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LETTER

Spectroscopic and Electrochemical Investigation of Strongly Luminescent Homobinuclear Re(I) Complexes

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Binuclear metal complexes have received considerable attention in recent years for a variety of reasons, including their potential utility as novel photosensitizers in energy storage schemes, as multi-electron redox agents, and as models for the study of intramolecular energy and electron transfer [1–9]. Although much of the published work involves ruthenium(II) polypyridines [1–4], there have been scattered reports regarding the spectroscopic and electrochemical properties of binuclear complexes containing other metals [5–9].

The photophysical properties of binuclear rhenium complexes are particularly intriguing, since few of these complexes are luminescent in room-temperature fluid solution [8, 9], in sharp contrast to the highly emissive nature of related monometallic species such as Re(bpy)$(CO)_3Cl$ (bpy = 2,2′-bipyridine) [10]. For example, $[Cl(CO)_3Re(bpym)Re(CO)_3Cl]$ (bpym = 2,2′-bipyrimidine) was found to be non-emissive even as a low-temperature solid, despite the fact that Re(bpym)$(CO)_3Cl$ *did* display emission under such conditions [7]. The lack of emission from the 'dimer' was attributed by the authors to the presence of a low-lying non-emissive metal-to-metal charge-transfer (MMCT) excited state. The absorption spectra also reveal substantial electronic differences between the binuclear complex and the corresponding mononuclear species, although no evidence for a MMCT state was observed [7].

We wish to report the synthesis of a series of bimetallic rhenium(I) complexes having the general formula $[(CO)_3(bpy)Re(L)Re(bpy)(CO)_3]^{2+}$, where L represents a pyridine-based bridging ligand such as pyrazine (pyz), 4,4′-bipyridine (4,4′-bpy), 1,2-bis(4-pyridyl)ethane (bpa), or 1,3-bis(4-pyridyl)propane (bpp). Unlike most earlier examples of binuclear rhenium complexes of this type, several of these new compounds are strongly luminescent even in room-temperature fluid solution. The photophysical properties of these molecules can be qualitatively understood using a simple model based in part on the energy-gap law [11].

Experimental

fac-Re(bpy)$(CO)_3Cl$ and *fac*-[Re(bpy)$(CO)_3(CH_3CN)](CF_3SO_3)$ were prepared according to established literature procedures [10–12]. The series of mononuclear complexes denoted by *fac*-[Re(bpy)$(CO)_3(L)](CF_3SO_3)$ (L = pyz, 4,4′-bpy, bpa and bpp) were synthesized by the direct reaction of an approximately ten-fold excess of the appropriate ligand with *fac*-[Re(bpy)$(CO)_3(CH_3CN)](CF_3SO_3)$ in refluxing THF solution over a period of 3 h. After cooling, ether was added to the solution in a dropwise fashion and the bright yellow precipitate which formed was collected by filtration, washed extensively with ether, and subsequently purified by recrystallization from CH_2Cl_2/ether.

The binuclear complexes $[(CO)_3(bpy)Re(L)Re(bpy)(CO)_3](CF_3SO_3)_2$ (L = pyz, 4,4′-bpy, bpa, bpp) were conveniently prepared by refluxing a THF solution containing a 2:1 ratio of *fac*-[Re(bpy)$(CO)_3(CH_3CN)](CF_3SO_3)$ and the desired bridging ligand for 5 to 6 h. During the course of this reaction, a yellow precipitate was formed, which was then collected, washed with THF and ether, and recrystallized from acetone/ether. The bimetallic nature of each product was confirmed by elemental analysis and NMR spectroscopy.

Absorption spectra were recorded on an AVIV Model 14DS spectrophotometer equipped for computerized data acquisition. Steady-state emission spectra were determined with either an Aminco-Bowman spectrophotofluorometer or a Spex Fluorolog system. The electrochemical experiments were carried out in freshly distilled, oxygen-free dimethyl sulfoxide (DMSO) containing dry tetraethylammonium hexafluorophosphate (TEAH) (0.1 M) as electrolyte. The working electrode was either a glassy carbon or a Pt disk, and the data were collected using an EG & G PAR Model 273 potentiostat/galvanostat. NMR spectra were obtained on a Varian Gemini-200 200 NMR spectrometer.

