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Spontaneous resolution of a diastereomeric ruthenium(II) complex with an atropisomeric 4,4′-biquinazoline ligand

Ljumni Ademi, Edwin C. Constable,* Catherine E. Housecroft, Markus Neuburger and Sylvia Schaffner

Department of Chemistry, University of Basel, Spitalstrasse 51, CH 4056 Basel, Switzerland. E-mail: edwin.constable@aaaunibas.ch; Fax: +41 61 267 1005; Tel: +41 61 267 1001

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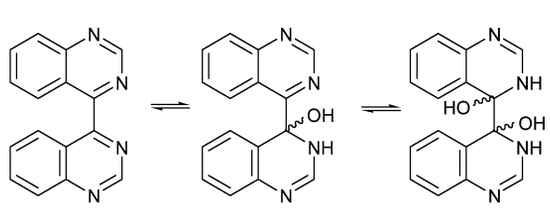
The ligand 4,4′-biquinazoline, 1, forms the complex [Ru(bipy)$_2$(1)]$^{2+}$ which consists of atropisomeric (Δλ/Λδ) and Δδ/Λλ) pairs of enantiomers but upon crystallization, spontaneous resolution of the major Δλ/Λδ pair occurs to give Δλ and Λδ crystals; although the free ligand is covalently hydrated in aqueous solution the ruthenium complex is not

Electron-poor aromatic nitrogen-containing heterocycles and quaternised derivatives can undergo reversible addition of water across C=N bonds in a process known as covalent hydration.[1] It was proposed by Gillard[2] that coordination to a transition metal activated heterocycles to covalent hydration although this proposal was strongly criticised.[3,4] In view of recent publications[5] which revive the discussion of covalent hydration of coordination compounds, we are prompted to report some unexpected results obtained in experiments designed to critically test the proposal by using ligands which are covalently hydrated in the non-coordinated state.

The ligand 4,4′-biquinazoline **1** is readily prepared in good yield by the reaction of quinazoline with KCN followed by oxidation of the intermediate with MnO_2.[6] We confirm that in weakly acidic aqueous solution, the ligand is hydrated across the 3,4 and 3′,4′-positions (Scheme 1) with the development of a highly shielded resonance at δ 6.1 in the ^{1}H NMR spectrum. Solutions of **1** in $CDCl_3$ exhibited a single solution species symmetrical about the C^4–$C^{4'}$ bond with a singlet assigned to H^2 at δ 9.58. The reaction of **1** with [Ru(bipy)$_2$Cl$_2$] in MeOH resulted in the formation of a dark green solution from which the complex [Ru(bipy)$_2$(**1**)][PF$_6$]$_2$ was precipitated as a green powder by the addition of NH_4PF_6.† The colour of the complex is unusual and arises from an MLCT absorption at 610 nm (ε 8,000 M^{-1} cm^{-1}) that is red shifted from the usual [Ru(diimine)$_3$]$^{2+}$ maximum close to 450 nm. Red shifting of this type has been observed with other extended aromatic systems and is attributed to a combination of steric interactions weakening the ligand field and the conjugation lowering the energy of the acceptor orbitals.[7,8] The related compound [Ru(bipy)$_2$(biq)][PF$_6$]$_2$ (biq = 1,1′-biisoquinoline) is reported to be dark purple but no spectroscopic data have been presented;[9] the additional red shifting in [Ru(bipy)$_2$(**1**)][PF$_6$]$_2$ is consistent with the incorporation of the additional heteroatom.[6,7] The ESMS spectrum of MeCN solutions of the complex exhibit peaks (with the expected isotopomer distribution) assigned to {Ru(bipy)$_2$(**1**)·PF$_6$}$^+$ (*m*/*z* 817), {Ru(bipy)$_2$(**1**)}$^{2+}$ (*m*/*z* 336), and {Ru(bipy)$_2$·PF$_6$}$^+$ (*m*/*z* 559) but no peaks which could be attributed to hydrated ligand species. The complex is electrochemically active and MeCN solutions exhibit a Ru^{II}/Ru^{III} process at +1.03 V and ligand-centred reductions at −0.76, −1.26, −2.01 and −2.30 V (*versus* Fc/Fc$^+$). The redox processes are fully reversible with the first reduction assigned to the electron deficient ligand **1**.



