Synthesis and Coordination Chemistry of 1-(2′,2″-bipyridyl-5′-yl-methyl)-1,4,8,11-tetraazacyclotetradecane L^1. Quenching of Fluorescence from $[Ru(bipy)_2(L^1)]^{2+}$ by Coordination of Ni^{II} or Cu^{II} in the cyclam Cavity (bipy = 2,2′-bipyridine; cyclam = 1,4,8,11-tetra-azacyclotetradecane)

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A novel bipy derivative of cyclam (L^1) designed for controlled and systematic polynuclear metal complex formation is reported; fluorescence quenching of the $[Ru(bipy)_3]^{2+}$ core of $[(bipy)_2Ru(L^1)]^{2+}$ upon coordination of Cu^{II} at the cyclam cavity is demonstrated.

Tris(2,2′-bipyridyl)ruthenium(II) complexes occur repeatedly in schemes for photochemical energy conversion (*i.e.* the conversion of light energy into chemical energy).[1] Several features make $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridyl) an attractive photosensitiser; it is stable and has an intense absorption band at 450 nm (ε = 15000 mol^{-1} dm^3 cm^{-1}), which coincides with the peak solar output. Following light absorption, rapid inter-system crossing produces a long-lived excited state, now universally recognised as a metal to ligand charge transfer (^{3}MLCT) state. This excited state is both a strong oxidant and a strong reductant, and is also luminescent. Its stability to collisional deactivation by solvent allows the

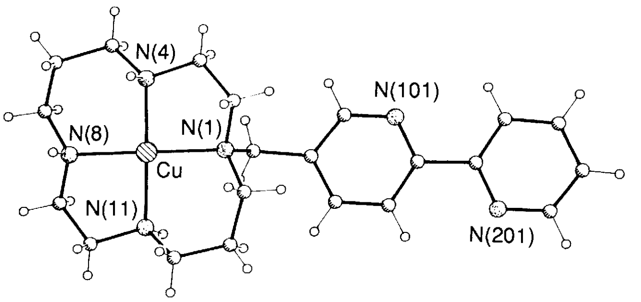
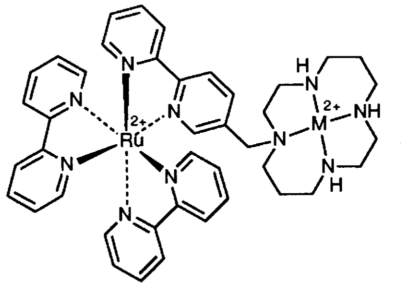
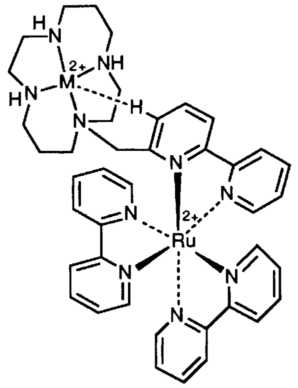


Fig. 1 Crystal structure of $[Cu(L^1)](ClO_4)_2$ **I**. Atoms are numbered sequentially around the macrocyclic ring [N(1), C(2), C(3), N(4), *etc.*]. The axial perchlorate anions are omitted for clarity.



IVa; M = Cu
IVb; M = Ni
IVc; M = Zn



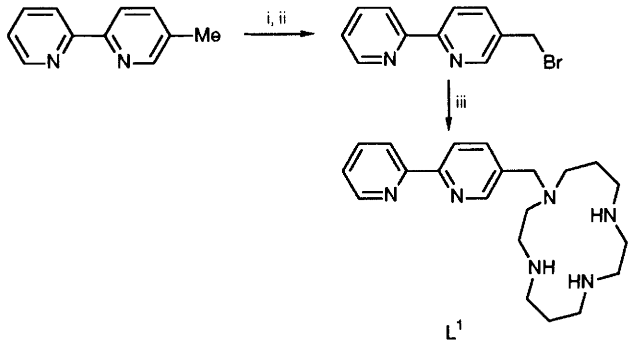
V

Fig. 2 Structures of **IVa–c**, and **V**

excitation energy of the ^{3}MLCT state to be efficiently and selectively transferred to other components of the solution *via* electron or energy transfer processes, rather than degrade uselessly to heat.