Results and Discussion

NMR Spectra

The ^1H NMR spectra of all compounds reported here are readily interpretable, and the integrated peak intensities closely match expected values. In general, the spectral pattern observed for the binuclear

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TABLE 1. Spectroscopic and electrochemical data for mononuclear and binuclear Re(I) complexes

Complex	MLCT absorption maxima[a], (nm) (ϵ, M^{-1} cm^{-1})	Emission maxima[b] (nm)	$E_{1/2}^{red}$ (1)[c] (V vs. SSCE)	$E_{1/2}^{red}$ (2)[c] (V vs. SSCE)	$E_{1/2}^{red}$ (3)[c] (V vs. SSCE)
$[Re(bpy)(CO)_3(pyz)]^{2+}$	346(sh) (5.37×10^3)	552	−1.11	−1.27	
$[Re(bpy)(CO)_3(4,4'\text{-}bpy)]^+$	348(sh) (7.39×10^3)	563	−1.09	−1.27	
$[Re(bpy)(CO)_3(bpa)]^+$	345 (3.89×10^3)	564	−1.09	−1.30	
$[Re(bpy)(CO)_3(bpp)]^+$	347 (4.49×10^3)	567	−1.09	−1.30	
$[(CO)_3(bpy)Re(pyz)Re(bpy)(CO)_3]^{2+}$	347 (1.78×10^4), 380(sh) (1.41×10^4)	d	−0.66	−1.12	−1.28
$[(CO)_3(bpy)Re(4,4'\text{-}bpy)Re(bpy)(CO)_3]^{2+}$	350 (1.74×10^4)	563	−0.96	−1.10	−1.26
$[(CO)_3(bpy)Re(bpa)Re(bpy)(CO)_3]^{2+}$	347 (7.44×10^3)	567	−1.08	−1.30	
$[(CO)_3(bpy)Re(bpp)Re(bpy)(CO)_3]^{2+}$	349 (8.56×10^3)	566	−1.08	−1.31	

[a] In acetonitrile at 25 °C; sh = shoulder. [b] Uncorrected spectra, in acetonitrile at 25 °C. [c] In DMSO/0.1 M tetraethylammonium hexafluorophosphate, 25 °C, glassy carbon disk working electrode; SSCE = saturated sodium Calomel electrode. [d] No emission detected.

complexes closely resembled that seen for the corresponding free ligand, while the mononuclear species displayed much more complex behavior. In the case of the pyrazine-bridged complex, some decomposition was noted in coordinating solvents over a period of several hours, and thus all necessary physical measurements were performed within 20 min of the preparation of a fresh sample solution. The mononuclear complex $[Re(bpy)(CO)_3(pyz)]^+$ also undergoes decomposition, but at a rate which is much slower than that observed for the binuclear complex. No decomposition was observed, at least on a timescale of several weeks, for any of the complexes containing bridging ligands other than pyrazine.

Absorption Spectra

In both mononuclear and binuclear complexes of this type, the lowest energy absorption is expected to arise from metal-to-ligand charge-transfer (MLCT) excitation [7–12], and our results are in accord with this expectation (Table 1). However, while only minor changes are observed upon attachment of the second metal center to the bpa and bpp bridging ligands, much larger effects are seen when L is pyz or 4,4′-bipyridine. Indeed, $[(CO)_3(bpy)Re(pyz)Re(bpy)(CO)_3]^{2+}$ exhibits a broad absorption at significantly lower energy than the lowest energy band seen in the spectrum of $[Re(bpy)(CO)_3(pyz)]^+$ (Fig. 1). This result suggests that coordination of a second Re(I) site to a small ligand such as pyrazine results in a substantial decrease in the electron density on the bridging ligand, and the Re → pyz MLCT state drops well below the Re → bpy MLCT level, a notion which is consistent with the electrochemical results presented below. It is worth noting that similar red shifts of the M → bpym absorption bands have been previously noted for species such as $[(bpy)_2Ru(bpym)Ru(bpy)_2]^{4+}$ [1] and $[Cl(CO)_3Re(bpym)Re(CO)_3Cl]$ [7]. This effect has been discussed in terms of the perturbation of the π^* orbital on bpym caused by attachment of the second metal for a series of binuclear ruthenium(II) complexes [1].

