Rapid electrochemically induced linkage isomerism in a ruthenium(II) polypyridyl complex†

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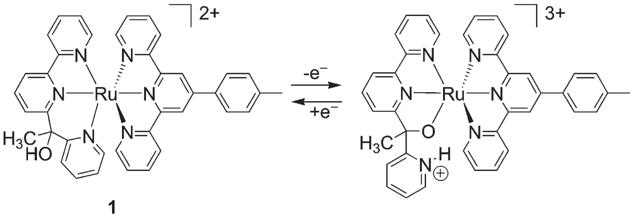
Rapid and complete switching between the N_6 and the N_5O donor set induced by changing the metal oxidation state has been observed for a new structural motif based on a ruthenium(II) polypyridyl complex.

The idea of building switches and memories on a molecular level has attracted great interest, as it would provide the basis for molecular electronic devices.[1] A principle requirement for any switch or memory is bistability,[2] *i.e.* the system has to exist in two stable states that can be reversibly interconverted by an external trigger. Coordination compounds featuring electrochemically induced linkage isomerism are interesting candidates as molecular memories.[3] In these compounds, the reversible rearrangement of for example an ambidentate ligand triggered by a metal-centered redox process results in a hysteresis-like bistable behavior, evident from a displacement of the voltammetric reduction peak compared to the oxidation peak. At any potential in between the two redox processes the state of the system depends on the electrochemical history of the system. Switching between the two states, that is writing or erasing the memory, is accomplished by a temporarily applied potential outside the range of bistability. Several such systems have been described, in particular for copper-based complexes where the oxidation states +1 and +2 have different geometric preferences leading to reversible monomer/dimer interconversions,[4] and $[Ru(NH_3)_5(sulfoxide)]^{3+/2+}$ complexes[5] where the ambidentate sulfoxide ligand is S-bound to Ru^{II} but isomerizes to O-bound after oxidation. Recently, also ruthenium(II) polypyridyl complexes containing sulfoxide ligands have been shown to undergo reversible linkage isomerization,[6] in which the favourable electrochromic behavior of these complexes offers a simple way to differentiate the redox states, *i.e.* to read the memory. However, most examples of bistability based on linkage isomerism in Ru complexes suffer from slow isomerization reactions (on the second timescale) and not in all systems conversions between the isomers are complete. These drawbacks would impede rapid writing and erasing and complicate reading of a memory. Here, we report linkage isomerism in a bistridentate heteroleptic ruthenium(II) polypyridyl complex containing the 1-[6-(2,2′-bipyridyl)]-1-(2-pyridyl)-ethanol ligand, where the electrochemically induced switching between a N_6 donor set and the N_5O analogue is rapid and complete in both directions (Scheme 1).

Reaction of $Ru^{II}(ttpy)(DMSO)Cl_2$ (ttpy is 4′-tolyl-2,2′:6′,2″-terpyridine) and one equivalent of 1-[6-(2,2′-bipyridyl)]-1-(2-pyridyl)-ethanol in a refluxing ethanol/water mixture produced the red $[Ru^{II}N_6(OH)]^{2+}$ complex **1**.[7] The ^1H NMR spectrum of **1** in CD_3CN revealed 23 signals in the aromatic region in accordance with the low symmetry of the complex (see ESI†). With the aid of COSY and NOESY techniques, all proton signals could be unambiguously assigned. The ^1H chemical shifts for the isolated pyridine are included in Table 1.



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Scheme 1

The redox properties of **1** were investigated by cyclic voltammetry, controlled potential electrolysis, and UV-Vis spectroelectrochemistry. In the cyclic voltammogram at low sweep rate ($0.100\ V\ s^{-1}$, CH_3CN), an irreversible anodic wave at $E_{p,a} = 0.79$ V (*vs.* $Fc^{+/0}$) was observed and an irreversible cathodic wave at $E_{p,c} = 0.34$ V was found on the reverse scan (Fig. 1). Both waves can be attributed to one-electron processes according to the coulometric data for exhaustive electrolysis at 0.92 V and re-reduction at −0.080 V. The UV-Vis spectroelectrochemical changes are shown in Fig. 2. Based on the spectral changes upon oxidation, in particular the bleach of the MLCT band at 480 nm, the anodic wave can be assigned to a metal-centered ($Ru^{II} \rightarrow Ru^{III}$) oxidation. All spectral changes were fully reversed by re-reduction at −0.080 V.

