# A Novel Cyclam–Nickel(II) Complex appended with a Tris-(2,2′-bipyridine)–Ruthenium(II) Complex (Cyclam = 1,4,8,11-tetra-azacyclotetradecane)

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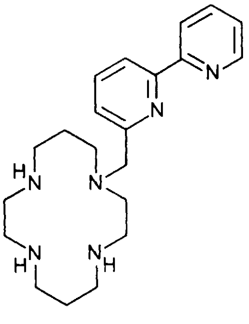
A new class of heterometallo-binuclear complex $[Ru^{II}(bpy)_2(bpy–cyclam)Ni^{II}]^{4+}$ (3) (bpy = 2,2′-bipyridine) has been synthesized as a new complex for use in photocatalysts; NMR and *X*-ray structural studies show a close contact between a hydrogen atom of the pendant bpy and $Ni^{II}$ in the cyclam.

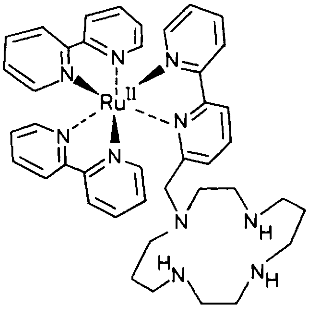
In the current efforts to combine cyclams (cyclam = 1,4,8,11-tetra-azacyclotetradecane) with other functional molecules,[1] we report a novel supermolecular ligand $[Ru^{II}(bpy)_2(bpy–cyclam)]^{2+}$ (**2**) [bpy = 2,2′-bipyridine, bpy–cyclam = 1-(2,2′-bipyridin-6-ylmethyl)-1,4,8,11-tetra-azacyclotetradecane], and a new prototype of heterometallo-binuclear complexes $[Ru^{II}(bpy)_2(bpy–cyclam)Ni^{II}]^{4+}$ (**3**) possessing two redox-active metal centres.[2]

Nickel(II)–cyclam complexes can act as catalysts for the reduction of $CO_2$ to CO,[3] the oxidation of alkenes to epoxides,[4] and a variety of other interesting transformations.[5] Similarly, $Ru^{II}(bpy)_3$ has been extensively studied for its facile photoexcitation properties.[6] Recently, Calvin *et al.* reported the photo-catalysed reduction of $CO_2$ to CO with a combination of $Ru^{II}(bpy)_3$ and $Ni^{II}$–cyclam.[7] We therefore considered that by intramolecularly linking these two functionalities, it might be possible to develop a novel photoredox catalysis system.

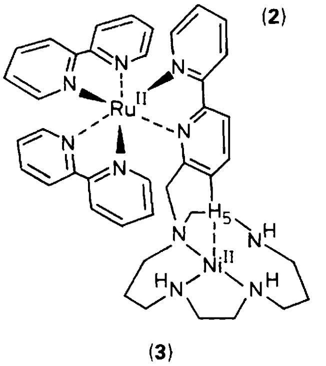
The bipyridine-pendant cyclam (**1**) was synthesized by the methods recently described.[8] When (**1**) (0.1 mmol) and $Ru^{II}(bpy)_2Cl_2$ (0.1 mmol) were heated at reflux for 24 h in ethanol–water (2:1; 20 ml) under Ar, red crystals were obtained, which were purified from aqueous solution (pH 3) as the diprotonated form, $[Ru^{II}(bpy)_2(bpy–H_2cyclam^{2+})]$-$(ClO_4)_4·3H_2O$. From this mono-metallated 'starting ligand,' (**2**)·2H+, the hetero-bimetallic complex (**3**) could then be prepared by stirring with $Ni(ClO_4)_2·2H_2O$ (1 equiv.) in methanol for 30 min at 60 °C. The resulting orange crystalline product (**3**) was then precipitated (yield 50%) either as $[Ru^{II}(bpy)_2(bpy–cyclam)Ni^{II}](ClO_4)_4·2H_2O$ (**3**)-$(ClO_4)_4·2H_2O$, or, upon the addition of $NH_4BF_4$, as (**3**)$(BF_4)_4·2H_2O$.†



(**1**)



(**2**)



(**3**)

The *X*-ray structure of (**3**)$(BF_4)_4·2H_2O$ is shown in Figure 1.‡ The Ru(bpy)$_3$ moiety possesses approximately $D_3$

