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A Phenanthroline Analogue of Tröger's Base as Bridging Ligand in the Synthesis of a Bimetallic Ruthenium (II) Complex

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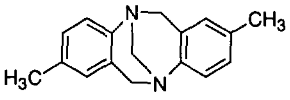
Abstract: Complexation of a Phenanthroline analogue of Tröger's Base 2 to $Ru(Bpy)_2^{2+}$ units results in the formation of a dinuclear complex 3. The spectroscopic data in absorption and emission indicate that the resulting dinuclear compound 3 behaves as two independent monometallic Ru(II) complexes.

Tröger's Base[1] 1 has been prepared for the first time in 1887 by condensation of para toluidine and formaldehyde in acidic medium. Due to the blocked conformation of the two nitrogens of the methanodiazocine bridge, the molecule is chiral with a C_2 axis of symmetry[2]. The geometry of Tröger's Base, with the two aromatic rings in almost perpendicular planes, has been used in molecular recognition and supramolecular chemistry[3]. If most of Tröger's base analogues have been prepared from substituted anilines, a few derivatives of heterocyclic amines have been recently described[4].



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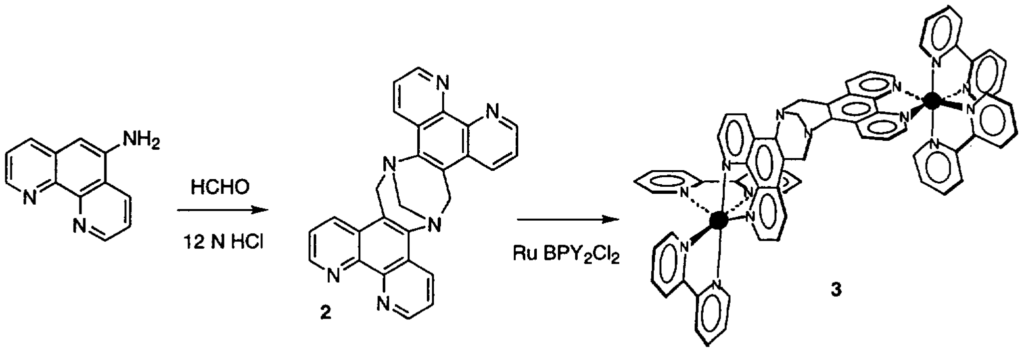
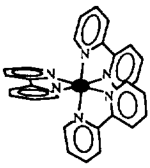
There are only a few examples of Tröger's Base-containing metal complexes reported in the literature. Transition metal complexes (Rhodium (III) or Iridium (III)) of Tröger's Base 1 have been used to catalyse the hydrosilylation of alkynes.[5] ^1H NMR spectra and elemental analysis data indicated that one molecule of the Tröger's Base forms a complex with two metal atoms, coordinated to the two nitrogens of the diazocine unit. The porphyrine analogue reported by Crossley *et al.* chelates different metal ions, palladium (II), Zinc (II), Cobalt (II), Nickel (II) and Copper (II)[4d]. From the X-ray structure of the dipalladium (II) derivative, it has been shown that the distance between the two metals complexed to the porphyrines, is 8.4-9.0 Å. These porphyrine derivatives have been used for the enantioselective recognition of histidine and lysine esters. In 1991, Yashima et al.[4a] reported the synthesis of a phenanthroline analogue 2 and showed that 2 could cleave

DNA in the presence of Copper (I). Compound **2** was prepared in 22 % yield by reaction of 5-aminophenanthroline with formaldehyde in acidic ethanol.

In this paper, we describe the synthesis of a dinuclear Ru(II) complex using the Tröger's base **2** as bridging ligand. Its absorption and luminescence properties are compared to those of the monometallic compounds $Ru(Bpy)_3^{2+}$ **4** and $Ru(Bpy)_2(Phen)^{2+}$ **5** [6] and to another dinuclear compound $[Ru(Bpy)_2]_2HAT^{4+}$ **6** [7] as references. It has been clearly demonstrated that the polycomplexation of the HAT ligand changes completely the absorption and luminescence properties of the resulting polynuclear complex. This has been attributed to an important stabilisation of the π* HAT orbital by the polycomplexation.





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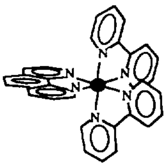

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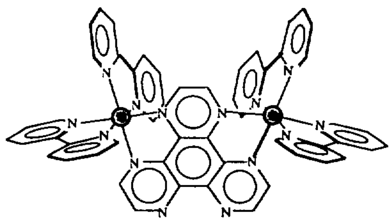

