Bi- and tri-nuclear ruthenium(II) complexes containing tetrapyridophenazine as a rigid bridging ligand

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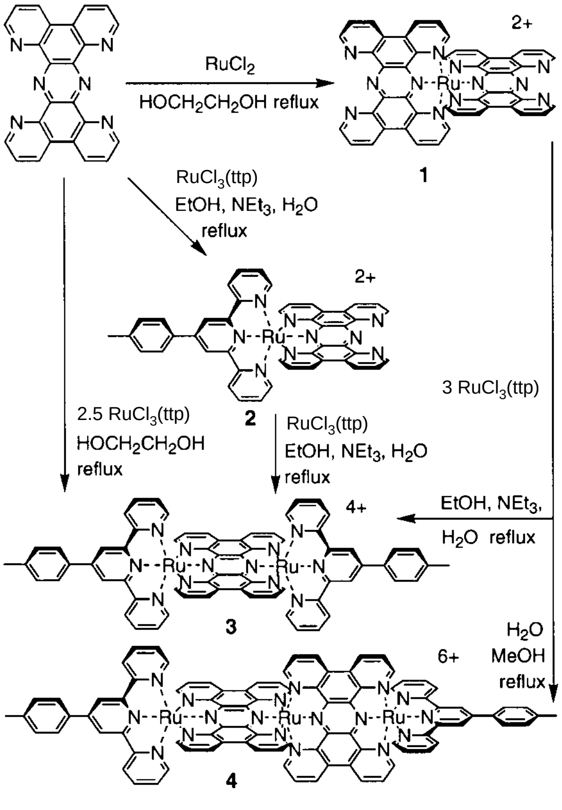
The rigid, aromatic bis-tridentate bridging ligand tetrapyrido[2,3-a:3′,2′-c:2″,3″-h:3‴,2‴-j]phenazine (tpp) allowed the preparation of linear, stable bi- and tri-nuclear complexes of ruthenium(II) exhibiting low energy Ru → tpp MLCT absorptions and a strong electronic coupling in the mixed-valence state.

Following the pioneering work of Creutz and Taube,[1] much interest has been devoted to the bridged bi- and poly-nuclear ruthenium complexes, particularly in their mixed valence state.[2,3] The short bridging ligands such as pyrazine,[1] *tert*-butylmalonitrile, dinitrogen, cyanogen[2] or 4,4-dithiodipyridine[4] provide often a strong enough coupling between ruthenium–amine centers to allow complete electronic delocalization in the mixed-valence (MV) state (class III MV complexes). On the other hand, polynuclear ruthenium–polypyridine complexes usually show weaker electronic coupling and are valence-trapped (class II).[5] Tetrakis(2-pyridyl)pyrazine (tppz) was up to now the only polyazine bridging ligand allowing a Ru–Ru coupling of a similar intensity as in the Creutz–Taube ion.[5–8] Polynuclear complexes of ruthenium(II) are valuable sensitizers for the conversion of light into chemical or electrical energy[9] as they are efficient MLCT chromophores in which the absorption maximum can be tuned to almost any wavelength of the visible spectrum.[10] In order to ensure a potentially good charge separation from an excited state in a donor–chromophore–acceptor triad, it is suitable to aim at linear, rigid assembly.[11] It is thus obvious that the most promising bridging ligands are the bis-tridentate ones, like tppz. In that class of polyazines, tetrapyrido[2,3-a:3′,2′-c:2″,3″-h:3‴,2‴-j]phenazine (tpp), is the representative which is at the same time the most rigid and the shortest intermetallic spacer. We have developed a straightforward synthesis of this compound[12] and report here on its outstanding properties as a bridging ligand between ruthenium–terpyridine units.

Attempts to react directly a blue solution of ruthenium(II) chloro complexes with tpp in various ratios in refluxing ethylene glycol led only to the mononuclear complex [Ru(tpp)$_2$]Cl$_2$ **1**. For the elaboration of polynuclear Ru–tpp complexes, we used RuCl$_3$(ttp) (ttp = 4′-*p*-tolyl-2,2′-6′,2″-terpyridine) as a starting ruthenium containing unit.[5,7,8,11,13] The advantage of ttp[14] over terpyridine is the availability of a methyl group for further linkage with electron donors or acceptors[11] and as a useful internal standard for NMR integration. Reaction of RuCl$_3$(ttp) with an excess of tpp in refluxing ethanol–water–triethylamine, followed by precipitation by NH$_4$PF$_6$ afforded the orange [Ru(tpp)(ttp)][PF$_6$]$_2$ **2** in 52% yield (Scheme 1). This complex reacted under the same conditions with RuCl$_3$(ttp) to give, after chromatography over SiO$_2$, the green binuclear complex [(ttp)Ru(ttp)Ru(ttp)][PF$_6$]$_4$ **3** in 39% yield. The same product was obtained by reacting tpp with RuCl$_3$(ttp) (28% yield). In the reductive solvents mentioned above, the main product obtained by reaction of **1** with 3 equiv. of RuCl$_3$(ttp) was surprisingly the binuclear complex **3**, and not the expected trinuclear species [(ttp)Ru(tpp)Ru(tpp)-Ru(ttp)][PF$_6$]$_6$ **4**. Similarly, the reaction of RuCl$_3$(ttp) with a slight excess of **1** afforded **2** only instead of the expected [(ttp)Ru(tpp)Ru(tpp)][PF$_6$]$_4$. The use of a less reducing mixture [water–methanol (3:1)] allowed finally the synthesis of **4** in 16% yield by reaction of **1** with RuCl$_3$(ttp). Even in this case, a small amount of the binuclear complex was formed. It appears thus that RuCl$_3$(ttp) is able to abstract a tpp ligand from [Ru(tpp)$_2$]$^{2+}$ under reducing conditions.§

