Can terdentate 2,6-bis(1,2,3-triazol-4-yl)pyridines form stable coordination compounds?†

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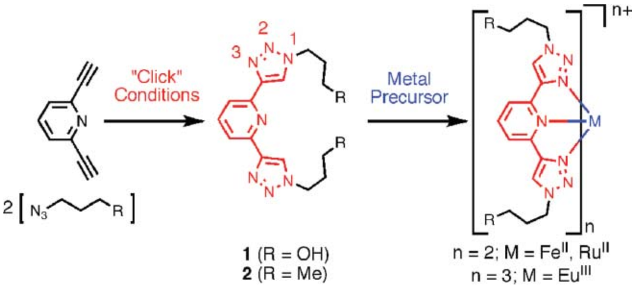
The first structurally characterized examples of the 1,2,3-triazole motif employed in a terdentate ligand display enhanced steric freedom and a facile receptivity towards a reversible aquation in the case of an electrogenerated Fe^{III} state.

One of the most widely studied classes of ligands in coordination chemistry is 2,2′:6′,2″-terpyridine[1] (terpy), and one reaction that has received a wide degree of recent interest is the Huisgen 1,3-dipolar cycloaddition,[2] one of the so-called Click reactions. Both the ligand[3] and reaction[4] provide access to a broad range of molecular materials, with applications in redox and photoactive systems, catalysis, and biologically active media. It is therefore of interest to examine whether the 1,2,3-triazole ring system resulting from the facile cycloaddition can be employed, not only as a labile ligand for catalysis,[2b] but also as a stabilizing multidentate ligand motif for coordination chemistry, particularly given that its 1,2,4-isomer has been extensively studied in this context.[5] For these reasons, we considered the viability of preparing terdentate ligands by employing the Huisgen cycloaddition as a means to (a) merge together these elementary building blocks, (b) ascertain if stable coordination compounds can be formed and, if so, (c) what properties emerge from this usage of the 1,2,3-triazole ring system.

Against this background, a readily accessible pair of ligands (Scheme 1) was prepared and their coordination with a supramolecular Fe^{II} motif,[6] a photoactive Ru^{II} moiety[7] and a luminescent Eu^{III} center was examined.[8] While favorable terdentate coordination properties are maintained, it is clear from the crystal structures that the sterically unhindered triazole N2 nitrogens, which are adjacent to the site of coordination, have a significant impact on the solid-state structure of all three complexes, and that in solution, this steric freedom exposes the redox-generated Fe^{III} center to a fully reversible, water-mediated structural change.



Scheme 1 Modular strategy to access coordination compounds from the terdentate ligands **1** and **2**, produced by Click chemistry.

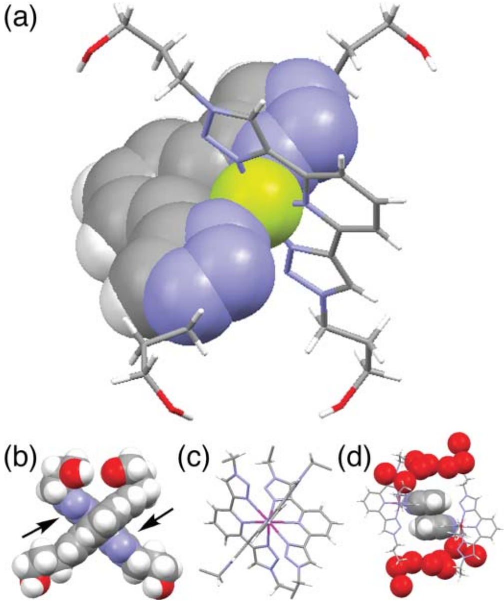


Fig. 1 Representations of the X-ray crystal structures of (a) $[Fe(\mathbf{1})_2]\cdot 2PF_6$, (b) $[Ru(\mathbf{1})_2]\cdot 2PF_6$ and (c) $[Eu(\mathbf{2})_3]\cdot 3ClO_4$ (there are *n*-butyl chains in the complex and the terminal $–CH_2CH_2CH_3$ groups have been omitted). Dimerization in the solid state structures of $[Fe(\mathbf{1})_2]\cdot 2PF_6$ and (d) $[Ru(\mathbf{1})_2]\cdot 2PF_6$ (shown) is mediated by hydrogen bonding (red oxygen atoms) and ring-over-bond π–π stacking between the pyridyl ring systems.

