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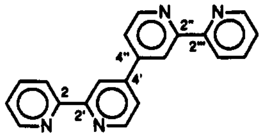
Synthesis and Properties of a Tris(2,2′-bipyridine)ruthenium(II) Dimer Directly Coupled at the C4 Carbon

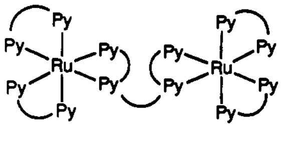
The spectroscopic and electrochemical properties of $Ru(bpy)_3^{2+}$ have been the subject of much attention for many years.[1] More recently, there has been considerable interest in binuclear and polynuclear analogues which contain bridging heterocyclic ligands that facilitate communication between the metal coordination sites via the π system of the bridging ligand.[2] Metal–metal interactions have been observed for complexes bridged by ligands such as 2,2′-bipyrimidine and 2,3-bis(2-pyridyl)pyrazine.[3,4] However such ligands, which contain diazine rings, have very low-lying π^* orbitals which significantly modify the properties of the resulting complexes. Although bridging ligands that contain isolated bpy subunits are known,[2,5] intermetal communication is usually prevented by the lack of conjugation between bpy subunits that are connected by saturated carbon chains. This problem might be overcome by the direct linking of two bpy groups. To date, the only such ligand whose ruthenium complexes have been studied is a substituted derivative of 2,2′:6′,2″:6″,2‴-quaterpyridine. However, a binuclear ruthenium(II) complex of this ligand[6] showed no metal–metal interactions, a fact that can be attributed to the inability of this ligand to bridge two octahedral metal centers and still maintain the conjugation between bpy subunits required for metal–metal interaction through the ligand π system. Since 4,4′-bipyridine can bridge with coplanar rings,[7] we felt that the direct linkage of two bpy groups at C4[8] would give a binucleating ligand with similar π-orbital properties to bpy that might allow metal–metal interactions. In this context, we herein report the preparation and properties of 2,2′:4′,4″:2″,2‴-quaterpyridine (**1**) and its binuclear complex with bis(2,2′-bipyridine)ruthenium(II).[9]



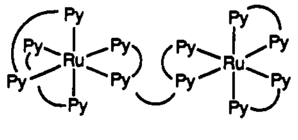
1

Ligand **1** was prepared in 50–60% yield by nickel(0)-catalyzed coupling[10] of 4-chloro-2,2′-bipyridine[11,12] and had spectroscopic properties[13] consistent with the structure shown for **1**, in which the bridging properties of 4,4′-bipyridine are combined with the chelating properties of 2,2′-bipyridine. The free ligand exists in two crystalline modifications that X-ray crystal structure determinations[14] have shown to differ only in the crystal packing. In the solid state the ligand is planar and in a conformation with transoid 2,2′- and 2″,2‴-linkages. Although coplanarity of the two central rings would favor communication between coordinated metals, it is likely that in solution the central rings would be twisted away from coplanarity in the free ligand.

The binucleating ligand readily forms complexes with a variety of metal ions. For example, reaction with excess $PdCl_4^{2-}$ gave in quantitative yield a dipalladium(II) complex that is insoluble in common solvents. Reaction with 1 equiv of $Ru(bpy)_2Cl_2$ gave a mixture of mononuclear complex **2** and binuclear complex **3**, which were isolated as the PF_6^- salts according to standard procedures[15] and separated by fractional crystallization. Binuclear complex **3** can be prepared more conveniently in high yield by reaction of **1** with 2 equiv of $Ru(bpy)_2Cl_2$. Although this complex undoubtedly exists as a mixture of meso (**3a**) and racemic (**3b**) diastereoisomers, the 300-MHz ^1H NMR spectrum was not sufficiently well resolved to identify the two isomers.



3a



3b

Mononuclear complex **2** shows electrochemical behavior[16] similar to that of $Ru(bpy)_3^{2+}$ with a reversible one-electron-oxidation wave at +1.22 V vs SCE and three reversible reduction waves at −1.32, −1.51, and −1.84 V (cf. +1.26, −1.35, −1.54, and −1.79 V for $Ru(bpy)_3^{2+}$).[17] The electrochemistry of binuclear complex **3** shows a chemically reversible two-electron-oxidation wave with ΔE_p = 85 mV centered at +1.24 V vs SCE. A reversible one-electron first reduction with $E^{\circ\prime} = -1.10$ V (ΔE_p = 60 mV) is followed by three further closely spaced single-electron reductions with $E^{\circ\prime} \approx -1.44$, −1.57, and −1.64 V, the last of which results in adsorption with associated stripping peaks.[18] The greater anodic to cathodic peak separation of the oxidation process (independent of scan rate over the range 10–100 mV s^{-1}) suggests that this actually represents two closely spaced one-electron

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[11] We have found that 4-chloro-2,2′-bipyridine can most conveniently be prepared by chlorination of 2,2′-bipyridine *N*-oxide[12] to give a 1:1 mixture of the 4-chloro and 6-chloro isomers, which are readily separated by extraction with nickel(II) ions. The nickel selectively complexes with the less sterically demanding 4-chloro isomer, which can then be released by addition of excess cyanide.

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[13] All new compounds gave spectral and analytical data consistent with the assigned structures. Selected data for **1** are as follows. Mp: 198–200 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.36 (ddd, H5), 7.70 (dd, H5′), 7.86 (dt, H4), 8.48 (dd, H3), 8.733 (ddd, H6), 8.81 (m, H3′ and H6′). ^{13}C NMR ($CDCl_3$): δ 119.0 (C3′), 121.3 (C3), 121.6 (C5′), 124.0 (C5), 136.7 (C4), 146.8 (C4′), 149.2 (C6), 150.0 (C6′), 155.7 (C2′), 157.1 (C2). The NMR assignments were made with the aid of homonuclear and heteronuclear 2D spectra.

