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A Bibenzimidazole-Containing Ruthenium(II) Complex Acting as a Cation-Driven Molecular Switch

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Introduction

Multinuclear ruthenium polypyridyl complexes are currently the subject of extensive investigations, their photophysical properties making them ideal components for photochemically and electrochemically driven molecular devices.[1] Among these compounds, mononuclear ruthenium complexes containing biimidazole or bibenzimidazole (bibzimH_2) type ligands[2] have been shown to be excellent building blocks for the synthesis of heteronuclear complexes of the type $\{(bpy)_nRu[(bibzim)M(bpy)_2]_{3-n}\}^{m+}$ (M = Ru, Os, Ni, Co).[3−5] This behavior makes these complexes prime candidates for application as luminophores for the detection of metal ions. The luminophore approach to the development of sensors has been widely used.[6] Ruthenium polypyridyl complexes have been proposed as luminescent sensors for the detection of anions.[7]

In this contribution, we wish to report the interaction of the nonluminescent compound [Ru(tbbpy)$_2$(bibzim)], **1** (see Figure 1), with a series of metal ions in solution. The results obtained show that the emission of **1** is switched on by the presence of metal ions such as Zn(II), Mg(II), and Cu(I). It is also shown that both the emission intensity and the emission wavelength are dependent on the concentration and the nature of the metal ion. Comparable results regarding the tuning of the emission maxima were recently obtained for substituted phenanthrolines.[8] To the best of our knowledge, there is only one other example where the emission intensity of a ruthenium complex is increased by binding of another metal.[9] The X-ray structure of **1** and of its protonated analogue [Ru(tbbpy)$_2$(bibzimH_2)]$^{2+}$, **2**, are also reported.

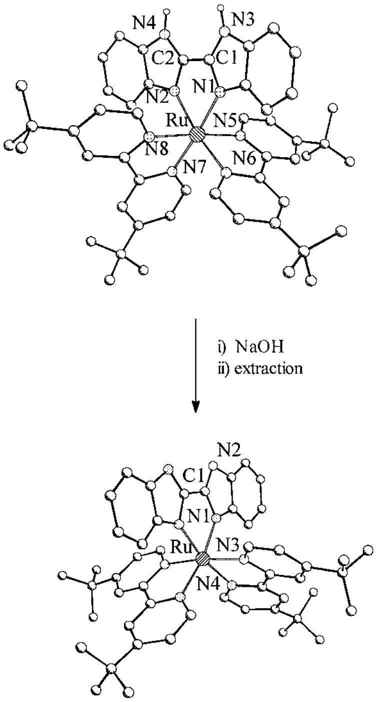

Figure 1. Synthesis of **1** from **2**. Anions, solvent molecules, and protons, except for the N3 and the N4 hydrogen in **2**, omitted from the X-ray structures for clarity.

Experimental Section

Methods and Materials. All synthetic work was performed using Schlenk techniques. Emission and absorption spectra were recorded using septum-equipped luminescent cells (Hellma). THF was dried and distilled over sodium/benzophenone, CH_3CN was dried over CaH_2 and distilled, and all other solvents were distilled prior to use. NMR spectra were recorded using Bruker 400 and 200 MHz spectrometers. UV−vis spectra were obtained using a Varian Cary 1 UV−vis or a Shimadzu UV 3100 UV−vis−NIR spectrometer. Emission spectra were not corrected and were recorded using a Perkin-Elmer LS50B spectrometer equipped with a Hamamatsu R928 red-sensitive detector. Luminescent lifetimes were measured by employing a Spectra Physics Nd:YAG frequency-tripled, Q-switched laser as the excitation source, coupled in a right-angled configuration with an Oriel iCCD. Laser power was measured as 30 mJ/20 ns pulse. IR spectra were recorded using a Perkin-Elmer 2000 FT-IR spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the University Jena. $RuCl_3 \cdot 3H_2O$, 4-*tert*-butylpyridine, $MgCl_2$, $ZnCl_2$, $ZnEt_2$, 1,2-diaminobenzene (Aldrich), oxamide (Fluka), $Cu(CH_3CN)_4BF_4$, and $Pd(CH_3CN)_2Cl_2$ (ABCR) were used as purchased without further purification. Ru(tbbpy)$_2$Cl$_2$,[10] tbbpy,[10] and bibzimH_2[11] were prepared by literature methods.