The electrochemical behavior of **1** can be rationalized in terms of a reversible follow-up reaction that is triggered by the $Ru^{II} \rightarrow Ru^{III}$ oxidation, resulting in a lowered potential for the $Ru^{III} \rightarrow Ru^{II}$ reduction. A linkage isomerization reaction that switches from the N_6 to the N_5O donor set upon oxidation, and back to the N_6 isomer upon re-reduction, could account for the considerable

Table 1 Electrochemical data, UV-Vis data and ^1H NMR shifts for **1** and **2** (PF_6^- salts)

	$E_{½}$/V (ΔE_p/mV)[a]		Absorption[b]	^1H NMR (CD_3CN)[c]			
	$Ru^{2+/1+}$[d]	$Ru^{3+/2+}$	λ_{max}/nm (ε/M^{-1} cm^{-1})	H_3	H_4	H_5	H_6
1	−1.59 (71)	0.79 (−)[e]	482 (14400)	8.26	7.68	6.87	7.40
2	−1.90 (73)	−0.10 (73)	518 (14200)[f]	6.95	7.07	6.95	8.35

[a] CH_3CN, $(n\text{-}C_4H_9)_4NPF_6$ (0.1 M), $0.1\ V\ s^{-1}$, *vs.* $Fc^{+/0}$. [b] MeOH. [c] 300 MHz, 298 K. [d] Reduction of the ttpy ligand, see Ref. 15. [e] Anodic peak potential. [f] ε obtained by *in situ* preparation.

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† Electronic supplementary information (ESI) available: Experimental details and Figs. S1–S5. See http://www.rsc.org/suppdata/cc/b5/b500946d/

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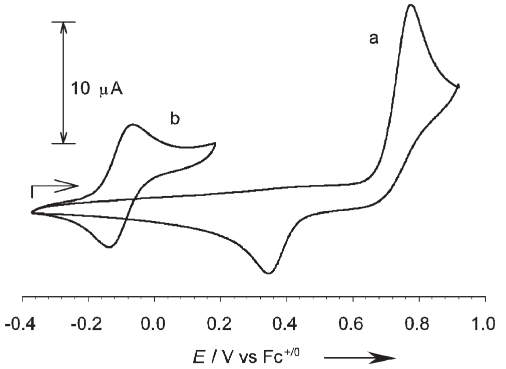


Fig. 1 Cyclic voltammograms (0.100 V s^{-1}) of **1** (a, 1 mM) and **2** (b, 0.8 mM) in CH_3CN with 0.1 M (n-$C_4H_9)_4NPF_6$.

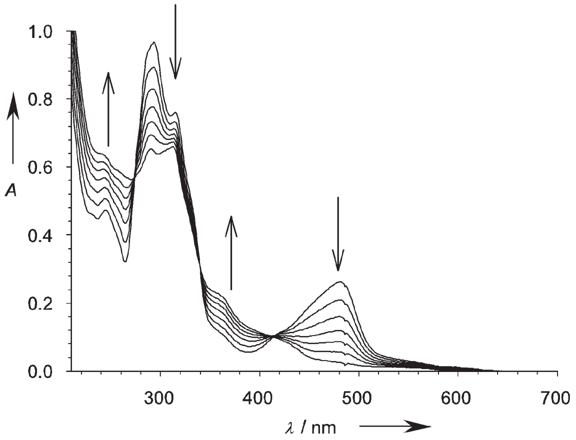
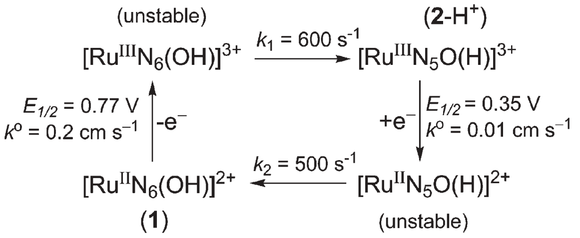


Fig. 2 Electronic spectrum of **1** ($\sim 1.6 \times 10^{-5}$ M) in CH_3CN with 0.1 M (n-$C_4H_9)_4NPF_6$ and spectral changes upon electro-oxidation at 0.92 V.