Two symmetrical terdentate ligands, **1** and **2**, containing the 2,6-bis(1,2,3-triazol-4-yl)pyridine (tripy) core and terminating with either hydroxyl or methyl groups, respectively, have been synthesized. These ligands were prepared under standard conditions[2] from 2,6-diethynylpyridine[9] and either 3-azidopropan-1-ol[4b]‡ or azidobutane[10] in excellent yields of 94 and 96%, respectively. The $[Fe(\mathbf{1})_2]\cdot 2PF_6$,[11] $[Ru(\mathbf{1})_2]\cdot 2PF_6$[12] and $[Eu(\mathbf{2})_3]\cdot 3ClO_4$[8]‡ metal complexes were also prepared in good yields (95, 92 and 54%, respectively) according to procedures employed for the coordination with terpy.[13] ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry confirmed the identity of each compound,† and X-ray crystallographic data was obtained for the Fe^{II}, Ru^{II} and Eu^{III} complexes,§ positively identifying these targeted structures.

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The crystal structures (Fig. 1) highlight the terdentate coordination geometries that emerge when using the tripy ligand. For each metal, the M–N bonds to the outer 1,2,3-triazole rings are longer than to the central pyridine, consistent with the structures of the terpy complexes.[13]† Inspection of the crystal structures of the Fe^{II} and Ru^{II} complexes indicate the different steric properties of the tripy ligand. The N2 nitrogen of the 1,2,3-triazole rings (see the arrows in Fig. 1b) replace C–H_3 protons of the terminal pyridine rings in terpy.[13] The absence of steric interactions in tripy can be observed in the heightened distortion from octahedral symmetry of $[Ru(\mathbf{1})_2]\cdot 2PF_6$ to C_1, which arises as a result of extensive hydrogen bonding, wherein each hydroxyl unit contributes to an infinite chain (Fig. 1d). This softening of the geometrical constraints around the metal center,† which are magnified by crystal packing forces, is also seen in the structure of $[Fe(\mathbf{1})_2]\cdot 2PF_6$, albeit to a lesser degree (C_2 symmetry). Intermolecular π–π stacking (Fig. 1d) is observed to arise as a result of the open sterics provided by the triazole N2 nitrogens of the Ru^{II} and Fe^{II}† crystal structures. The π–π stacking (~3.3 Å) is observed between the central pyridine ring systems of adjacent pairs of complexes in the form of ring-over-bond overlap, facilitated by the close approach of the H4 proton of the pyridine. The impact of steric freedom afforded by the 1,2,3-triazole rings is seen most acutely in the tricapped trigonal prism crystal structure of the $[Eu(\mathbf{2})_3]\cdot 3ClO_4$ complex. By way of contrast, in the $[Eu(terpy)_3]\cdot 3ClO_4$ complex,[13] each pyridyl ring is tilted at an angle of ~16° to the adjacent one in order to minimize the interligand steric interactions arising from the C–H_3 protons. However, the use of 1,2,3-triazole rings leads to a situation in which each entire tripy ligand is almost planar, and the planes defined by each of the three ligands are mutually orthogonal to each other. As a result, the overall tris-chelated structure is more isotropic than it is in the tris-terpy Eu^{III} complex.[14]

The effects of coordination on the electronic structure of the ligand were investigated by undertaking UV-vis spectroscopy (Fig. 2) on the Fe^{II} and Ru^{II} complexes, and obtaining emission spectra of the Eu^{III} complex. The ligand-centered (LC) band of ligand **1** blue-shifts ~10 nm from 301 nm upon complexation. This finding suggests that the ligand adopts a near coplanar *transoid* arrangement in its unbound state (Scheme 1) to minimize steric interactions with the H5 triazole protons.[13] Coordination of the Fe^{II} leads to a visibly red-colored compound with an intense metal-to-ligand charge-transfer (MLCT) band at 443 nm, while Ru^{II} coordination produces an MLCT transition at 393 nm. These bands, and the LC band, are all blue-shifted by ~4500 cm^{-1} compared to the terpy complexes, although the band shapes are similar. The phosphorescence† of $Eu(\mathbf{2})_3^{3+}$ in MeCN displays peaks at 594 and 617 nm, whose intensity, relative to the fluorescence of **2**, decreases with concentration.[8] Together, these data indicate that the effects of coordination on the optical properties of the complexes are similar to the terpy analogs, albeit with higher energy excited states being accessible in the case of the Fe^{II} and Ru^{II} complexes. This effect is attributed to the lowest unoccupied molecular orbital (LUMO) of the tripy core being located at a higher energy than for terpy.

