Metallamacrocycles

Switchable Electron-Transfer Processes in a Mixed-Valence, Kinetically Locked, Trinuclear Ru^{II} Metallamacrocycle[**]

*Naz Shan, Steven J. Vickers, Harry Adams, Michael D. Ward, and Jim A. Thomas**

The use of metal ions to template the self-assembly of discrete molecular structures has attracted a great deal of attention,[1] and an area of particular recent interest has been the assembly of metallamacrocyclic complexes, which, in addition to their appealing structures, can act as highly specific hosts and sensors for neutral molecules, cations and anions.[2] Bowl-shaped metallamacrocyclic complexes such as **1** were first described by Fish and co-workers; these contain adenine-based units as bridging ligands and cationic [Cp*Rh^{III}] units as vertices and act as effective hosts for guests such as aromatic amino acids.[3]

Consequent work by Yamanari et al. resulted in higher order macrocycles,[4] and Sheldrick and co-workers reported the structures of related [(arene)Ru^{II}] and [(arene)Ir^{III}] systems.[5] Using Ir^{III}, Rh^{III}, and Ru^{II} metal centers and pyridyl-based ligands, Severin and co-workers prepared analogous neutral metallamacrocycles, such as **2**, which function as highly specific hosts and sensors for cations and anions.[6]

Apart from their host–guest chemistry, triangular complexes such as these are appealing targets for the study of redox properties and metal–metal interactions because of their unusual topology. The triangular arrangement of the redox centers means that two different mixed-valence states can, in principle, be generated. However, solution studies on previously reported Ru macrocycles reveal that they are in equilibrium with their monomeric building blocks[5] and that they are unstable towards substitution reactions.[7] These observations are reflected in reports of their electrochemistry, in which the metal-based redox couples exhibit poor reversibility.[6]

Herein we describe the synthesis of a *kinetically inert* triangular electroactive bowl, which displays well-behaved reversible electrochemical behavior and demonstrates two mixed-valence states with substantially different characters. The [([9]-ane-S_3)Ru^{II}] moiety was selected as a precursor for the corner units; previous work has demonstrated that this fragment exhibits suitable electronic and electrochemical properties,[8] and that self-assembly at high temperatures

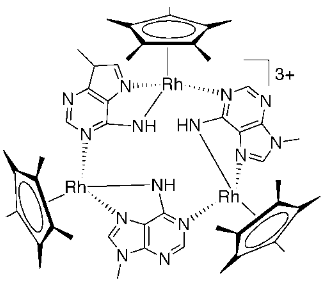
---

[*] N. Shan, S. J. Vickers, H. Adams, Prof. M. D. Ward, Dr. J. A. Thomas
Department of Chemistry
University of Sheffield, Sheffield S3 7HF (UK)
Fax: (+44) 114-273-8673
E-mail: james.thomas@sheffield.ac.uk

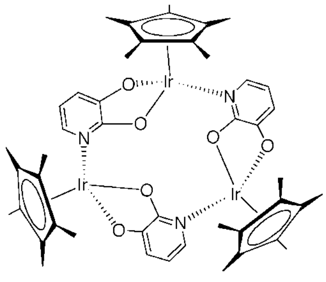
[**] We gratefully acknowledge the support of The Royal Society (J.A.T), EPSRC (N.Z, S.J.V) and the Leverhulme Trust (S.J.V).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

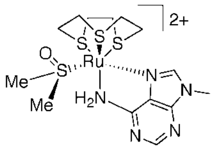
DOI: 10.1002/ange.200460022



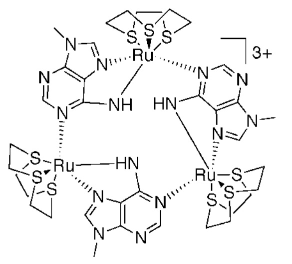
1



2



3



4

allows the thermodynamic assembly of species that become “kinetically locked” at room temperature,[9] thereby avoiding the kinetic lability of previously reported systems.