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[18] In dichloromethane solution there was no adsorption on reduction. However the fourth reduction was an irreversible multielectron process.

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transfers. Indeed simulation[19] of the observed response gave a best fit for two individual one-electron transfers with $\Delta E^{\circ\prime} = 56 \pm 3$ mV, indicating a weak metal–metal interaction in the complex.[20,21] The weakness of the metal–metal interaction can be attributed to the ability of the complex to rotate about the 4′–4″ bond which links the two $\mathrm{Ru(bpy)_3}^{2+}$ subunits, thereby disrupting the overlap of the π systems of the subunits. This is similar to the recently reported[8] noninteracting dimer of $\mathrm{Ru(terpy)_2}^{2+}$ units but is in marked contrast to a recently reported[22] strongly interacting binuclear complex containing a bridging tetraiminobiphenyl ligand that also has the potential for free rotation between the bridged components. Although the metal–metal interaction is not strong in **3**, there is extensive electronic coupling between the two bpy groups of the bridging ligand, as evidenced by the large separation between the potentials of the first and subsequent one-electron reductions in **3** and the 210-mV difference in the first reduction potentials of **2** and **3**.[21] This first reduction of **3** is assigned as quaterpyridine-centered by comparison with related literature data.[23]

The electronic absorption spectrum of mononuclear complex **2** is also similar to that of $\mathrm{Ru(bpy)_3}^{2+}$ with a maximum at 455 nm ($\epsilon = 1.2 \times 10^4$) in acetonitrile (cf. 451 nm for $\mathrm{Ru(bpy)_3}^{2+}$). Binuclear complex **3** showed maxima at 471 nm ($\epsilon = 2.2 \times 10^4$) and 445 nm ($\epsilon = 2.0 \times 10^4$), corresponding to d–$\pi^*$ MLCT transitions into the quaterpyridine and bpy ligands respectively, as well as the usual intense π–π^* absorptions at 287 nm ($\epsilon = 1.1 \times 10^5$) and 244 nm ($\epsilon = 5.2 \times 10^4$). The small red shift of the lowest energy MLCT absorption relative to $\mathrm{Ru(bpy)_3}^{2+}$ confirms the weak metal–metal interaction, as binuclear complexes with strong metal–metal interactions usually exhibit much greater red shifts. Thus the electrochemical and spectroscopic data show that the new ligand, **1**, has the intended similar π-orbital energy to bpy, exhibits electronic coupling between the two bpy subunits, and permits weak metal–metal interactions.

Meyer and co-workers[24] very recently reported a structurally related complex in which the rutheniums are bridged by a ligand containing bpy groups linked through C4 by an ethenyl group. Relative to **3**, this complex has a greater intermetal separation and an extra rotational degree of freedom and, not surprisingly, a weaker metal–metal interaction. However, electronic delocalization in the bridging ligand was observed, and this was proposed to account for the unexpectedly long excited-state lifetime of the complex. In accord with this, a long excited-state lifetime was also observed in a recently reported highly conjugated but noninteracting diruthenium complex containing bpy units linked through a 1,4-diethenylbenzene bridge.[21] Our more strongly interacting complex, **3**, which dispenses completely with the bridging moiety, emits at $\lambda_{\max} = 685 \pm 5$ nm with a surprisingly long excited state lifetime of 2.0 ± 0.2 μs (acetonitrile, 295 K). Hence, **1** is a new example of a binucleating ligand that leads to enhanced excited state lifetimes by way of electron delocalization. Furthermore this lifetime is much longer than those reported for strongly interacting binuclear ruthenium complexes with bridging diazine ligands such as 2,2′-bipyrimidine and 2,3-bis(2-pyridyl)pyrazine.

In summary, the new binucleating ligand **1** has been prepared and its diruthenium(II) complex (**3**) shown to display a weak metal–metal interaction. Electron transfer into the bridging ligand results in extended delocalization and an increased excited-state lifetime. Further studies of other complexes of **1**, including heterobinuclear examples and complexes of higher nuclearity, are in progress.

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Articles

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Absorption Bands of the $\mathrm{S_3}^-$ and $\mathrm{S_6}^{2-}$ Polysulfide Ions in Liquid-Ammonia Solutions

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The absorption spectra of $\mathrm{Li_2S_6}$–$\mathrm{NH_3}$ solutions have been resolved at various temperatures and concentrations. It has been shown previously that in these solutions $\mathrm{S_6}^{2-}$ is not disproportionated but is in equilibrium with $\mathrm{S_3}^-$. In various previous studies, $\mathrm{S_3}^-$ and $\mathrm{S_6}^{2-}$ were characterized by a single absorption band in the visible range at 610 and 440 nm, respectively. It is shown that the radical $\mathrm{S_3}^-$ also has an absorption band at 268 nm, while $\mathrm{S_6}^{2-}$ absorbs also at 330, 288, and 244 nm. The molar extinction coefficient of these bands was determined. The value of the equilibrium constant between $\mathrm{S_6}^{2-}$ and $\mathrm{S_3}^-$ was determined; this value confirms previous determinations.

Introduction

The identification of the $\mathrm{S_3}^-$ radical anion was clarified about 15 years ago.[1] This radical has been observed in many solutions. It has been found in alkali-metal polysulfides in solution in various solvents (HMPA,[2,3] DMF,[3] $\mathrm{NH_3}$,[4–6] amines[7]). It was also ob-

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