1

Scheme 1

The complex has two elements of chirality: firstly the Δ/Λ chirality at the stereogenic ruthenium in a tris(chelate) and secondly, the chirality of the atropisomeric ligand resulting in the possibility of four diastereomers which will exist as two enantiomeric pairs (Δδ, Λλ) and (Δλ, Λδ) of differing thermodynamic stability (Fig. 1). Solutions of the green complex in

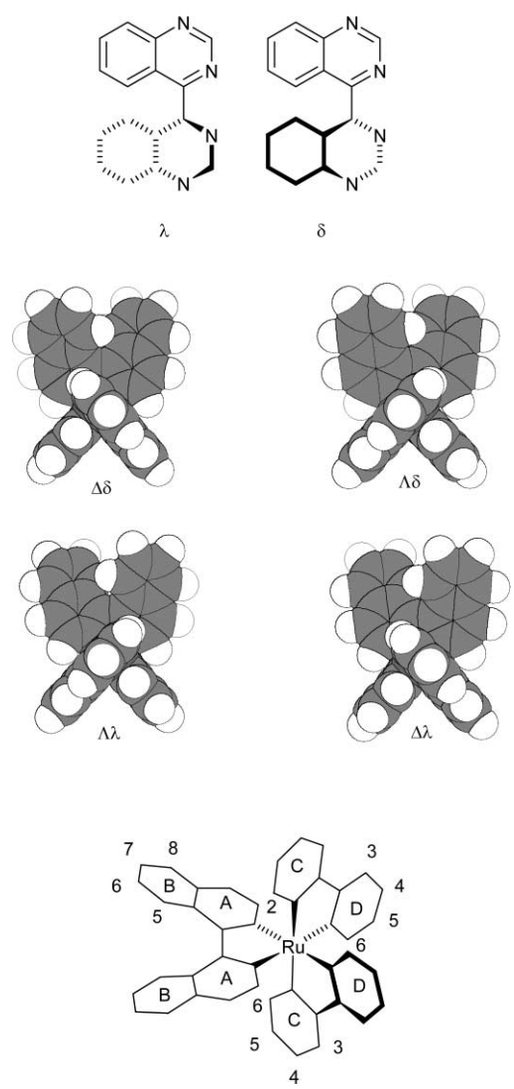


Fig. 1 The atropisomeric ligand **1** can adopt a δ or λ configuration in the complex. The complex can exist as four diastereoisomers comprising two pairs of enantiomers (Δδ, Λλ) and (Δλ, Λδ) which are expected to have different energies and be present in different amounts in an equilibrium mixture. The final structure shows the numbering scheme adopted for the discussion of the NMR spectra.

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CD_3CN exhibited complicated ^1H NMR spectra containing two species in differing amounts. Some of the resonances were significantly broadened at room temperature, but sharpened up on cooling the solution to 245 K giving a 3 : 1 ratio of major to minor component (Fig. 2). The spectra were fully assigned from COSY and NOESY spectra at 245 K giving the assignments presented in the footnote.† Upon heating to 350 K only the major diastereomer was present in solution allowing unambiguous confirmation of the COSY results at 245 K (Fig. 3), although at 350 K H^{D6} is in coalescence. The two subspectra correspond to the enantiomeric pairs of compounds (Δδ, Λλ) and (Δλ, Λδ) which are present. Modelling, NOESY spectroscopy and comparison with the behaviour of [Ru(bipy)$_2$(biq)][PF$_6$]$_2$[9] suggested that the major species would be the (Δλ, Λδ) pair in which the interactions of H^{C6} and H^{D6} with the A ring of **1** is minimised. The assignment of the C and D rings is on the basis of observed NOE's between these protons and H^{A2}.

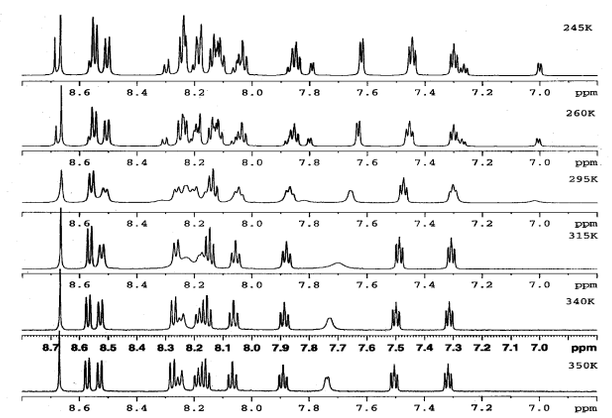

Fig. 2 The variable temperature 600 MHz ^1H NMR spectra of a CD_3CN solution of [Ru(bipy)$_2$(**1**)][PF$_6$]$_2$ showing the sharpening up of the spectrum at 245 K and conversion to the major species at 350K. Assignments are given in the footnote.†