$[Ru(bipy)_3]^{2+}$ has been covalently linked to numerous other units to produce more sophisticated photochemical molecular devices. In particular diad, triad and even tetrad systems have been constructed, which funnel the excitation energy to other chromophores.[2] Much effort has also been expended on the problem of converting the excitation into physically separated oxidising and reducing equivalents, much as occurs during photosynthesis.[3] Significantly less attention has focused on the attachment of $[Ru(bipy)_3]^{2+}$ to catalytic sites that could potentially use the energy stored in the ^{3}MLCT state. Since metal macrocyclic complexes catalyse a number of reactions[4] and allow close stereoelectronic control of metal-ion reaction sites, we synthesised the novel ditopic ligand L^1 (Scheme 1), and examined the photochemistry of the derived complexes L^2 (Scheme 2) and **IVa–c** (Fig. 2).

L^1, which bears two independent, divergent binding sites, was synthesised in two steps from 5-methyl-2,2′-bipyridyl[5] (Scheme 1). This ligand is unable to bind a single metal ion simultaneously in the macrocyclic cavity and at the pendent arm. Instead, metal ions choose between the bipy unit and the macrocycle on the basis of their own kinetic and thermodynamic preferences, and the exact nature of the metallic precursor.



Scheme 1 *Reagents and conditions*: i, *N*-bromosuccinimide, CCl_4, tungsten light; ii, recrystallization, iii, cyclam (5 equiv.), PhCl, 100 °C

Reaction of L^1 with one equivalent† of Cu^{II}, Ni^{II} or Zn^{II} yields, respectively, the complexes **I**, **IIa** and **IIb**, in which the metal occupies the macrocyclic cavity and the bipy pendent arm is free (Scheme 2). This is shown by optical spectroscopy {consistent with presence of $[M(cyclam)]^{2+}$ and free bipy chromophores}, mass spectra, and the X-ray crystal structure of **I** as its nitromethane solvate (Fig. 1).‡

In $[Cu(L^1)](ClO_4)_2$, **I**, the cyclam moiety circumscribes the square-planar Cu^{II} ion, adopting the unstrained *RRSS* configuration (Fig. 1). Copper–nitrogen distances average 2.026 Å, although the longest (2.062 Å) is associated with the tertiary nitrogen atom, N(1), which bears the pendent arm. The bipyridyl unit takes no part in coordination to Cu, and is oriented diametrically away from it. Instead, coordination to copper is completed by axial perchlorate groups [Cu–O(1) = 2.81 Å, Cu–O(14) = 2.47 Å]. Interestingly, the longer of these two distances is associated with the perchlorate anion on the same side of the cyclam ring as the pendent arm. The pyridine rings of the bipyridyl moiety are essentially coplanar, but their nitrogen atoms are oriented *trans* with respect to the central C–C bond [C(102)–C(202)], as is usual when not chelating.