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We have greatly improved the synthesis of compound **2**. Reaction of 5-aminophenanthroline with a stoechiometric amount of paraformaldehyde in 12 N hydrochloric acid at room temperature gave compound **2** in 81 % yield. The ^1H NMR spectrum was in agreement with the literature data[4a] and the purity was checked by HPLC. Complexation has been achieved by adding slowly $Ru(Bpy)_2Cl_2$, prepared as already described[8], to a solution of compound **2** in ethylene glycol. The reaction was monitored by HPLC. The same product **3** was obtained using different stoechiometries of Ru(II) precursor (1 or 2 equivalents). The new complex, purified on a cation exchanger Sephadex column, eluted with aqueous NaCl and precipitated by KPF_6, was examined by ^1H NMR. Due to the chirality of the Ru(II) precursors and of the Tröger's Base unit, the spectrum appeared as very complicated to analyze in detail. However, two sets of signals could be attributed : the aromatic C-H between 6.95 and 9.05 ppm and the CH_2 groups of the methano diazocine between 4.7 and 5.35 ppm. The relative integration of the methanodiazocine protons (3 CH_2) compared to the aromatic signals (4 Bpy and 2 Phen) confirmed the bimetallic structure of compound **3**. A 2D COSY experiment allowed the attribution of the multiplet centered at 5.35 ppm to the two *exo* protons of the benzylic CH_2 and the signal centered at 4.8 ppm to the methano bridge of the Tröger's Base. The *endo* benzylic protons appeared as two sets of signals, centered at 4.83 ppm and 4.97 ppm. This complexity of the spectrum is thus in agreement with a mixture of diastereoisomers.

The complex ($[Ru(Bpy)_2]_2BTPhen_2(PF_6)_4$) **3** was also analyzed by electrospray mass spectrometry. In the spectrum, three peaks corresponding to $M\text{-}4(PF_6^-)^{4+}$, $M\text{-}3(PF_6^-)^{3+}$ and $M\text{-}2(PF_6^-)^{2+}$ (M = most important isotopic peak) were observed at 313.77 $^{(100)}$ (calc 313.55), 466.41 $^{(20)}$ (calc 466.39) and 771.5 $^{(5)}$ (calc 772.08) respectively (in superscript: relative intensity).

The absorption and emission data for $[Ru(Bpy)_2]_2BTPhen_2^{4+}$ and for the reference compounds are collected in table 1.

Table 1: Absorption and Emission Data of Complexes 3-6.

Complex	λmax abs (nm) ($10^{-3}\varepsilon\ M^{-1}cm^{-1}$)	λmax em.(nm)		τ_{Ar} (ns)	
	H_2O	H_2O	MeCN	H_2O	MeCN
$RuBPY_3^{2+}$ **4**	242, 285, 428, 452 (14.6)[8]	622$^{(a)}$	616$^{(a)}$	595	940
$RuBPY_2Phen^{2+}$**5**	264, 285, 424, 450 (15.9)	619$^{(a)}$	613$^{(a)}$	688	848
$[RuBPY_2]_2BTPhen_2^{4+}$ **3**	253, 280, 430, 454 (37)	620$^{(a)}$	611$^{(a)}$	950	1090
$[RuBPY_2]_2HAT^{4+}$ **6**	206, 276, 405, 490, 572 (15)[9]	800$^{(b)}$	800 $^{(b)}$	170	550

The luminescence lifetimes were measured under argon. (a): corrected, (b): non corrected for the photomultiplier response. The absorption spectra were recorded with a HP 8452A UV-visible diode array spectrophotometer. The ε (molar extinction coefficients) were determined by Ru titration by plasma emission with a Spectrometric Spectrospan IV instrument. The emission lifetimes were determined with a laser kinetic apparatus as described in reference 7; ≈ 2 % error on the lifetimes.

For **3**, as for the other Ru(II) complexes, the usual stabilisation of the ^{3}MLCT excited state (Metal to Ligand Charge Transfer) in water as compared to MeCN is indicated by the slight red shift of λmax of emission in water relatively to MeCN. Similarly, for **3**, as for the other compounds, the usual lengthening of luminescence lifetime from water to MeCN is also present.[8] The most important conclusion from the comparison of the data in table 1 is the similarity of the photophysical properties of the dinuclear complex **3** with the two mononuclear compounds, **4** and **5**. Moreover in absorption, the coefficient ε of the MLCT band at 454 nm is approximately the double of that of the mononuclear complexes. These absorption and emission data show quite clearly that the properties of **3** are controlled by the MLCT transition Ru-Phen (similar to that of Ru-Bpy) which is quasi not affected by the diazocine ring and the presence of the other metallic unit. The slight increase of luminescence lifetime of **3** as compared to **5** should simply be attributed to the effect of the amino group on each of the Phen ligands in **3**. This conclusion is based on data for other complexes. Indeed, it has been observed that τ for $Ru(Bpy)_2acPhen^{2+}$ (acPhen = 5-acetamido-phenanthroline) in water under argon reaches 900 ns as compared to 688 ns for $Ru(Bpy)_2Phen^{2+}$ in the same conditions.[10] This absence of important difference in absorption and emission of **3** vs **5** is in contrast to the case of the dinuclear compound **6**, where the π^* orbital of the HAT ligand is stabilized by the complexation of a second $Ru(Bpy)_2^{2+}$ unit.[7]

In conclusion, we have shown that the Tröger's base **2** can behave as a bridging ligand for the preparation of bimetallic complexes where the two bridged metallic units behave quasi independently.

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