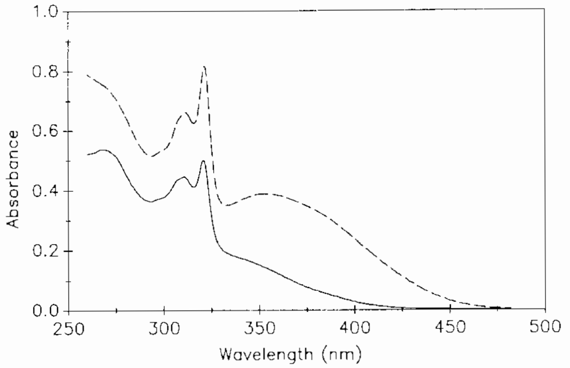


Fig. 1. Electronic absorption spectra recorded in CH_3CN: (——) $[Re(bpy)(CO)_3(pyz)]PF_6$; (– – –) $[(CO)_3(bpy)Re(pyz)Re(bpy)(CO)_3](CF_3SO_3)_2$.

Electrochemistry

The electrochemistry of these complexes reveals some interesting features. Each complex displays two essentially reversible reductions, at roughly −1.1 and −1.3 V versus SSCE. These processes are attributed to the reduction of 2,2′-bipyridine and of Re, respectively [10–12], and the measured potentials remain relatively constant throughout this series of complexes (Table 1). For the binuclear complexes, the reductions at −1.1 and −1.3 V are net two-electron processes, and each is probably best described as two closely spaced one-electron reductions originating from weakly interacting mononuclear $-Re(bpy)(CO)_3^+$ fragments.

Two of the binuclear complexes, $[(CO)_3(bpy)Re(pyz)Re(bpy)(CO)_3]^{2+}$ and $[(CO)_3(bpy)Re(4,4'\text{-}bpy)Re(bpy)(CO)_3]^{2+}$, exhibit an additional reversible reduction at more positive potentials (Fig. 2). In these cases, this first reduction is found to be a one-electron process which we have tentatively assigned to reduction of the bridging ligand. Thus, while the reduction potentials of the 2,2′-bipyridine ligand and the Re center are virtually unchanged by the attachment of the second metal center, the reduction of the bridging ligand can be greatly facilitated, at least for the two shortest bridges (pyz and 4,4′-bpy). In other words, the π^* orbital energy of the bridge is decreased upon metal coordination, and the magnitude of the perturbation caused by the second metal is largest for small, fully conjugated bridging ligands [1]. On the other hand, the two pyridine moieties appear to act essentially independently in the binuclear complexes containing bpa or bpp, owing to the 'insulating' nature of these bridging ligands [9]. The loss of the anodic wave of the $pyz/pyz^{\cdot -}$ couple in $[(CO)_3(bpy)Re(pyz)Re(bpy)(CO)_3]^{2+}$ which occurs upon extension of the scan range to −1.5 V is dependent on scan rate, and is most likely due to cleavage of the Re–pyz bond following rhenium reduction [9, 10].

