)_2(CN)_2$ to I to II is indicative of an increasing degree of bridge formation in this series, consistent with similar observations made on a large number of related systems.[14,27–29] In detail, the spectra in Figure 2 contain the following information: (i) $Ru(bpy)_2(CN)_2$ exhibits a doublet of closely spaced bands at 2053 and 2067 cm^{-1}, characteristic of two monodentate cyanide groups, in a cis configuration.[30] (ii) Compound II exhibits a doublet of closely spaced, broader bands at higher frequencies (2108 and 2129 cm^{-1}), consistent with the presence of two bridging cyanide groups in a cis configuration. (iii) Compound I shows two well-separated broad bands, one in the frequency range of the monodentate cyanides (2058 cm^{-1}) and the other in that of the bridged ones (2108 cm^{-1}).

A comparison of the absorption and emission spectra of the three complexes shows that, except for the shifts in the energy scale, all the spectra (Table I and Figures 1 and 3) look very similar. Even the low-temperature emission spectra (Figure 4), which have a relatively well-resolved vibrational structure, are almost exactly superimposable for the three complexes, with constant vibrational spacings. This shows that (i) cyanide bridging to the platinum moieties does not introduce new, low-energy, states in the system and (ii) cyanide bridging does not alter the relative energy ordering in the original chromophore to a sufficient extent to change the nature of the emitting state. While point i is largely as expected, point ii is worthy of mention, since Peterson and Demas[26] showed that excited-state protonation of the cyanide ligands could lead to a change in nature of the emitting state from d–π^* to π–π^*. Thus, for I and II the emitting state can be confidently assigned, as in the $Ru(bpy)_2(CN)_2$ case[24] as a Ru → bpy d–π^* "triplet" state.

The solvent shifts in both the room-temperature and low-temperature emission spectra (Table I and Figures 3 and 4) show a definite trend, decreasing from $Ru(bpy)_2(CN)_2$ through I to II, which actually exhibits an almost solvent-independent emission. This trend could be analyzed according to standard models[31] in terms of effective ground-state dipole moment of the $Ru(bpy)_2(CN)_2$ chromophore in the three complexes and of the change in dipole moment on going from the ground to the excited state. However, perhaps the simplest view is that taken long ago by Burgess[32,33] for analogous iron(II) chromophores, that the solvent effect (possibly via hydrogen bonding) is operating at the cyanide ends of the chromophore. As the cyanide groups are progressively engaged in bridging to the platinum moieties, the solvent effects decrease to vanishing.

The lifetimes of the emitting states exhibit a quite complicated pattern, as a function of the type of complex and of the solvent. This is not surprising, since the lifetime is expected to be a very sensitive function of the relative energetic situation of the various excited states of the $Ru(bpy)_2(CN)_2$ chromophore. In particular, the lifetime of the lowest emitting ^{3}(d–π^*) triplet state is expected to decrease with (i) decreasing energy of the emitting ^{3}(d–π^*) state (energy gap law), (ii) decreasing energy gap between the ^{3}(d–π^*) and the upper d–d states (due to an activated deactivation pathway, which is well established for $Ru(bpy)_3^{2+}$ and other Ru–diimine complexes[34–36]), and (iii) increasing the energy gap between the d–π^* and the upper π–π^* states (due to the decrease in ^{3}(π–π^*) character acquired via configuration mixing[26]). Changing the solvent and making cyanide bridges to platinum moieties may drastically affect the above sketched energetic situation. In fact, while the π–π^* levels of the chromophore should hardly be sensitive to these changes, increasing the solvent polarity and increasing the number of cyanide bridges certainly moves the d–π^* states toward higher energies. The effect of solvent polarity and cyanide bridge formation on the energy of the d–d state is less clearly predictable, although some increase in energy should

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be expected if the main effect is one of enhancing the π^*-acceptor ability of the cyanides.[26] A further factor potentially affecting the lifetimes is that introducing platinum atoms near to the chromophore is expected to increase the spin–orbit coupling, leading to a further weakening of the spin forbiddenness of several relevant transition. In view of the degree of complexity (and flexibility) of the picture, it does not seem worthwhile to make detailed speculations on the reason for the particular lifetime variations observed (Table I).

As far as the redox properties are concerned (Table I), the one-electron reduction potentials are almost constant, with a small increasing trend throughout the $Ru(bpy)_2(CN)_2$, I, and II series. This result is quite reasonable, if one considers that reduction in these types of complexes largely coresponds to reduction of a bipyridine ligand.[23] The small increase in reduction potentials along this series is most likely associated with the increasing overall positive charge of the complexes. As for the one-electron oxidation potentials, the substantial increase observed on going from $Ru(bpy)_2(CN)_2$ to I is as expected,[14,26] since oxidation in these complexes is essentially localized on the ruthenium center[23] and cyanide bridge formation efficiently drains electronic charge from the metal (or stabilizes the t_{2g} HOMOs). On the other hand, the inversion in the oxidation potentials on going from I to II is quite unexpected, in view of the regular variation in other properties (e.g., spectral shifts) connected with electronic effects of bridge formation on the metal orbitals. Tentatively, it could be suggested that the presence of two platinum centers in complex II introduces a new oxidizable center, possibly arising from Pt–Pt axial interactions.