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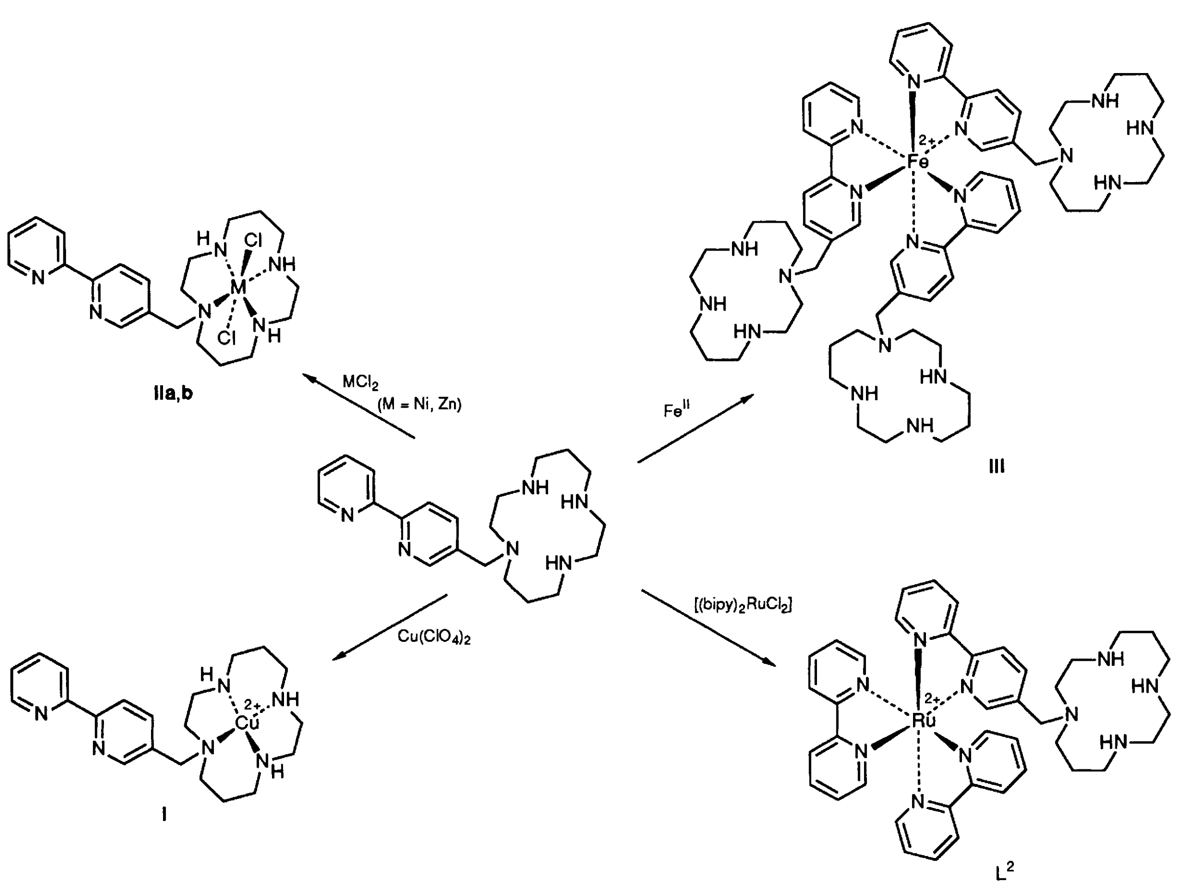
† Use of an excess of metal enables both bipy and cyclam groups to bind separate ions. This approach allows us to build up polynuclear complexes in a controlled and systematic fashion.

‡ *Crystal data* for $[Cu(L^1)](ClO_4)_2 \cdot MeNO_2$; $C_{22}H_{35}N_7CuCl_2O_8$; $M_r = 691.5$; triclinic, $P\bar{1}$; $a = 8.730(2)$; $b = 12.434(4)$; $c = 14.768(4)$ Å; $\alpha = 98.04(2)$; $\beta = 106.15(2)$; $\gamma = 101.78(2)°$; $V = 1474$ Å^3; $Z = 2$; $D_c = 1.56$ g cm^{-3}. Mo-Kα radiation ($\lambda = 0.71073$ Å). μ(Mo-Kα) = 9.7 cm^{-1}. $T = 290$ K. $R = 7.53\%$, $R_w = 7.89\%$ for 3305 unique reflections with $I > 2\sigma(I)$.

Red blocks suitable for diffraction studies were obtained by vapour diffusion of diethyl ether into a nitromethane solution of the complex. Since loss of solvent occurs slowly in air, the selected crystal was sealed inside a Lindemann tube. Data were collected using a Siemens R3m diffractometer in ω-2θ mode and corrected for absorption.

