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Bipyrimidine-bridged Rhenium(I)/Rhenium(I) and Ruthenium(II)/Rhenium(I) Complexes. Synthesis, Electronic Absorption and Emission Spectra

A. VOGLER* and J. KISSLINGER

Universität Regensburg, Institut für Anorganische Chemie, Universitätsstr. 31, D-8400 Regensburg, F.R.G.

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Abstract

The binuclear complexes [Cl(OC)$_3$Re^I(bipym)Re^I(CO)$_3$Cl] (bipym = 2,2′-bipyrimidine), [(bipy)$_2$Ru^{II}(bipym)Re^I(CO)$_3$Cl](PF$_6$)$_2$ (bipy = 2,2′-bipyridine) and their mononuclear component [Re(bipym)(CO)$_3$Cl] were prepared. The electronic absorption spectra of these complexes display low-energy Re(I) $\rightarrow \pi^*$(bipym) and Ru(II) $\rightarrow \pi^*$(bipym) charge transfer (CT) bands. While [Re(bipym)(CO)$_3$Cl] shows a strong emission from its lowest CT state, the dimer [Cl(OC)$_3$Re(bipym)Re(CO)$_3$Cl] is not luminescent. The cation [(bipy)$_2$Ru(bipym)Re(CO)$_3$Cl]$^{2+}$ emits from the lowest-energy Ru $\rightarrow$ bipym CT state. The emission behavior of the binuclear complexes is described in terms of intramolecular excited state electron or energy transfer.

Introduction

The electronic interaction between the mononuclear components of ligand-bridged binuclear complexes has been investigated extensively during recent years. If the two metal centers are weakly coupled both complex fragments can be considered as independent chromophores [1]. In addition, optical metal-to-metal charge transfer (MMCT) or intervalence (IT) transitions may occur when one metal is reducing and the other one oxidizing [1–8]. In this case electronic excitation involves both chromophores simultaneously. Light absorption by one chromophore can be followed by energy [9–13] or electron transfer [11, 14–22] to the other one. An excited state electron transfer between both chromophores may also occur if the two mononuclear components are rather redox inert in the ground state [21]. Photochemical reactions of binuclear complexes following intramolecular energy [9, 10, 12, 13] or electron transfer [14–17, 23–25] have received much attention during recent years.

A variety of bridging ligands was used for the design of appropriate binuclear complexes. Many rather stable complexes are formed with 2,2′-bipyrimidine (bipym) which coordinates as a bidentate bridging ligand to both metals [13, 26]. We report here on the synthesis, electronic absorption and emission spectra of the binuclear complexes [Cl(OC)$_3$Re(I)(bipym)Re(I)(CO)$_3$Cl], [(bipy)$_2$Ru(II)(bipym)Re(I)(CO)$_3$Cl]$^{2+}$ (bipy = 2,2′-bipyridine) and their mononuclear constituent [Re(I)(bipym)(CO)$_3$Cl]. The emission behavior of the binuclear compounds is discussed in terms of excited state electron or energy transfer between the mononuclear components.

Experimental

Materials

Spectrograde dimethylsulfoxide (DMSO) from Merck (Uvasol) was used as solvent for measuring electronic absorption spectra. The ligand 2,2′-bipyrimidine (Ventron) was a commercial reagent grade product. The compounds [Ru(bipy)$_2$(bipym)](PF$_6$)$_2$ [27, 28] and [Re(CO)$_5$Cl] [29] were prepared according to published procedures.

Syntheses

[Re(bipym)(CO)$_3$Cl]

0.75 g of [Re(CO)$_5$Cl] and 0.35 g of bipym were dissolved in 40 ml of toluene. Upon heating the color of the solution changed from yellow to orange and the crude product precipitated. It was collected by filtration, washed with toluene and ether, and dried. For purification the product was heated in 30 ml of acetone and then filtered. To the filtrate 150 ml of hexane were added. The mixture was cooled to −10 °C. The yellow material was collected by filtration, washed with hexane, and dried under vacuum: yield 0.33 g. *Anal.* Calc.: C, 28.48; H, 1.3; N, 12.08. Found: C, 28.36; H, 1.26; N, 12.09%.

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*Author to whom correspondence should be addressed.

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[Cl(OC)$_3$Re(bipym)Re(CO)$_3$Cl]

0.19 g of [Re(bipym)(CO)$_3$Cl] and 0.29 g of [Re(CO)$_5$Cl] were heated to boiling in 20 ml of toluene for 10 min. The solution was filtered and poured into 500 ml of boiling acetone. After filtration the volume of the solution was reduced to about 10 ml by vacuum evaporation. A red–brown solid precipitated. It was washed with ether and dried under vacuum: yield 0.29 g. *Anal.* Calc.: C, 21.8; H, 0.8; N, 7.8. Found: C, 22.3; H, 0.8; N, 6.9%.