Scheme 2

separation of the two $Ru^{III/II}$ redox couples (Scheme 2). At high sweep rates ($v \geqslant 50$ V s^{-1}), the reverse peak for the $Ru^{III/II}$ couple in **1** started to appear suggesting that the re-reduction can compete with isomerization (Fig. 3). This peak became more pronounced with increasing sweep rate and at values of $v > 1000$ V s^{-1}, the cathodic wave attributed to the $Ru^{III} \rightarrow Ru^{II}$ reduction of the isomer **2**-H^+ almost completely disappeared. At the highest scan rates a minor anodic peak at *ca.* 0.5 V also emerges (Fig. 3 and ESI†) that can be attributed to the oxidation of the unstable $[Ru^{II}N_5O(H)]^{2+}$ isomer. The rate constants of the isomerization reactions were obtained from digital simulations[8] of the cyclic voltammograms (Fig. 3) based on an ECEC mechanism according to Scheme 2. The simulations with the parameters from Scheme 2 consistently reproduced the experimental voltammograms over the whole range of sweep rates between 50 and 1700 V s^{-1} (see ESI†).[9]

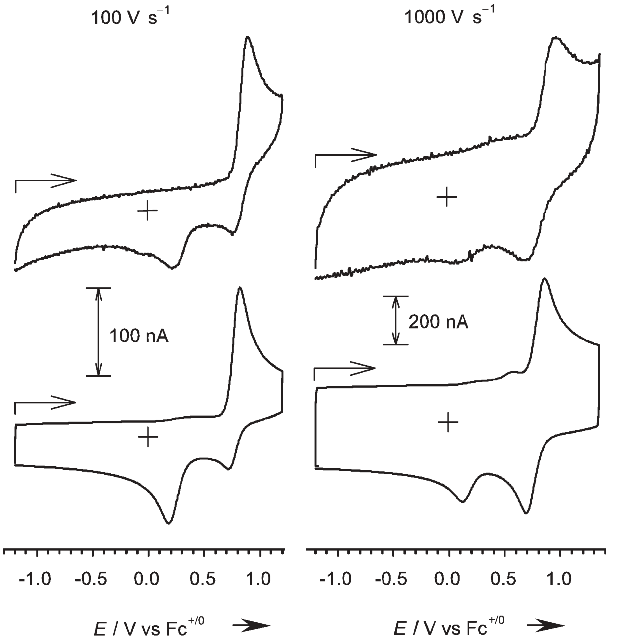


Fig. 3 Cyclic voltammograms of **1** (5 mM) in CH_3CN with 0.5 M (n-$C_4H_9)_4NPF_6$ and digital simulations with the parameters given in Scheme 2.

Similar homogenous rate constants, $k_1 = 600$ s^{-1} ($[Ru^{III}N_6(OH)]^{3+} \rightarrow [Ru^{III}N_5O(H)]^{3+}$) and $k_2 = 500$ s^{-1} ($[Ru^{II}N_5O(H)]^{2+} \rightarrow [Ru^{II}N_6(OH)]^{2+}$), respectively, were obtained for the two isomerization reactions.[10] For the reverse reactions of both chemical steps a product of $k_{-1} \times k_{-2} = 0.03$ s^{-2} could be obtained from the thermodynamics of the square scheme. Both rate constants are negligibly small compared to the forward reactions, as the isomerization equilibria are basically completely on the side of the N_6 and N_5O isomers in the Ru^{II} and Ru^{III} states, respectively. This is evidenced by the absence of any peaks for oxidation of the N_5O isomer and re-reduction of the N_6 isomer in CVs at sufficiently low scan rates (Fig. 1), and by the ^1H NMR spectrum of **1** which shows no detectable signals from the $[Ru^{II}N_5O(H)]^{2+}$ isomer.[11]

Further support for the suggested N_6 to N_5O linkage isomerization was obtained from the successful preparation of the $[Ru^{II}N_5O]^+$ complex **2** (inset Fig. 4), isolated after treatment of a solution of **1** in DMF with potassium *tert*-butoxide and subsequent precipitation with diethylether. The ^1H NMR spectrum of **2** (CD_3CN) showed the expected changes for the non-coordinating pyridine (Table 1). The H_6 proton in **1** appears at 7.40 ppm reflecting a position in a shielding region above the orthogonal terpyridine ligand.[12] In **2**, in contrast, H_6 resonances at 8.35 ppm. The effect on H_3 is even larger ($\Delta\delta = -1.3$), suggesting a conformation in **2** where H_3 is located over the terpyridine ligand.

The kinetics of the base-induced $[Ru^{II}N_6(OH)]^{2+} \rightarrow [Ru^{II}N_5O]^+$ isomerization was followed spectrophotometrically after addition of sodium methoxide to a methanolic solution of **1** (see ESI† for kinetic data). The solution gradually changed from an orange to a purple colour, indicating a change from the N_6 to the N_5O donor set, and showed isosbestic points at 497, 419, and 346 nm (Fig. 4). The red-shift of the ^{1}MLCT band is expected due to stabilization of the $Ru^{III}(ttpy^-)$ and $Ru^{III}(bpy^-)$ excited states by the alkoxide