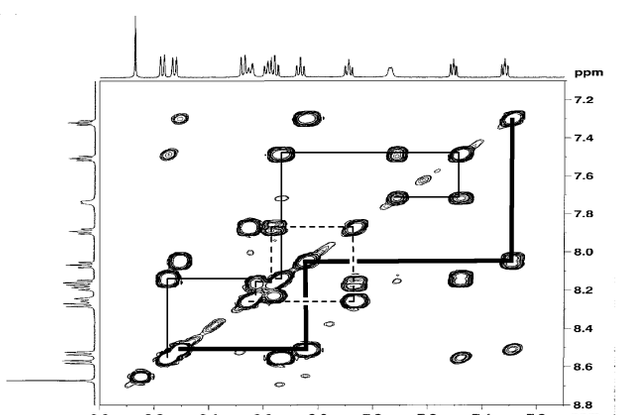

Fig. 3 The 600 MHz COSY spectrum of a CD_3CN solution of [Ru(bipy)$_2$(**1**)][PF$_6$]$_2$ at 350K where only the major pair of enantiomers (Δλ/Λδ) is present showing the connectivity of the B (solid line), C (broken line) and D (bold line) rings

Recrystallisation of the green solid from MeCN by the slow diffusion of diethyl ether vapour gave deep purple dichroic crystals of stoichiometry [Ru(bipy)$_2$(**1**)][PF$_6$]$_{5/3}$Cl$_{1/3}$·2MeCN, Fig. 4).‡ The crystal structure revealed that the chosen crystal contained only one enantiomer (Δλ) of the proposed major (Δλ, Λδ) enantiomeric pair. The spontaneous resolution into Δλ and Λδ enantiomers has occurred upon crystalisation. There are short contacts between H^{C6} and H^{A2} (3.636 Å), H^{C6} and H^{D6} (3.542 Å), and H^{D6} and H^{A2} (3.685 Å) responsible for the NOE's used in the assignment of the NMR spectra. Bond

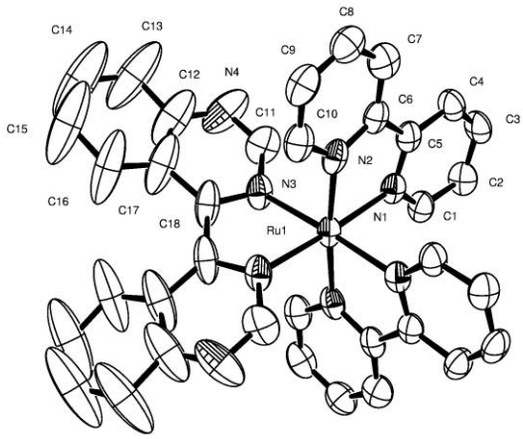

Fig. 4 The Δλ cation present in the crystal of [Ru(bipy)$_2$(**1**)][PF$_6$]$_{5/3}$-Cl$_{1/3}$·2MeCN showing the numbering scheme adopted. The unlabelled atoms are generated by symmetry operator 46 ($x+1, -y+1, -z+1/2$) and designated A. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1–N1 2.052(4), Ru1–N2 2.049(5), N1–Ru1–N1A 84.1(2), N1–Ru1–N2 79.12(18), N1A–Ru1–N2 96.35(18), N2–Ru1–N2A 174.0(2), N1–Ru1–N3 99.76(16), N1A–Ru1–N3 176.13(17), N2–Ru1–N3 84.53(19), N2A–Ru1–N3 100.26(19), N3–Ru1–N3A 76.4(3).

lengths within the coordination sphere are as expected and the Ru–N bonds to the bipy ligands are remarkably similar to those of the **1** ligand. The ligand **1** is twisted about the C18–C18A bond with an interplanar angle of 35.1° between the least squares planes of the A rings. The result is to minimise the interaction between H^{B5} and the symmetry related $H^{B5'}$ to 2.380 Å. The heterocyclic ring of **1** in the complex is somewhat riffled, primarily as a result of C18 lying 0.337 Å out of the plane of the least square plane of all six atoms in the ring.