The Cu atom was located by the Patterson interpretation section of SHELXTL, and the light atoms then found on successive Fourier syntheses. The nitromethane was disordered, and refined isotropically. Anisotropic temperature factors were used for all remaining non-hydrogen atoms. The non-coordinating O atoms of the perchlorate anions also showed disorder, as evidenced by their high thermal parameters and unusual Cl–O bond distances and angles, but no attempt was made to model this further. Hydrogen atoms were given fixed isotropic temperature factors, $U = 0.07$ Å^2; those defined by molecular geometry were inserted at calculated positions and not refined. Hydrogen atoms on the methyl group of the nitromethane were not included in the model.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 2

Reaction of L^1 with *cis*-$[(bipy)_2RuCl_2]$ in water followed by cation exchange chromatography yields the ligand L^2 (Scheme 2), which comprises a $[Ru(bipy)_3]^{2+}$ core with a covalently attached free cyclam moiety, as shown by optical and NMR spectroscopy. At neutral pH, two protons occupy the macrocyclic cavity. Interestingly, L^1 also binds Fe^{II} at the bipy centre, to yield the ferroin-type complex **III** (Scheme 2). ^{13}C NMR spectroscopy shows that in this diamagnetic $[Fe(a\text{-}b)_3]^{2+}$ chelate, the less crowded *mer*-isomer predominates over the *fac*-isomer.

Reaction of the free bipy group of **I** (in EtOH), **IIa** or **IIb** (in water) with *cis*$[(bipy)_2RuCl_2]$, followed by cation exchange chromatography, yields the diads **IVa–c** (Fig. 2), which were isolated as their hexafluorophosphate salts by addition of NH_4PF_6 and recrystallised from ethanol–water. They each show UV/VIS spectra characteristic of $[Ru(bipy)_3]^{2+}$, and cyclic voltammograms consistent with the presence of non-interacting $[Ru(bipy)_3]^{2+}$ and $[M(cyclam)]^{2+}$ units. FAB mass spectra (3-nitrobenzyl alcohol matrix) show the presence of $\{[(bipy)_2Ru(L^1)M](PF_6)_2\}^+$ at *m/z* 1 129 (M = Ni) and 1 135 (M = Cu), and also the presence of $\{[(bipy)_2Ru(L^1)Ni](PF_6)_3\}^+$ at *m/z* 1 274. Microanalyses also agree with the formulations. **IVa** presumably retains the *RRSS* configuration at the $[Cu(cyclam)]^{2+}$ centre as established for **I**.

Irradiation of L^2 or **IVc** at any of their absorption bands (but especially the CT band at 450 nm) yields strong fluorescence centred on 600 nm, characteristic of the $[Ru(bipy)_3]^{2+}$ chromophore. The fluorescence lifetime of L^2 in acetonitrile, measured by laser flash photolysis, is 700 ns (compare 600 ns for $[Ru(bipy)_3]^{2+}$ itself), whilst the fluorescence intensity in water approaches 75% that of $[Ru(bipy)_3)]^{2+}$. The zinc complex **IVc** behaves similarly. The ready fluorescence of L^2 contrasts the very weak fluorescence of **V** (M = $2H^+$, Ni^{2+}, Fig. 2), where the macrocycle is attached to the 6-position of the bipy, rather than the 5-position.[6] The 6-substitution generates considerable (0.1 Å) elongation of the Ru–N distance for the neighbouring pyridine N atom. Such distortions of the RuN_6 coordination sphere reduce the energy of certain Ru-centred d–d levels below that of the ^{3}MLCT excited state, providing a ready non-radiative relaxation pathway.