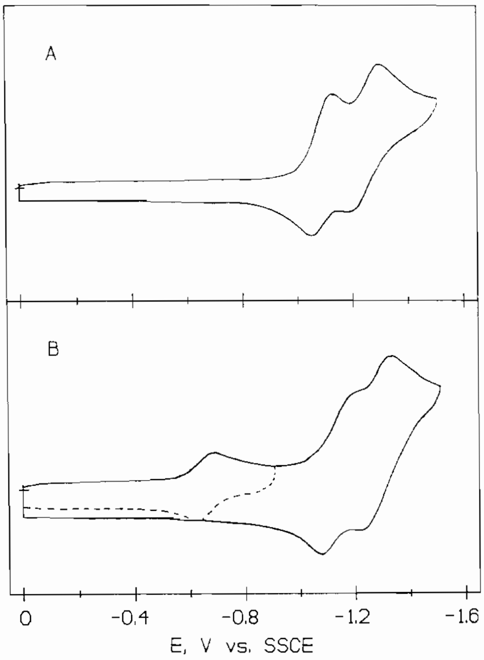
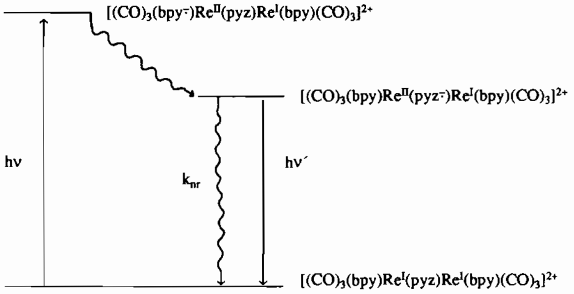


Fig. 2. (A) Cyclic voltammogram for $[Re(bpy)(CO)_3(pyz)]PF_6$ in DMSO/0.1 M tetraethylammonium hexafluorophosphate (TEAH); scan rate = 10 mV/s. (B) Cyclic voltammogram for $[(CO)_3(bpy)Re(pyz)Re(bpy)(CO)_3](CF_3SO_3)_2$ in DMSO/0.1 M TEAH; scan rate = 50 mV/s.

Emission Properties

With the exception of $[(CO)_3(bpy)Re(pyz)Re(bpy)(CO)_3]^{2+}$, all of the complexes display strong luminescence in room-temperature fluid solution. The emission spectra are broad and featureless, consistent with an MLCT origin, and based on these results and those of previous studies, we attribute the emission to the Re → bpy MLCT excited state. However, we cannot rule out emission from the Re → 4,4′-bpy MLCT level in the binuclear complex $[(CO)_3(bpy)Re(4,4'\text{-}bpy)Re(bpy)(CO)_3]^{2+}$, since the two important MLCT states in this complex appear to have similar energies. In any event, the key observation is the lack of detectable emission from the pyrazine-bridged bimetallic complex, at least within our accessible wavelength range (300–750 nm). Such behavior is readily explained by a simple energy diagram as in Scheme 1. In $[(CO)_3(bpy)Re(pyz)Re(bpy)(CO)_3]^{2+}$, the lowest energy excited state is the Re → pyz MLCT level, and this state is rapidly populated by internal conversion after initial excitation into the Re → bpy MLCT band. The relatively low energy of this excited state results in a substantial increase of the non-radiative decay rate (k_{nr}) as described by the energy-gap law [11], and a corresponding decrease in the quantum yield for emission.

The energy-gap law also serves to explain the lack of emission from $[Cl(CO)_3Re(bpym)Re(CO)_3Cl]$, since the presence of two rhenium centers bound to the bridging bpym ligand drastically lowers the energy of the π^* orbital on bpym relative to $Re(bpym)(CO)_3Cl$. This lower energy is manifested



Scheme 1.

in a much longer wavelength MLCT absorption [7], more positive reduction potential [9], and (presumably) reduced emission quantum yield. Importantly, no low-lying MMCT state need be proposed. The present model is more attractive than that suggested by Vogler and Kisslinger [7], since electrochemical and spectral measurements indicate that the intermediate MMCT state postulated by these authors actually lies at considerably higher energy than the Re → bpym MLCT level [9].

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