[(bipy)$_2$Ru(bipym)Re(CO)$_3$Cl](PF$_6$)$_2$

0.43 g of [Ru(bipy)$_2$(bipym)](PF$_6$)$_2$ and 0.18 g of [Re(CO)$_5$Cl] were refluxed in 50 ml of acetone for 12 h. The volume of the solution was reduced to 5 ml by vacuum evaporation. Upon addition of toluene the dark-brown compound precipitated. It was collected by filtration, washed with toluene, and dried under vacuum: yield 0.14 g. *Anal.* Calc.: C, 31.9; H, 1.9; N, 9.6. Found: C, 32.0; H, 2.0; N, 9.0%.

Instrumentation

Electronic absorption spectra were obtained on a Varian-Techtron Super Scan 3 Recording Spectrophotometer. Emission spectra were recorded on a Hitachi 850 Fluorescence Spectrophotometer.

Results and Discussion

Syntheses

One of the mononuclear components, [Ru(bipy)$_2$(bipym)]$^{2+}$, was prepared according to Hunziker and Ludi [27]. The synthesis of the other constituent, [Re(bipym)(CO)$_3$Cl], was accomplished by heating the ligand bipym and [Re(CO)$_5$Cl] in toluene. At room temperature the crude product precipitated. Recrystallization from acetone/hexane yielded the yellow analytically pure material.

The neutral binuclear complex [Cl(OC)$_3$Re(bipym)Re(CO)$_3$Cl] was formed by boiling [Re(bipym)(CO)$_3$Cl] and [Re(CO)$_5$Cl] in toluene. The solution was added to boiling acetone. After filtration the solution was partially evaporated under vacuum. The pure compound precipitated as a red–brown powder.

The binuclear cation [(bipy)$_2$Ru(bipym)Re(CO)$_3$Cl]$^{2+}$ was obtained by refluxing [Ru(bipy)$_2$(bipym)](PF$_6$)$_2$ and [Re(CO)$_5$Cl] in acetone for 12 h. Upon addition of toluene the salt [(bipy)$_2$Ru(bipym)Re(CO)$_3$Cl](PF$_6$)$_2$ precipitated as a dark-brown material. Further purification was not required.

Absorption Spectra

The absorption spectrum of [Re(bipym)(CO)$_3$Cl] in DMSO displays its longest-wavelength band at λ_{max} = 371 nm (ϵ = 2967). This band is assigned to a metal-to-ligand (ML) CT transition from Re(I) to bipym(π^*). Similar complexes such as [Re(1,10-phenanthroline)(CO)$_3$Cl] show this CT band at comparable energies [30].

In the case of the binuclear complex [Cl(OC)$_3$Re(bipym)Re(CO)$_3$Cl] in DMSO, this MLCT band from Re(I) to the bridging bipym ligand is shifted to longer wavelength at λ_{max} = 450 nm (ϵ = 4283) tailing out at about 600 nm. Such a red shift is generally observed when ligands such as pyrazine or bipyrimidine undergo coordination to a second metal center by the formation of binuclear complexes [13, 27, 28, 31].

The absorption spectrum of [(bipy)$_2$Ru(bipym)Re(CO)$_3$Cl]$^{2+}$ in DMSO is presented in Fig. 1. On the basis of the arguments given above, this spectrum should not be composed of the absorption spectra of the mononuclear components [Ru(bipy)$_2$(bipym)]$^{2+}$ and [Re(bipym)(CO)$_3$Cl]. Rather, it is expected to be approximately a superimposition of the spectra of both binuclear complexes [Cl(OC)$_3$Re(bipym)Re(CO)$_3$Cl] and [(bipy)$_2$Ru(bipym)Ru(bipy)$_2$]$^{4+}$. The absorption spectrum of the latter displays the Ru(II)-to-bipy CT band at λ_{max} = 408 nm while the Ru(II)-to-bipym CT absorption occurs at λ_{max} = 606 nm [27] (592 nm [28]) including a shoulder at 560 nm [27] (Fig. 2 of ref. 27). It is apparent that this spectrum is rather similar but not identical to that of Fig. 1. This similarity suggests that the absorption spectrum of [(bipy)$_2$Ru(bipym)Re(CO)$_3$Cl]$^{2+}$ consists essentially of the Ru(II)-to-bipy (λ_{max} = 420 nm; ϵ = 8730) and Ru(II)-to-bipym (λ_{max} = 556 nm; ϵ = 2167) CT bands. However, it is assumed that the deviation of the spectrum of the binuclear Ru/Re complex is mainly caused by a modification in the region between 450 and 600 nm due to the presence of the Re(I)-to-bipym CT band as it occurs in the case of the Re/Re dimer.

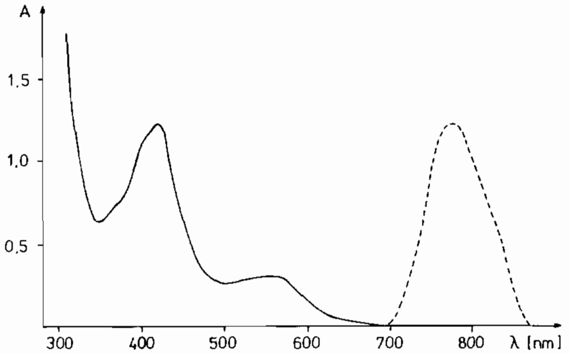


Fig. 1. Electronic absorption and emission spectrum of [(bipy)$_2$Ru(bipym)Re(CO)$_3$Cl](PF$_6$)$_2$. Absorption (——): 1.41 × 10^{-4} M complex in DMSO, 298 K, 1 cm cell; emission (- - - - -): solid complex, 77 K, λ_{exc} = 480 nm, intensity in arbitrary units.