Ground-state redox potentials are usually coupled with spectrosopic excitation energies to obtain theoretical values of the excited-state redox potentials.[1,37,38] This procedure relies on the identification of a definite zero–zero spectroscopic energy of the excited state and on the assumption that the differences in entropic terms between ground and excited state are negligible.[39] Applying this procedure to the complexes studied in this work presents some problems. At least in $Ru(bpy)_2(CN)_2$ and in I, the relevant transitions are highly polar ones. This is reflected not only in the solvent shifts (Table I and Figure 1) but also in the relatively high shifts between the structured, low-temperature emission maxima and the broad, room-temperature emission maxima (1700 and 1400 cm^{-1}, respectively, for $Ru(bpy)_2(CN)_2$ and I in aqueous solvent; to be compared, e.g., with 800 cm^{-1} for $Ru(bpy)_3^{2+}$). This is no doubt caused by room-temperature relaxation of the solvent to a situation adapted to the new excited-state polarity. A substantial part of the driving force for this relaxation must be entropic in nature so that enthalpy and free energy differences may not be safely interchangeable in these cases. Moreover, in these systems any zero–zero spectroscopic energy taken from emission spectra is likely to be a poor approximation to the enthalpic content of the excited state. In fact, the differnece in enthalpy between the excited and the ground states refers to a solvent-relaxed situation for both states, while low-temperature or room-temperature emission reflect ground-state or excited-state solvation, respectively, by virtue of the Franck–Condon principle.

As a consequence, the zero–zero spectroscopic energy from the structured low-temperature emission spectra represents an upper limit to the free energy content of the excited state, while the onset energy of the unresolved room-temperature emission spectra should set a lower limit for that. In Table III, zero–zero energies from low-temperature spectra have been used to calculate the excited-state redox potentials, with the understanding that the resulting values may be somewhat overestimated (to the maximum extent, in DMF, of ca. 0.07 V in the case of $Ru(bpy)_2(CN)_2$).[40]

The calculated excited-state redox potentials indicate that $Ru(bpy)_2(CN)_2$, I, and II[41] are all expected to behave as very powerful excited-state reductants (compare with $^*E_{1/2}(S^+/^*S) = -0.84$ V for the popular $Ru(bpy)_3^{2+}$ sensitizer[1]). The experiments carried out with the standard electron-acceptor methylviologen (Table II) indicate that the kinetic factors for the excited-state electron-transfer reaction

$$^*S + MV^{2+} \xrightarrow{k_q} S^+ + MV^+ \qquad (1)$$

where S stands for $Ru(bpy)_2(CN)_2$, I, or II are also quite good. In fact, the rate constants k_q are in all cases essentially diffusion controlled, as expected for substantially exoergonic, adiabatic electron-transfer reactions,[38] the variations in rates being easily accounted for by the changes in the electric charges of the reactants. Thermal back-electron-transfer reactions (eq 2) are also in the diffusion-controlled range

$$S^+ + MV^+ \xrightarrow{k_q} S + MV^{2+} \qquad (2)$$

(Table III). This is consistent with the lower than unity limit quantum yields (Table II) for the formation of kinetically free products in reaction 1, as a consequence of lower than unity cage escape yields.[2,42,43] Although the models for these effects[42,43] are not accurate enough for actual calculations, the steady increase in cage escape yield observed on going from $Ru(bpy)_2(CN)_2$ to I and II seems clearly to be the consequence of the increasing electric charge of the oxidized complex in this series.

In conclusion, this study shows that the $Ru(bpy)_2(CN)_2$ chromophore can be easily functionalzied via cyanide bridge formation by a suitable choice of the bonded moieties. If, as in the present case, these moieties are inert from the redox point of view, this functionalization does not destroy the original excited-state properties of the chromophore, its effect being limited to some alteration of the lifetime, energy, and redox properties of the excited state. Much more profound consequences are expected when the bonded moieties behave as redox active sites. In this event, the vectorial nature of the excitation in the $Ru(bpy)_2(CN)_2$ chromophore might turn out to play a major role in determining the occurrence of specific intramolecular electron-transfer processes. Studies in this direction are in progress.

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(41) If, as tentatively suggested above, the relatively low ground-state oxidation potential of II (0.86 V) may be related to the presence of some low-energy oxidizable site other than Ru(II), the question arises as to whether this potential is appropriate for calculating the excited-state redox potential of this species. Thermodynamically, the use of this potential is correct. However, it may well be that oxidation at Ru(II) is kinetically favored relative to that of a more remote site in the oxidative quenching of the excited state. In that case, a more anodic (unknown) ground-state potential should be used in order to obtain a kinetically significant redox potential for the excited state of II, which would thus turn out to be a poorer effective excited-state reductant than estimated on thermodynamic grounds.