In the solid state the coordinated **1** ligand is clearly in a non-hydrated form and the upfield shifting of the resonance at δ 7.0 assigned to H^{D6} (in the minor pair of enantiomers) is due to the proton lying in the shielding region above an aromatic ring rather than to the formation of a hydrate. The addition of D_2O to a CD_3CN solution of [Ru(bipy)$_2$(**1**)][PF$_6$]$_2$ results in no observable change in the ^1H NMR spectrum. We can thus conclude that even in the case of a compound such as **1**, which is strongly activated towards covalent hydrate formation, coordination of the ligand to a transition metal does not result in the formation of covalently hydrated complex. Disregarding steric influences, we can now state that the electronic influence of coordination to the ruthenium(II) centre cannot be equated to protonation of the free ligand.

We have demonstrated that the complex [Ru(bipy)$_2$(**1**)][PF$_6$]$_2$ is not covalently hydrated and reiterate our earlier conclusion "it is possible that covalent hydrates are of importance in the reactions of transition metal complexes of bipy and phen, but there is, as yet, no unambiguous evidence for their formation."[4] We are currently investigating the dynamic process involving the diastereomeric complexes.

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Notes and references

† [Ru(bipy)$_2$Cl$_2$] (170.3 mg, 0.1 mmol) and **1** (88.7 mg, 0.1 mmol) were suspended in ethane-1,2-diol (3 cm^3) and the mixture heated to reflux for 2 min in a modified domestic microwave oven for 2 min (600 W) to give a deep blue solution. The solution was cooled, diluted with MeOH (3 cm^3) and filtered. The filtrate was treated with a solution of [NH$_4$][PF$_6$] (100 mg) in MeOH (1 cm^3) to give a deep green preciptate of [Ru(bipy)$_2$(**1**)][PF$_6$]$_2$ that was collected by filtration and dried *in vacuo* (342 mg, 98.5%) mp 340–345 °C (dec). ^1H NMR (600 MHz, CD_3CN,

245 K): δ Major pair of enantiomers ($\Delta\lambda/\Lambda\delta$) 8.67 (s, 2H, H^{A2}), 8.55 (d, 2H, H^{C3}), 8.51 (d, 2H, H^{D3}), 8.25 (d, 2H, H^{B8}), 8.23 (d, 2H, H^{D6}), 8.19 (dd, 2H, H^{B5}), 8.13 (d, 2H, H^{B6}), 8.12 (t, 2H, H^{C4}), 8.04 (4, 2H, H^{D4}), 7.85 (t, 2H, H^{B7}), 7.62 (br d, 2H, H^{C6}), 7.45 (td, 2H, H^{C5}), 7.30 (td, 2H, H^{D5}); minor pair of enantiomers ($\Delta\delta/\Lambda\lambda$) 8.69 (s, 2H, H^{A2}), 8.57 (d, 2H, H^{C3}), 8.54 (d, 2H, H^{D3}), 8.30 (dd, 2H, H^{B5}), 8.20 (d, 2H, H^{B8}), 8.19 (d, 2H, H^{B6}), 8.10 (t, 2H, H^{C4}), 8.05 (4, 2H, H^{D4}), 7.87 (t, 2H, H^{B7}), 7.79 (br d, 2H, H^{C6}), 7.44 (td, 2H, H^{C5}), 7.27 (td, 2H, H^{D5}); 7.00 (d, 2H, H^{D6}).

‡ Crystal data for $[Ru(bipy)_2(\mathbf{1})][PF_6]_{5/3}Cl_{1/3}\cdot 2MeCN$, $C_{20}H_{16}Cl_{0.17}F_5Ru_{0.5}N_5P_{0.83}$, $M = 503.63$, cubic, space group $I\,41\,3\,2$, $a = 30.143(2)$ Å, $U = 27387.4$ Å^3, $Z = 24$, $D_c = 1.466$ Mg m^{-3}, μ(Mo-Kα) = 0.503 mm^{-1}, $T = 173$ K, 109941 (5543 independent) reflections collected on an Enraf Nonius Kappa CCD instrument. Refinement of 3597 reflections (349 parameters) with $I > 3.0\sigma(I)$ converged at final $R1 = 0.0546$, $wR2 = 0.0602$, Flack parameter −0.046. CCDC reference number 220745. See http://www.rsc.org/suppdata/dt/b3/b312125a/ for crystallographic data in CIF or other electronic format.

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