To investigate further the energy differences of the excited states, and to determine the effect of the tripy core on the redox properties of the Fe^{II} and Ru^{II} complexes, their electrochemistry was determined using cyclic voltammetry (CV, Fig. 3a). As suggested from the UV-vis spectroscopy, the primary difference to the terpy complexes lies with the ligand. For $Fe(\mathbf{1})_2^{2+}$, the reduction processes of the coordinated ligand start at −1.5 V *vs.* SCE and are cathodically-shifted ~250 mV compared to the terpy

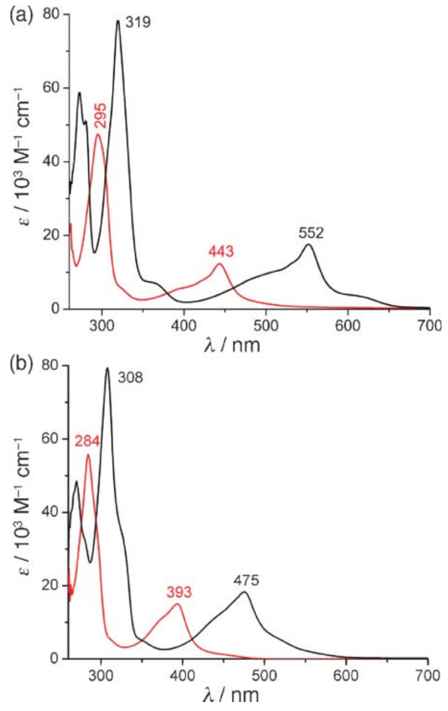

Fig. 2 UV-vis spectra in MeCN of (a) $Fe(\mathbf{1})_2^{2+}$ (red) and (b) $Ru(\mathbf{1})_2^{2+}$ (red), compared with their associated terpy analogs (black).

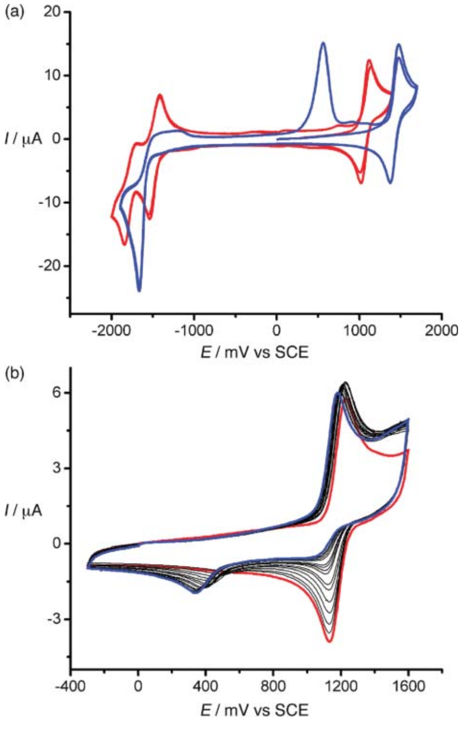

Fig. 3 CV of (a) $Fe(\mathbf{1})_2^{2+}$ (red) and $Ru(\mathbf{1})_2^{2+}$ (blue), and of (b) $Fe(\mathbf{1})_2^{2+}$ with increasing amounts of H_2O added from none (red) through to 1.25 molar equivalents (blue) (~1 mM, 200 mV s^{-1}, MeCN, 0.1 M $TBAPF_6$).

complex,† whereas the metal-based oxidation process occurs at similar potentials of $\sim$1.0 V. The Ru^{II} complex displays similar oxidation behavior to the related terpy compound. However, for the reduction, a quasi-reversible process is observed as a two-electron peak at -1.7 V, and its re-oxidation peak occurs at +0.6 V. A comparison of the redox potential differences $\Delta E = E_{ox} - E_{red}$ for the Fe^{II} and Ru^{II} complexes correlates with their MLCT transition energies: 2.56 V $\approx$ 2.81 eV and 3.10 V $\approx$ 3.15 eV, respectively. This observation indicates that the electronic structure of the frontier orbitals of both the terpy and tripy complexes Fe^{II} and Ru^{II} complexes are similar to each other, with the highest occupied molecular orbitals (HOMOs) being metal-based dπ orbitals and the π^* LUMO being localized on the ligand. This description is consistent with their similar UV-vis absorption profiles. Therefore, the blue-shifted MLCT absorption for the tripy-based complexes does, in fact, result from a ligand-based π^* LUMO that is higher in energy than for terpy. This interpretation is consistent with the absence of aromaticity and the presence of simple conjugation from the pyridyl ring out onto the two 1,2,3-triazole ring systems in tripy.