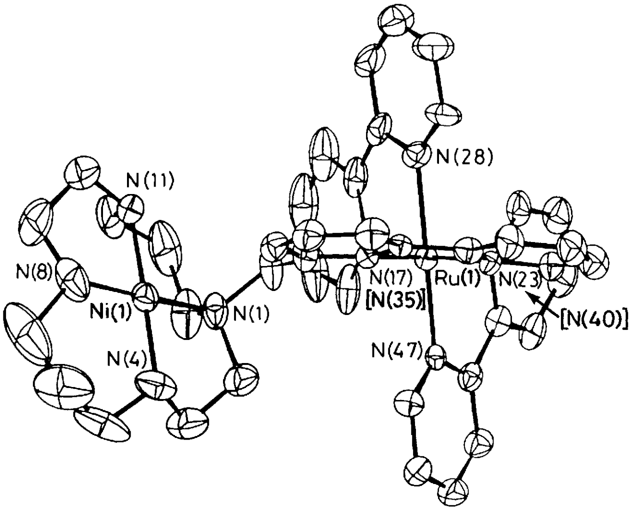


**Figure 1.** ORTEP view of (**3**). Atoms are drawn with 20% probability ellipsoids. Ni–N and Ru–N distances (Å) are as follows: Ni(1)–N(1), 1.949(8); Ni(1)–N(4), 1.931(13); Ni(1)–N(8), 1.942(12); Ni(1)–N(11), 1.978(11); Ru(1)–N(17), 2.143(6); Ru(1)–N(23), 2.033(7); Ru(1)–N(28), 2.074(10); Ru(1)–N(35), 2.077(7); Ru(1)–N(40), 2.050(6); Ru(1)–N(47), 2.053(9). The H(5)···Ni distance is 2.41 Å (see text). Important bond angles (°) are as follows: N(1)–Ni(1)–N(8), 177.5(5); N(4)–Ni(1)–N(11), 176.8(5); N(17)–Ru(1)–N(40), 173.5(3); N(23)–Ru(1)–N(35), 171.8(3); N(28)–Ru(1)–N(47), 174.5(3).

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† Elemental analyses of these metal complexes were satisfactory.

‡ *Crystal data* for (**3**)$(BF_4)_4·2H_2O$ at 293 K: $C_{41}H_{52}B_4F_{16}O_2N_{10}NiRu$, triclinic, space group $P\bar{1}$, $a = 12.152(7)$, $b = 19.296(10)$, $c = 11.817(7)$ Å, $\alpha = 85.80(5)$, $\beta = 106.52(6)$, $\gamma = 104.29(6)°$, $U = 2573$ Å$^3$, $Z = 2$, $D_c = 1.580$ g cm$^{-3}$, $\mu = 7.6$ cm$^{-1}$. Using a dark orange crystal (0.02 × 0.05 × 0.1 mm$^3$), 6811 unique reflections with $|F_o| > 2\sigma(F_c)$ were collected of the possible 9033 points (Philips PW1100 diffractometer, Mo-$K_\alpha$, $6° < 2\theta < 50°$), and used for refinement by the heavy-atom method (without absorption correction), H atoms not being included; $R = 0.092$, $R_w = 0.100$. As shown by the anisotropic thermal vibrations of the F atoms, the four $BF_4$ groups have a strong tendency to rotate. Many residual electron density peaks (*ca.* 0.8 e Å$^{-3}$) were found at distances of 0.9—1.7 Å from B. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

symmetry with an average Ru–N length (2.07 Å) close to normal.[3b,9] The $Ni^{2+}$ ion is bound within the $N_4$ plane, with the average Ni–N distance being 1.95 Å, the normal range for diamagnetic low-spin $Ni^{II}$–N bonds.[10] The configuration of the cyclam system was found to be of the (*R*,*S*,*R*,*S*)-type,[11] in which the three protons and the benzyl carbon bound to the cyclam nitrogens all face in the same direction. Molecular models suggest that this configuration is most likely to minimize the effects of steric repulsion between the $Ni^{II}$(cyclam) and the $Ru^{II}(bpy)_3$ units. The spatial distance between Ru and Ni is 6.4 Å. The most remarkable feature of the structure of (**3**) is the anomalously close distance, 2.41 Å, between H(5) of the pendant bipyridine and the $Ni^{II}$ bound in the cyclam cavity (assuming a C–H bond length of 1.07 Å).[12]