By contrast with L^2 and **IVc** (which fluoresce readily), the Cu^{II} and Ni^{II} analogues **IVa** and **b** show *no detectable fluorescence* on irradiation at 450 nm. This presumably reflects a very rapid quenching of the ^{3}MLCT excited state, which could arise by either electron transfer or energy transfer mechanisms.[7] In the former case the excited $[Ru(bipy)_3]^{2+}$ moiety would donate an electron to (or receive an electron from) the attached macrocyclic complex, forming a transient Ru^{III}–M^I (or Ru^I–M^{III}) species. This intermediate would then undergo rapid back-transfer to regenerate the ground state. This mechanism is unlikely for **IVa** and **b** in aqueous solution as neither $[Ni(cyclam)]^{2+}$ nor $[Cu(cyclam)]^{2+}$ are oxidised or reduced with sufficient facility. In addition, there was no evidence for absorptions owing to transient $[Ru(bipy)_3]^{3+}$ or $[Ru(bipy)_3]^+$ chromophores following flash photolysis of these diads in acetonitrile. This implies that electron-transfer intermediates either do not form (as expected) or that they undergo back-transfer within the timescale of the laser pulse (1 ns).

Prolonged illumination of **IVa** in *acetonitrile*, however, causes the build up of a small amount of fluorescence, characteristic of L^2. This implies that some oxidative quenching of the excited $[Ru(bipy)_3]^{2+}$ unit by the attached $[Cu(cyclam)]^{2+}$ group occurs under these conditions, as allowed by the $[Cu(cyclam)]^{2+/+}$ redox potential in acetonitrile.§ Oxida-

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§ The relevant potentials are (V *vs.* normal hydrogen electrode, MeCN); $^*[Ru(bipy)_3]^{2+/+}$, +0.84; $^*[Ru(bipy)_3]^{2+/3+}$, −0.86; $[Cu(cyclam)]^{2+/+}$, −0.85; $[Cu(cyclam)]^{2+/3+}$, +1.60; $[Ni(cyclam)]^{2+/+}$, −0.90; $[Ni(cyclam)]^{2+/3+}$, +1.48.

tive quenching would yield a transient Ru^{III}–Cu^{I} intermediate; the $[Cu(cyclam)]^+$ moiety, which is known to be unstable,[8] could then dissociate (to the free ligand, L^2, and $[Cu(MeCN)_4]^+$) before back-transfer takes place.

Most likely, the quenching in **IVa** and **b** occurs predominantly *via* an energy transfer mechanism, *i.e.* the excited $[Ru(bipy)_3]^{2+}$ group initiates an electronic transition in the attached $[M(cyclam)]^{2+}$ unit. Both $[Cu(cyclam)]^{2+}$ and $[Ni(cyclam)]^{2+}$ have d–d transitions which match the excitation energy of $[Ru(bipy)_3]^{2+}$, but the Zn^{II} analogue lacks such transitions. In general, energy transfer can be mediated either through a dipole–dipole interaction (Forster's mechanism) or an exchange interaction (Dexter's mechanism). In view of the presence of a heavy atom in both chromophore and quencher portions of **IVa** and **b**, the latter seems the most likely. Dexter's mechanism can be viewed as a dual electron transfer process, necessitating orbital overlap between excited state and quencher. Indirect evidence for the orbital overlap required can be found in the crystal structure of **V**, which indicates a significant interaction between H(5) of the bipy group and Ni in the macrocyclic ring.[6]

The $[Ru(bipy)_3]^{2+}$ moiety in the diads **I** and **IVa–c** acts essentially as a reporter group for the presence of metal ions in the cyclam cavity; when Ni^{II} and Cu^{II} are encapsulated there, the fluorescence is switched off. This prompts the question: can L^2 act as a fluorescent sensor for these ions? Such sensors attract attention because of their enormous potential sensitivity. Unfortunately, addition of Cu^{II} to L^2 under conditions suitable for sensor operation (10^{-1} mol dm^{-3} aqueous solution, room temperature) causes only slow and incomplete quenching of the fluorescence. It appears that an unstable, incompletely quenched adduct forms, which reverts to the stable, fully quenched diad **IVa** only under forcing conditions.

Further studies addressing the mechanism and the generality of the quenching of L^2 and analogues by metal ions are underway in this laboratory. In addition we are utilising receptor groups other than cyclam with a view to improving the kinetics of metal uptake, and extending the range of target ions. The results of these studies will be published shortly.

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