This absorption of the binuclear Ru/Re complex is apparently not intense enough to show up as a distinct maximum.

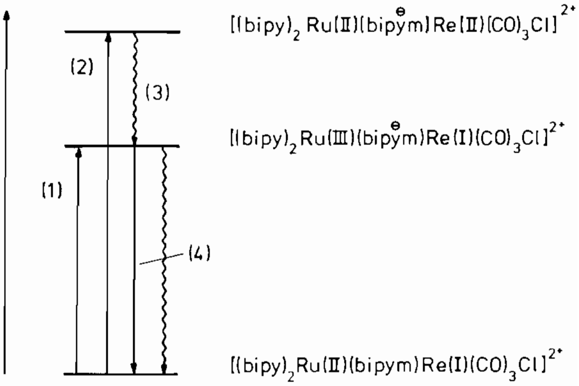
Emission Spectra

All emission spectra were recorded for samples of the solid complexes since luminescence of solutions was much weaker and sometimes hard to detect. Irrespective of the exciting wavelength, the mononuclear complex $[Re(bipym)(CO)_3Cl]$ shows a strong emission at $\lambda_{max} = 567$ nm even at room temperature. Compared to similar compounds such as $[Re(1,10\text{-phenanthroline})(CO)_3Cl]$ [30], the emitting state of $[Re(bipym)(CO)_3Cl]$ is certainly the lowest Re(I)-to-bipym CT state.

The dimer $[Cl(OC)_3Re(bipym)Re(CO)_3Cl]$ does not show any detectable emission in the solid state or in low-temperature glasses even at temperatures as low as 4 K [31]. This observation is rather unusual because other binuclear complexes with comparable electronic structures such as $[(OC)_5W(pyrazine)W(CO)_5]$ [32] or $[(bipy)_2Ru(bipym)Ru(bipy)_2]^{4+}$ [27] undergo emission from their lowest-energy metal-to-bridging-ligand CT states. We suggest that an excited state of a different origin lies below the Re-to-bipym CT state and quenches the CT emission of $[Cl(OC)_3Re(bipym)Re(CO)_3Cl]$. The only candidate for such an intervening excited state must be associated with the binuclear structure. Otherwise $[Re(bipym)(CO)_3Cl]$ should also not emit. It seems possible that the absence of emission of the dimer is due to a low-energy Re(I)-to-Re(I) IT state. An optical IT band was not detected in the absorption spectrum.

But if this band is of low intensity it could be obscured by the long-wavelength MLCT bands. Nevertheless, a Re(I)-to-Re(I) IT transition generating Re(II) and Re(0) in the excited state may occur at reasonable low energies. Re(II) is well known to be formed in Re(I)-to-ligand CT excited states [30]. Re(0) exists in unstable intermediates such as $Re(1,10\text{-phenanthroline})(CO)_3$ radicals which can be formed photochemically [33].

Independent of the excitation wavelength, the binuclear cation $[(bipy)_2Ru(bipym)Re(CO)_3Cl]^{2+}$ shows an emission at $\lambda_{max} = 774$ nm (Fig. 1) which can be detected only at low temperatures (77 K). This luminescence appears at almost the same energy as that of $[(bipy)_2Ru(bipym)Ru(bipy)_2]^{4+}$ at $\lambda_{max} = 769$ nm [27]. It is concluded that in both cases the lowest-energy Ru(II)-to-bipym CT state undergoes the observed emission. Light absorption by $[(bipy)_2Ru(bipym)Re(CO)_3Cl]^{2+}$ in the region between 450 nm and 600 nm should lead partially to the population of a Re(I)-to-bipym CT excited state as discussed above. This state is then apparently deactivated to the emitting Ru(II)-to-bipym CT excited state. This deactivation process can be explained as an energy transfer between both mononuclear components of $[(bipy)_2Ru(bipym)Re(CO)_3Cl]^{2+}$ according to Scheme 1. The Re(I)-to-bipym CT state which is reached by direct light absorption (2) is located on the mononuclear constituent $[(bipym)Re(CO)_3Cl]$. By energy tranfer (3) the Ru(II)-to-bipym CT state is populated. The energy is thus transferred to the second component $[(bipy)_2Ru(bipym)]^{2+}$ which undergoes emission (4) to the ground state. Of course, the emitting state may also be populated by direct light absorption (1). Interestingly, the energy transfer (3) can also be described as an intramolecular excited state electron transfer from Ru(II) to Re(II). Related observations on excited state metal-to-metal electron transfer in polynuclear metal complexes were recently reported by the research groups of F. Scandola [22] and T. J. Meyer [21].



Scheme 1.

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