The close H(5) to $Ni^{2+}$ distance observed in the *X*-ray structure appears to persist in solution. The $^1H$ NMR spectrum of (**3**) in $D_2O$ is sharp and shows a one-proton resonance (d, $J_{HH}$ 7.8 Hz) at the unusually low field of δ *ca.* 12, assignable to H(5) proximate to $Ni^{II}$.§ As expected, in (**2**) (as $2H^+$), no such low-field shift for H(5) was apparent. Such a close contact would be useful in any electron transfer between the two metal-containing systems.[13]

The absorption spectra of (**2**) and (**3**) (in $H_2O$) are similar to that of $[Ru(bpy)_3]Cl_2$.[14] The steady-state emission maxima of (**2**) and (**3**) in vacuum-degassed $H_2O$ at room temperature (excited at 450 nm; $\lambda_{max}$ 622 nm) are almost identical to that of $Ru^{II}(bpy)_3$ itself ($\lambda_{max}$ 625 nm).[3b] However, the emission intensities of (**2**) and (**3**) are drastically reduced [to *ca.* 1/170 and 1/160, respectively, of that of $Ru^{II}(bpy)_3$], suggesting that efficient quenching of the excited state occurs by virtue of the intramolecular attachment to a diprotonated or nickel-chelated cyclam.¶

The electrochemical properties of the ground-state supercomplex (**3**) were also studied. The cyclic voltammogram in MeCN (0.1 M $Bu^n_4NClO_4$; 25 °C) shows three quasi-reversible redox waves {$E_{1/2}$ −1.33, −1.54, and −1.81 V *vs.* saturated calomel electrode (SCE) for +2/+1, +1/0, and 0/−1 redox couples, respectively; these potentials parallel those for $[Ru^{II}(bpy)_3]Cl_2$: −1.33, −1.52, and −1.78 V *vs.* SCE}. An additional irreversible reduction wave for $Ni^{II}$ to $Ni^I$ was observed at −1.10 V, ‖ which is much less negative than that of $Ni^{II/I}$–(*R*,*R*,*S*,*S*)-cyclam ($E_{1/2}$ < −1.7 V). Similarly, the $Ni^{III/II}$ potential of (**3**) (> +1.4 V) far surpassed that of the (*R*,*R*,*S*,*S*)-cyclam complex ($E_{1/2}$ +0.99 V). These redox changes of Ni may reflect the attachment of the hydrophobic tris(bpy) complex to the cyclam as well as the unusual (*R*,*R*,*S*,*S*)-cyclam configuration. The $Ru^{III/II}$ potential of (**3**) is moved to +1.39 V, significantly more positive than that (+1.29 V) of $[Ru^{II}(bpy)_3]Cl_2$.**

Recently, several $Ru^{II}(bpy)_3$ complexes intramolecularly attached (at the 4,4′-positions) with organic redox molecules have been designed.[15] Our supercomplex (**3**), however, has a catalytic site in the Ni(cyclam) unit. Furthermore, versatile structural modifications may be conceived; other redox-active and photoactive metal ions may be substituted at either site, or bipyridine may be replaced by other polypyridine ligands such as phenanthroline.

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§ Sodium 2,2-dimethyl-2-silapentane-5-sulphonate was used as reference. Occurrence of the other four satellite doublet signals (all minor, accounting overall for <23% intensity) further suggests the presence of four minor cyclam conformers (*e.g.*, *R*,*R*,*S*,*S*) which could co-exist in solution.

¶ Addition of ten equivalents of $Ni^{II}$–(*R*,*R*,*S*,*S*)-cyclam complex does not quench the metal-to-ligand charge-transfer (MLCT) excited state of $[Ru(bpy)_3]Cl_2$. We are currently studying whether the results with (**2**) and (**3**) are due to electron transfer or energy transfer.

‖ The irreversibility suggests that a fast chemical reaction also occurs when the $Ni^I$ complex is generated. If scanned in the limited range of −0.8 to −1.3 V, this became a quasi-reversible wave at −1.01 V ($E_p$ 190 mV, scan speed 200 mV $s^{-1}$).

** The excited state redox potentials of (**3**) are calculated from the electrochemical data and the MLCT excited-state energy: $E_{1/2}$ ($^*Ru^{2+}/Ru^{3+}$) = $E_{1/2}$ ($Ru^{2+}/Ru^{3+}$) − $E_{MLCT}$ = −0.62 V, $E_{1/2}$ ($^*Ru^{2+}/Ru^{+}$) = $E_{1/2}$ ($Ru^{2+}/Ru^{+}$) − $E_{MLCT}$ = +0.68 V.