For all the investigated compounds, the first one-electron cathodic wave observed by cyclic voltammetry¶ was attributed to the tpp-centered reduction. It shifts from −1.23 V *vs.* SCE in the free ligand to −0.80 V in **2** and further to −0.38 V in **3**. The oxidation waves corresponding to the Ru$^{2+/3+}$ couple appeared at 1.52 V in **2** but at 1.32 and 1.71 V in **3**. This splitting ΔE of 0.39 V between the (Ru–Ru)$^{4+/5+}$ and the (Ru–Ru)$^{5+/6+}$ redox potentials, symmetrically above and below the potential of **2**, indicates a strong degree of interaction between the two metallic centers. It corresponds to a comproportionation constant $K_c = [(\mathrm{Ru–Ru})^{5+}]^2/\{[(\mathrm{Ru–Ru})^{6+}][(\mathrm{Ru–Ru})^{4+}]\} = \exp(\Delta EF/RT) = 4 \times 10^6$ which is identical to the value reported for the Creutz–Taube ion[1] and higher than the value obtained for [(ttp)Ru(tppz)Ru(ttp)]$^{5+}$ ($K_c = 10^5$).[5] The insolubility of **1** and **4** in the presence of supporting electrolytes prevented any determination of their electrochemical properties.



Scheme 1

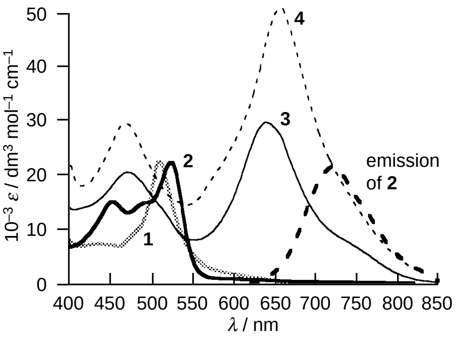


Fig. 1 Visible absorption spectra of **1**, **2**, **3** and **4** as well as emission spectrum of **2** (arbitrary units), in acetonitrile

Table 1 UV–VIS spectral data in MeCN and attribution

	λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1})		
Complex	LC	Ru⟶ttp	Ru⟶tpp
1[a]	254(92.0) 276(87.4) 316(82.3) 364(48.1)		508(22.6)
2	251(61.0) 280(79.4) 306(75.3) 366(40.2)	450(15.1)	522(22.2)
3	282(103.2) 309(112.1) 371(33.8)	470(20.7)	644(29.9)
4	230(110.0) 276(148.0) 310(156.0) 376(58.4)	470(29.5)	658(50.7)

[a] As hexafluorophosphate.

The visible absorption spectra of **1**, **2**, **3** and **4** as well as the emission spectrum of **2** are shown in Fig. 1 and the corresponding parameters are given in Table 1. The monometallic complexes show a sharp Ru⟶tpp MLCT band around 520 nm. In **2**, an additional Ru⟶ttp MLCT band appears at 450 nm and the complex emits at room temperature at 738 nm, with a yield of $1.2 \pm 0.2 \times 10^{-4}$ and a lifetime $\tau = 60$ ns. No emission was detected from **1**. In **3** and **4**, the low-energy absorption band is attributed to the Ru⟶tpp MLCT. It is strongly red-shifted compared to those of the monometallic species, while the Ru⟶ttp band is only slightly affected. This shift is attributed both to the strong stabilization of the π* orbital of the tpp ligand by the chelation of the second Ru^{II}, as shown by the associated low reduction potential, and to the splitting of the t_{2g} orbitals, the d_{xy} set engaged in the bonds with the π* orbital on the pyrazine ring of tpp being destabilized by the metal–metal interaction, while the other sets linked to ttp are less (d_{yz}) or not at all (d_{xz}) affected. From **3** to **4**, the Ru⟶tpp MLCT band only red-shifts by 14 nm but grows by 70%, which means that the set of t_{2g} orbitals does not undergo a significant additional splitting by addition of a third Ru^{II} center, certainly because the environment is different for the central and for the two terminal metals. While solutions of **3** in acetonitrile could be stored for weeks at room temperature without degradation, **4** was observed to break down quite rapidly, its solution showing after 7 days essentially the spectrum of **2**. No emission was detected below 900 nm for **3** and **4** which could emit further in the IR. The photophysical study of these complexes will be published elsewhere. Oxidation of **3** by Ce^{4+} in acetonitrile acidified by 0.5 M CF_3CO_2H led to the disappearance of the Ru⟶tpp MLCT band accompanied by the rise of a new absorption at 592 nm, attributed to a tpp⟶Ru ligand-to-metal charge transfer. Concomitantly, an 'intervalence' absorption band appeared at 1388 nm (7206 cm^{-1}). Its width at half-intensity $\Delta\nu_{1/2}$ is only 2000 cm^{-1}, half the value calculated by the Hush model for a class II complex (4080 cm^{-1}).[2,15] This discrepancy indicates that **3** is a class III complex. In such a case, the electron coupling matrix element V_{ab} is half the energy of the band maximum, *i.e.* 0.447 eV.

In conclusion, tpp appears to form stable mono- and binuclear ruthenium complexes and to mediate a strong interaction between the metallic centers. The intense low-energy Ru⟶tpp MLCT absorption could prove useful for the development of supramolecular systems and for the photochemical conversion of solar energy.

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Notes and References

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§ All compounds gave satisfactory elemental and/or FABMS and/or plasma-desorption MS analyses. The corresponding data and NMR spectra will be published elsewhere.

¶ Medium: MeCN + 0.1 M NBu_4BF_4; working electrode: glassy carbon disk; reference: SCE. The given half-wave potentials correspond to reversible processes.

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