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Acknowledgment. We are indebted to Professor P. Courtot for a collaboration that triggered this work. We thank Dr. M. T. Indelli for her assistance in the laser work and for helpful discussions. We are also grateful to Professors F. Fagioli and A. De Battisti for help with elemental analyses and cyclic voltammetry. The work was supported by the Commission of the European Communities (Contract ESD-026-I) and by the Consiglio Nazionale delle Ricerche (Progetto Finalizzato Chimica Fine e Secondaria, Tematica Ah1).

Registry No. I, 88360-14-9; II, 88377-85-9; [Pt(dien)Br]Br, 15633-95-1; $Pt(dien)(H_2O)^{2+}$, 48102-16-5; $Ru(bpy)_2(CN)_2$, 20506-36-9; MV^{2+}, 1910-42-5.

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Electronic Excited States of Arylphosphine Complexes of Copper(I) Halides

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Received June 9, 1983

Perturbation of the electronic transitions of aromatic phosphine ligands upon coordination to copper(I) has been investigated. The lowest electronic transition $(l \rightarrow a_\pi)$ of arylphosphines associated with an electron excitation from the lone electron pair of the phosphorus to an antibonding phenyl π orbital can be enhanced by coordination to copper(I). The phosphine–copper(I) electronic transition is classified as a $\sigma,d \rightarrow a_\pi$ transition. The transition is described as an electron excitation from the metal–phosphorus bond with a concerted donation of electron density from the metal to the phosphorus via d–d orbital back-bonding. The photophysical properties of the methyldiphenylphosphine complexes of the isoelectronic d^{10} metals Ni(0), Cu(I), and Zn(II) are shown to be consistent with the $\sigma,d \rightarrow a_\pi$ classification. The Ph_3P and $MePh_2P$ complexes of CuX have phosphorescence lifetimes of 2–6 ms which are decreased from those of the free ligands where the lifetimes are 17 ms for Ph_3P and 40 ms for $MePh_2P$. By comparison, the phosphorescence lifetime of $(MePh_2P)_2ZnCl_2$ and $(MePh_2P)HCl$ are 55 and 49 ms, respectively.

Introduction

Copper(I), having an electronic d^{10} structure, exhibits no low-energy ligand-field excited states.[1-3] Cuprous compounds are normally white[4] unless color results from an internal ligand or charge-transfer excitation band. The few articles that have suggested electronic transition assignments for phosphine–cuprous halide complexes[3,5-7] all seem to agree that the electronic transitions of the complexes are internal ligand processes that are only slightly perturbed by the bonding of the ligand to the metal. Since the electronic transitions are considered internal ligand processes, the same confusion recently described for the electronic transition assignments of the aromatic phosphines[8a,b] also appears in the literature for the arylphosphine–cuprous halide complexes. Our study of the solution dissociation properties of L_3CuX (L = Ph_3P, $MePh_2P$; X = Cl, Br, I) complexes[8a,c] indicated that the dissociation of the complexes has apparently masked a proper interpretation of the effect of metal coordination on the electronic transitions of the arylphosphines. The results of this study clearly show that coordination of arylphosphines to copper(I) halides has a pronounced effect on the lowest excited electronic state transition $(l \rightarrow a_\pi)$[8a,b] of the ligands.

Experimental Procedures

Materials and Synthesis of Inorganic Complexes. Materials and the synthesis of the Ph_3P and $MePh_2P$ complexes of CuX were the same as described previously,[8a,c]

$[Ph_2P(CH_2)_2PPh_2]CuCl$. The (diphos)CuCl complex, diphos = $Ph_2P(CH_2)_2PPh_2$, appears in the literature with the empirical formula given;[9] however, osmometry data indicate that the complex actually exists in the trimer form.[9a] The molecular weight of 1500 measured in benzene at 37 °C during this study (empirical formula weight equals 497) is in agreement with the literature. The exact structure of the trimer form is still not known. In order to be consistent with the current literature, the diphos complex will be referred to in this article by the empirical formula.

$(MePh_2)_2ZnCl_2$. This complex was prepared in the same manner as the copper complexes; mp 179–181 °C. Anal. calcd for $C_{26}H_{26}P_2ZnCl_2$: C, 58.30; H, 4.89; P, 11.56; Cl 13.24. Found: C, 58.43; H, 5.01; P, 11.69; Cl 13.03. $(Ph_3P)_2ZnCl_2$ has been reported and studied extensively;[10] however, no reference could be found for $(MePh_2P)_2ZnCl_2$.

$(MePh_2)HCl$. The protonated phosphine is assumed to be the product made by bubbling a 5–10-mL phosphine solution (benzene or EPA (ethyl ether–isopentane–ethanol)) with dry HCl for 1–2 min. The HCl was dried just prior to use by bubbling it through concentrated sulfuric acid. From the large change in the absorption spectra (see Results) essentially all of the phosphine was probably in a protonated form. No analysis or isolation of the salt was attempted. The phosphine solutions had to be rather dilute (less than approximately 5×10^{-4} M) or a white precipitate would be formed while the solution is bubbled with the dry HCl.

Spectra and Phosphorescence Lifetimes. The various spectra reported and phosphorescence lifetime measurements were accomplished with the same procedures as described for the arylphosphines.[8a,b] The 77 K absorption spectra were obtained by using the square quartz-tip

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