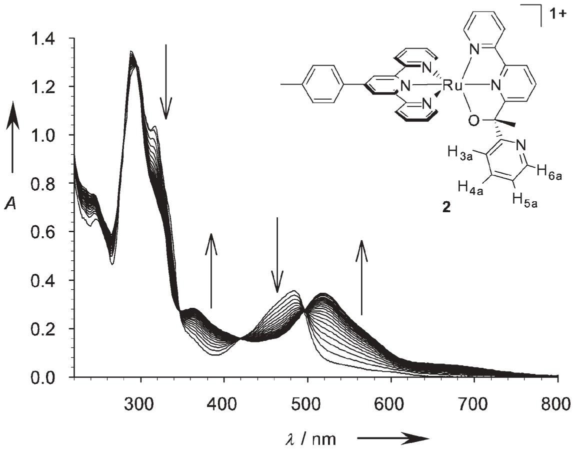


Fig. 4 Spectral changes of **1** (2×10^{-5} M) in MeOH containing 250 equiv. NaOMe at 292.5 K. Arrows indicate increasing reaction time from 0 to160 min. Inset: Structure and proton numbering of complex **2**.

ligand.[13] The rate of the forward reaction $\mathbf{1} \rightarrow \mathbf{2}$ is independent of the base concentration with a first order rate constant of $k_{\text{iso}} = (7.5 \pm 0.3) \times 10^{-4}\ \text{s}^{-1}$ (at 295 K).[14] This indicates that a rate limiting isomerization step is preceding a rapid deprotonation reaction. The electrochemical and ^{1}H NMR data show that in the absence of base only an undetectable fraction could reside in the N_5O form, but in the presence of base subsequent deprotonation completely shifts the reaction to the product **2**. The reversibility of the process was confirmed by the addition of acid (*p*-TsOH) that instantaneously regenerated the starting spectrum of the $[\text{Ru}^{\text{II}}\text{N}_6(\text{OH})]^{2+}$ complex.

In the cyclic voltammogram of **2** (Fig. 1), a reversible redox couple was observed at -0.10 V ($\Delta E_{\text{p}} = 73$ mV at $v = 0.100\ \text{V s}^{-1}$) assigned to the $\text{Ru}^{\text{III/II}}$ redox couple in accordance with previous results in ruthenium(II) polypyridyl complexes with oxygen donors.[13] The substantially lower potential of the $\text{Ru}^{\text{III/II}}$ couple in the deprotonated complex **2** as compared to the electrogenerated isomer (**2**-H$^+$) indicates that the electrochemically induced isomerization does not involve deprotonation of the complex and it can be anticipated that the electrogenerated isomer is protonated at the pyridyl moiety.

In summary, we have shown that the ruthenium(II) bistridentate complex **1** containing the ambidentate ligand 1-[6-(2,2′-bipyridyl)]-1-(2-pyridyl)-ethanol rearranges reversibly from the N_6 to the N_5O analogues **2**-H$^+$ (Ru^{III}) and **2** (Ru^{II}) upon oxidation or treatment with base, respectively. The electrochemically induced process is rapid in both directions and both interconversions between the isomers are complete. Due to the tridentate nature of the ambidentate ligand the isomerization is an intramolecular process in contrast to those systems where bimolecular steps such as dimerization or re-binding of a monodentate ligand are involved that would hamper isomerization in surface confined or solid state systems. Both isomers can be easily distinguished owing to the favourable electrochromic properties of the ruthenium complex or, alternatively, the state of the system could be inferred from its electrochemical response by sufficiently fast voltammetric reading that avoids isomerization. With these favourable properties complex **1** represents an interesting new structural motif for linkage isomerism and variations of this motif should be explored in view of factors that affect the rates of isomerization.

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8 The electrochemical simulation package (ESP v. 2.4) was provided by Dr Carlo Nervi, University of Torino, and can be retrieved free of charge from http://www.lem.ch.unito.it.

9 For the heterogenous electron transfer reactions the simulations require a significantly lower value of the standard rate constant k^0 for the N_5O isomer to account for the larger scan rate dependency of the cathodic peak potential associated with the $\text{Ru}^{\text{III/II}}$ couple at $E_{1/2} = 0.35$ V.

10 The relative high value of k_2 explains the absence of a voltammetric peak, except at the highest scan rates applied, arising from the oxidation of the N_5O isomer $[\text{Ru}^{\text{II}}\text{N}_5\text{O(H)}]^{2+}$.

11 Upper limits of $k_{-1} \leqslant 10\ \text{s}^{-1}$ and $k_{-2} \leqslant 2\ \text{s}^{-1}$ follow from the simulated voltammograms at slow scan rates (see ESI†).

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