Synthesis of [Ru(tbbpy)$_2$(bibzimH$_2$)]Cl$_2$ (2). The synthesis was performed using standard procedures[2] with 265 mg (1.13 mmol) of bibzimH_2 and 510 mg (0.71 mmol) of Ru(tbbpy)$_2$Cl$_2$. Crystals of **2** suitable for X-ray studies were grown from an acetonitrile solution of [Ru(tbbpy)$_2$(bibzimH_2)]Cl$_2$. To obtain the complex as its perchlorate, the product was redissolved in water and precipitated by the addition of aqueous $LiClO_4$. *Note*! Perchlorates are potentially explosive. Yield: 740 mg (0.64 mmol). Anal. Calcd. for [Ru(tbbpy)$_2$(bibzimH_2)](ClO$_4$)$_2 \cdot 2H_2O \cdot Me_2CO$: C, 54.60; H, 5.84; N, 9.62. Found: C, 54.70;

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Table 1. ESI-MS and Photophysical Data for Investigated Complexes Based on **1**

	λ_{max}, nm	λ_{em}, nm	τ, ns	ESI-MS signal (m/z)
$[Ru(tbbpy)_2(bibzim)]^0$	580			$[Ru(tbbpy)_2(bibzimH)]^+$ (871)
$[Ru(tbbpy)_2(bibzimH_2)]Cl_2$	480	645	130	$[Ru(tbbpy)_2(bibzimH)]^+$ (871)
$[\{Ru(tbbpy)_2\}_2(bibzim)](PF_6)_2$	510	700	70	$[\{Ru(tbbpy)_2\}_2(bibzim)](PF_6)^+$ (1654)
$[Ru(tbbpy)_2(bibzim)ZnCl_2]$	500	675	80	$[Ru(tbbpy)_2(bibzim)ZnCl]^+$ (971)
$[Ru(tbbpy)_2(bibzim)ZnEt_2]$	510	675	*a*	$[Ru(tbbpy)_2(bibzim)ZnEt]^+$ (963)
$[\{Ru(tbbpy)_2(bibzim)\}_2ZnCl_2]$	530	710	*a*	$[\{Ru(tbbpy)_2(bibzim)\}_2ZnCl]^+$ (1841)
$[Ru(tbbpy)_2(bibzim)CuBF_4]$	500	685	60	*a*
$[Ru(tbbpy)_2(bibzim)MgCl_2]$	500	675	40	
$[Ru(tbbpy)_2(bibzim)NiBr_2]$	505			$[Ru(tbbpy)_2(bibzim)NiBr]^+$ (1009)
$[Ru(tbbpy)_2(bibzim)CoBr_2]$	492			$[Ru(tbbpy)_2(bibzim)CoBr]^+$ (1010)
$[Ru(tbbpy)_2(bibzim)PdCl_2]$	462			$[Ru(tbbpy)_2(bibzim)PdCl]^+$ (1012)

[a] Not measured.

H, 5.90; N, 9.88. ^{1}H NMR for $[Ru(tbbpy)_2(bibzimH_2)]Cl_2$ (CH_3CN-d_3; δ ppm): 8.55 (1H, s), 8.45 (1H, s), 7.78 (3H, m), 7.47 (1H, d), 7.31 (2H, m), 7.01 (1H, t), 5.64 (1H, d), 1.46 (9H, s); 1.34 (9H, s). ES-MS (m/z): 871 (M − H$^+$ − 2Cl).