Reaction of the readily available starting material $[RuCl_2(dmso)([9]\text{-ane-S3})]$[10] with 9-methyladenine (9-MA) in an aqueous buffered solution (pH 7) heated at reflux for several hours afforded a single product, which was isolated as a hexafluorophosphate salt. ^1H NMR spectroscopy and FAB-MS studies revealed that the new compound was the mononuclear dicationic complex **3**$(PF_6)_2$ The structure of the cation was confirmed by X-ray crystallographic analysis of its triflate salt (Figure 1).

An analysis of this structure reveals why the anticipated self-assembly into a metallamacrocycle is inhibited: the exocyclic NH_2 group in complex **3** is still intact and has not been deprotonated. In contrast to the $[Cp^*Rh^{III}]$ center, the coordinated $[Ru([9]\text{-ane-S3})]^{2+}$ moiety is not a strong enough Lewis acid to initiate deprotonation of N6. Consequently, the N1 position of 9-MA is not a sufficiently good donor to compete for the metal-coordination site occupied by dmso in **3**.

To deprotonate the exocyclic NH_2 site and attain bridged polynuclear structures, we repeated the reaction under more basic conditions. In the presence of the sterically hindered base pentamethylpiperidine (PMP), which is a very strong Brønsted base but a weak nucleophile, reaction of $[RuCl_2(DMSO)([9]\text{-ane-S3})]$ with 9-MA afforded (as the hexafluorophosphate salt) a single product whose ^1H NMR, FAB-MS, and high-resolution mass spectra as well as elemental analysis were all consistent with the metallamacrocycle of formula **4**$(PF_6)_3$. Although attempts at growing crystals suitable for X-ray crystallographic studies were unsuccessful, the m/z values and isotope-distribution models of the FAB-MS and ES-MS peaks corresponding to the fragments obtained for both the hexafluorophosphate and triflate salts of **4** confirm the trinuclear formulation.

The redox properties of **4**$(PF_6)_3$ were investigated by means of cyclic voltammetry (CV). Between 0.6–1.6 V (versus the Ag/AgCl couple) the new complex undrgoes three metal-based $Ru^{III/II}$ oxidation processes (Figure 2). In contrast to previously reported Ru^{II} species[6] and **3** (which displays a single irreversible oxidation), each of these couples is reversible with $\Delta E = 100$ mV and $|I_{Pa}/I_{Pc}| = 1$. Interestingly, although $\Delta E_{1/2}(1,2)$ is 175 mV, $\Delta E_{1/2}(2,3)$ is much larger with a value close to 380 mV. Comproportionation constants (K_c) derived from these figures indicate that the $[Ru^{II}/Ru^{III}/Ru^{III}]$ $\mathbf{4}^{5+}$ state has a stronger intermetallic interaction ($K_c = 2.8 \times 10^6$) than the $[Ru^{III}/Ru^{II}/Ru^{II}]$ $\mathbf{4}^{4+}$ state ($K_c = 760$). This observation is in contrast to other redox-active triangular complexes in which the spacings are approximately constant, as would be expected if there was no variation in the individual pairwise metal–metal interactions across the redox series. This implies that on moving from $\mathbf{4}^{4+}$ to $\mathbf{4}^{5+}$, there is a much greater delocalization of the positive charges which render the final oxidation more difficult than it would otherwise be.

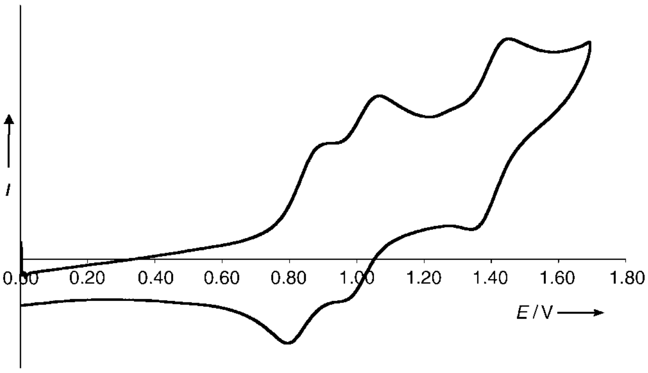


Figure 2. Cyclic voltammogram of oxidative processes for **4**$(PF_6)_3$ in $MeCN/Bu_4NPF_6$ (0.1 M) (versus Ag/AgCl).