Beyond these electronic effects, the electrochemistry of the $Fe(\mathbf{1})_2^{2+}$ complex revealed a scan-rate dependent quasi-reversible oxidation upon addition of H_2O (Fig. 3b). Confirming† that this relationship was not related to a coordination mode of the electrogenerated Fe^{III} center with the hydroxyl end groups of **1**, studies on the methyl-terminated complex $Fe(\mathbf{2})_2^{2+}$ displayed the same effect. Neither the $Ru(\mathbf{1})_2^{2+}$ nor the $Fe(terpy)_2^{2+}$ complexes displayed this behavior. Secondly, standard aliquots of H_2O were added to the MeCN solution, with a concomitant increase in the degree of quasi-reversible behavior up to the addition of 1 equivalent. Based upon coincident traces in ten consecutive CV cycles,† these observations indicate that after oxidation to Fe^{III} at +1.2 V, the complex undergoes a structural rearrangement,[15] which can be reversed upon reduction to the Fe^{II} state at +0.4 V. This effect is attributed to the coordination of H_2O to either produce, or pass through, a not uncommon 7-coordinate complex. There are a variety of solution phase studies implicating iron aquation[16] and more than 12 heptacoordinate water-bound Fe^{III} crystal structures,[17]† whereas 7-coordinate Ru^{III} complexes are rare.[18] Therefore, this effect is facilitated by the opening-up of the iron center in its +3 oxidation state in the presence of the sterically unhindered 1,2,3-triazoles.

In summary, we have established that the synthesis of the tripy ligand provides facile access to a new class of terdentate ligands, which provide stable coordination environments resembling terpy, but with distinctive favorable differences. The reduced steric bulk provided by the N2 nitrogen of 1,2,3-triazole makes an impression upon the crystal structures of all three complexes, as well as the reversible redox switching of the Fe^{II} complex. This preliminary study confirms the effectiveness of the tripy ligand as a coordination environment for transition metals, and we intend to explore further its preparation and properties for the construction of supramolecular systems.

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Notes and references

‡ **Safety note:** Low molecular weight organic azides and the perchlorate salt of the europium complex are potential explosives.

§ *Crystallographic data* for $[Fe(\mathbf{1})_2]\cdot 2PF_6\cdot H_2O$: $C_{30}H_{40}F_{12}FeN_{14}O_5P_2$, M_r = 1022.51, monoclinic, space group = $C2/c$, a = 11.156(3), b = 26.836(3), c = 14.153(3) Å, β = 104.726(5), T = 173 K, Z = 4, μ = 0.556 mm^{-1}, R_F (R_{wF}) = 0.042 (0.102) for 872 observed independent reflections. *Crystallographic data* for $[Ru(\mathbf{1})_2]\cdot 2PF_6$: $C_{30}H_{38}F_{12}RuN_{14}O_4P_2$, M_r = 1049.75, monoclinic, space group = $P2_1/c$, a = 12.2491(8), b = 23.2119(15), c = 14.9526(10) Å, β = 108.375(2), T = 125 K, Z = 4, μ = 0.580 mm^{-1}, R_F (R_{wF}) = 0.0299 (0.0729) for 1965 observed independent reflections. *Crystallographic data* for $[Eu(\mathbf{2})_3]\cdot 3ClO_4$: $C_{51}H_{71}Cl_3EuN_{21}O_{13}$, M_r = 1444.60, orthorhombic, space group = $Pbcn$, a = 19.2068(17), b = 28.499(3), c = 24.321(2) Å, T = 135 K, Z = 8, μ = 1.136 mm^{-1}, R_F (R_{wF}) = 0.0638 (0.1915) for 2045 observed independent reflections. CCDC 639381–639383. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703301j

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