Synthesis of [Ru(tbbpy)$_2$(bibzim)] (1). A 500 mg sample of $[Ru(tbbpy)_2(bibzimH_2)]Cl_2$, **2**, was dissolved in ca. 200 mL of methanol. A 200 mL portion of a 5 M aqueous NaOH solution was added, and the violet mixture was stirred at room temperature for 15 min. The solution was then extracted three times with CH_2Cl_2, and the organic layers were combined. The solvent was immediately removed by vacuum distillation at room temperature. A small sample was crystallized from dry CH_3CN to yield X-ray-suitable crystals. ES-MS (m/z): 871 (M + H$^+$). FT-IR spectra (Nujol emulsion and KBr disk) showed no NH or OH signals. ^{1}H NMR (THF-d_8; δ, ppm): 8.56 (1H, s), 8.45 (1H, s), 7.85 (2H, m), 7.40 (2H, m), 7.26 (1H, d), 6.66 (1H, t), 6.37 (1H, t), 5.38 (1H, d), 1.45 (9H, s), 1.30 (9H, s).

Investigation of the Luminescence Properties of Mixed-Metal Solutions Containing 1. A 9 mL portion of a concentrated solution of the corresponding metal compound in THF was added to 1 mL of a 10^{-4} M THF solution of **1**. The resulting mixture was stirred for 30 min and then was analyzed by UV−vis and emission spectrometry. To investigate the concentration dependence of the luminescence, a dilute zinc solution (5.4×10^{-3} M) was gradually added via a microsyringe to 10 mL of a 10^{-5} M solution of **1**. All mixtures obtained were analyzed by electrospray mass spectrometry as described below.

X-ray Structure Determinations. The intensity data for the crystals of compounds **1** and **2** were collected on a Nonius KappaCCD diffractometer at $T = -90$ °C, using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects but not for absorption.[12]

The structures were solved by direct methods (SHELXS[13]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[14]). Two *tert*-butyl groups of **2** were found to be disordered, but the disorder could be solved. For **2**, the hydrogen atoms of the amine group in the bibenzimidazole system were located by a difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[14] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Mass Spectroscopy. Mass spectra were recorded on a Finnigan MAT 95 XL spectrometer. In the ESI process, the sample used for the photochemical investigation (ca. 10^{-5} M solution in THF) was introduced into the ESI ion source with a Harvard Apparatus syringe infusion pump, model 22, with a flow rate of 5−20 μL/min. The positive-ion ES mass spectra were obtained with potentials of 3−4 kV applied to the electrospray needle. The resolution was usually about 2000 at m/z 750.

Results and Discussion

Compound **2** was prepared using standard synthetic methods.[2] The deprotonated complex **1** was then obtained conveniently by reaction of **2** with NaOH and subsequent extraction with dichloromethane. 4,4′-*tert*-Butyl-2,2′-bipyridyl was used to improve the solubility of the compounds in organic solvents such as THF. The molecular structures of compounds **1** and **2** as obtained from X-ray analysis are shown in Figure 1.

As expected, Ru(II) possesses in both cases a distorted octahedral coordination sphere. Except for a widened N−C−N angle of 117.2(3)° at the bridging carbon of the bibenzimidazole ligand in **1** compared with 113.2(3)° in **2**, no significant structural changes are induced through the deprotonation. Ruthenium−nitrogen (tbbpy) distances in both **1** and **2** are ~2.045 Å (except in **2**, where Ru−N6 = 2.024(2) Å) and are within the range expected, whereas ruthenium−nitrogen (bibzim) distances are 2.094(2) Å for **2** and 2.101(3) Å for **1**.[15]

Deprotonation of **2** yields a significant bathochromic shift in the absorption spectrum of about 100 nm and also results in a total quenching of emission (see Table 1). Addition of a series of various metal salts to **1** in THF results in a hypsochromic shift of the absorption maxima from 580 to ca. 500 nm, depending on the nature of the metal ion (see Table 1). In addition, the luminescence is “switched on” upon addition of $ZnCl_2$, $ZnEt_2$, $MgCl_2$, or $Cu(CH_3CN)_4BF_4$. Interestingly, the wavelength of the emission maximum is metal dependent, varying from 670 nm for Mg(II) to 710 nm for the trinuclear $ZnCl_2$ complex (see Figure 2). Upon addition of metal salts such as $NiCl_2$ and $PdBr_2$, a hypsochromic shift in the absorption spectra is observed as well but no emission is detected, which is in contrast to recently published data for a Ru−Pd complex.[16] These results, especially for $ZnEt_2$, show that the spectral changes cannot be explained by protonation of the imidazole ring. The maxima observed for both absorption and emission spectra are however quite similar to those found for the Ru−Ru dimer (see Table 1).

The spectroscopic changes observed can, therefore, be attributed to binding of the transition metal ions to the free bibenzimidazole binding site. In this case, we can expect 1:1, 1:2, or 1:3 complexes to be formed. To identify the compositions of the compounds obtained, electrospray mass spectrometry was carried out on the reaction mixtures. The results obtained are given in Table 1. The mass spectral data clearly indicate the compositions of the metal complexes. All reaction mixtures, except for those of magnesium species, show a signal that can be attributed to a binuclear species with an overall charge of

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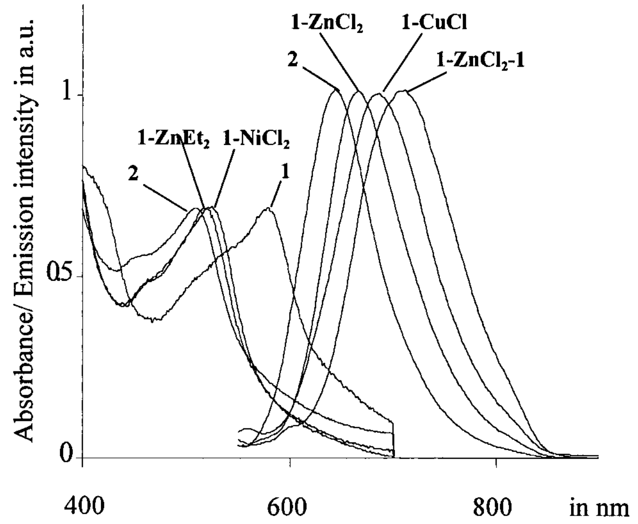

Figure 2. Selected UV−vis and emission spectra recorded in THF for some of the heteronuclear complexes discussed in the test.

$+1$, resulting from the loss of one counterion. This observation suggests that when an excess of metal ions is present, a 1:1 complex is obtained. Also organometallic complexes are found to bind. **1** forms a complex with $ZnEt_2$ that has properties very similar to those observed for its $ZnCl_2$ analogue. The absorption maximum is slightly shifted, but this organometallic complex emits at the same wavelength as the **1**−$ZnCl_2$ complex (see Table 1).

If **1** is reacted with small amounts of $ZnCl_2$ (up to 3 equiv/equiv of **1**), the absorption maximum gradually shifts from 580 to 530 nm and at the same time a rise of the emission at 710 nm is observed. This represents a bathochromic shift of 30 nm in both absorption and emission wavelength maxima with respect to those observed at high $ZnCl_2$:**1** ratios, suggesting that, at low zinc concentrations, a trinuclear complex is formed as shown in Figure 3. This hypothesis is confirmed by electrospray mass spectroscopy, which indicates that, at low zinc concentrations, a product with the composition $\{[Ru(tbbpy)_2(bibzim)]_2ZnCl_2\}$ is formed. When **1** is reacted with more than a 10^4-fold excess of $ZnCl_2$ a complex of the composition $[\{Ru(tbbpy)_2(bibzim)\}ZnCl_2]$ is obtained (see Figure 3).

One of the most striking observations is that the maxima of both absorption and emission spectra are dependent on the nature and concentration of the metal ion added. The absorption features of ruthenium polypyridyl complexes in the visible region are explained by the presence of a singlet metal-to-ligand charge-transfer (^{1}MLCT) transition, while the emission is normally assumed to occur from a ^{3}MLCT state. The shifts observed in both absorption and emission spectra indicate therefore that the energies of both the ^{1}MLCT and the ^{3}MLCT transitions are affected by binding of the transition metal ions. In all cases, the absorption maxima are shifted to higher energy than observed in the spectra of **1**. All are however at lower energy than found for **2**. The emission wavelengths follow a similar trend.

An initial interpretation of these results suggests that the behavior observed can be explained by a stabilization of the metal-based ground state in the heteronuclear compounds with respect to **1**. This is not unexpected, and such behavior has been observed for other complexes with negatively charged bridges.[3,17] The emission observed can then be explained by the increased energy gap between the emitting triplet state and the ground state. This increased energy gap is expected not only to shift the emission to higher energy but also to increase the emission lifetime. The variations in emission and absorption energies are therefore measures of the electron-withdrawing properties of the metal ions added. However, a second factor that needs to be taken into account is the location of the deactivating triplet metal-centered (^{3}MC) state. Upon binding of a second metal ion, the energy of this state will be reduced, since the electron density on the negatively charged bridge is now shared by two metal centers, leading to a decrease of the emission lifetime. This is, for example, clearly the case for the mononuclear and dinuclear $Ru(bpy)_2$ complexes of the ligand 3,5-bis(pyridin-2-yl)-1,2,4-triazole (Hbpt). For this ligand, which deprotonates upon binding, forming bpt, the emission shifts to higher energy upon binding of a second ruthenium center, but the emission lifetime decreases from 160 to 100 ns because of a lowering of the ^{3}MC level.[18] The emission lifetimes observed for these complexes will therefore be governed by both the energy gap law and by the relative energies of the emitting triplet state and the deactivating ^{3}MC state.

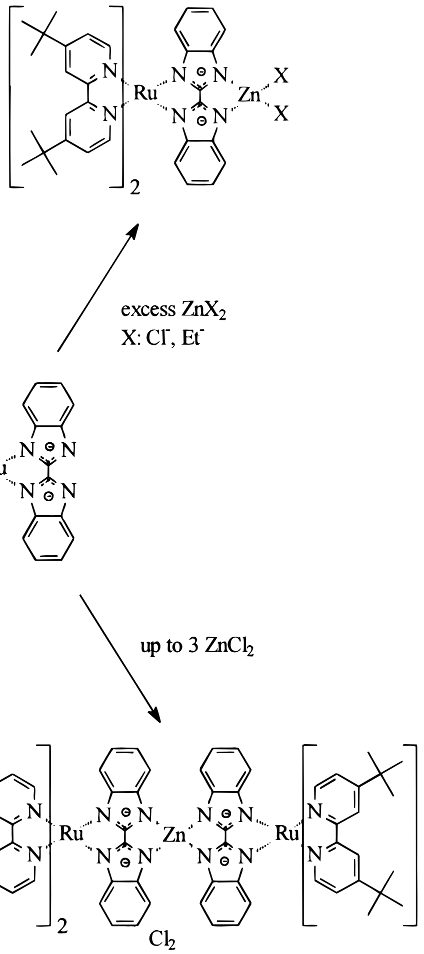

Figure 3. Proposed pathways for the reactions of **1** with different zinc compounds.

In conclusion, we report here a neutral ruthenium complex that can act as a ligand for different metal centers, thus creating different heterobi- and heterotrinuclear complexes. Also, organometallic compounds such as $ZnEt_2$ can be complexed by **1**, which might allow the tuning of the reactivity of the Zn−Et bond through the interaction with the ruthenium complex. The

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heteronuclear bibenzimidazole complexes show a remarkable "2-fold" tunability. The emission, which can be "switched on" by complexation with closed-shell metal ions such as Zn^{2+} and Mg^{2+}, can also be "fine-tuned" in both *wavelength* (λ_{max}) and *intensity* (τ) simply by choosing a suitable metal ion. These properties are very promising in view of the continuing search for components to be used in molecular-level devices and might also lead to the design of novel luminescence-based sensors.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structures of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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