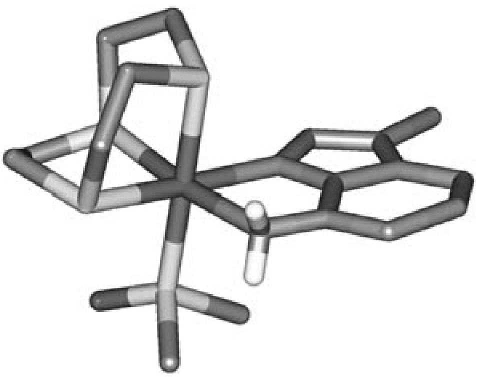


Figure 1. X-ray crystal structure of cation **3**, determined from **3**$(CF_3SO_3)_2$, showing the coordinating NH_2 group. All other hydrogen atoms and lone pairs have been removed for clarity.

On their own, K_c values are not always a true indication of the strengths of metal–metal electronic couplings; more accurate information can be obtained from the intensity, position, and shape of any observable intervalence charge-transfer (IVCT) bands. Therefore, the optical properties of the two mixed-valence and isovalent Ru^{III} states were investigated by UV/Vis/NIR spectroelectrochemistry in an OTTLE cell.

The evolution of electronic spectra through the redox series $\mathbf{4}^{3+}$ to $\mathbf{4}^{6+}$ is shown in Figure 3. In all cases, clean isosbestic points were observed, and at the end of the experiment the spectrum of $\mathbf{4}^{3+}$ was regenerated to confirm the full chemical reversibility of all the processes. The spectrum of $\mathbf{4}^{3+}$ shows only a Ru(d)→L(π*) metal-to-ligand charge-transfer (MLCT) band (313 nm) involving the adenine ligands. On one-electron oxidation to $\mathbf{4}^{4+}$ this MLCT band, whose origin is Ru^{II}, diminishes in intensity. A lower energy band centered at 800 nm was assigned to a thiacrown(S)→Ru^{III} ligand-to-metal charge transfer (LMCT). Furthermore, the spectrum of $\mathbf{4}^{4+}$ above 950 nm is dominated by a broad, low intensity absorption ($\varepsilon = 2950\ \mathrm{mol^{-1}\,dm^3\,cm^{-1}}$), which we assign as an IVCT band.

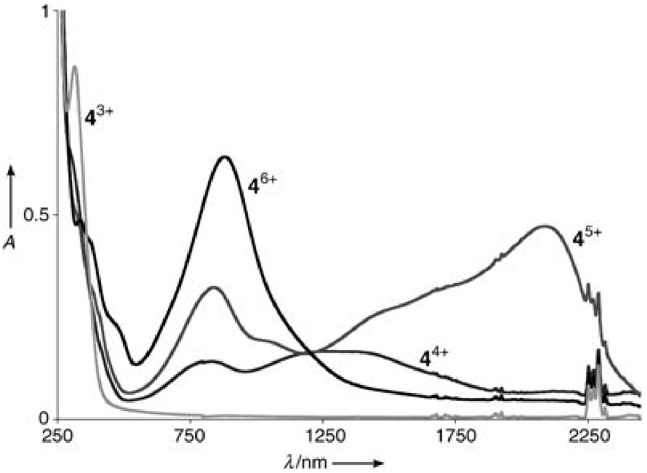


Figure 3. UV/Vis/NIR spectra of $\mathbf{4}^{3+}$, $\mathbf{4}^{4+}$,$\mathbf{4}^{5+}$, and $\mathbf{4}^{6+}$.

Further oxidation to $\mathbf{4}^{5+}$ results in the further collapse of the Ru^{II}→adenine MLCT band accompanied by the simultaneous growth of the S→Ru^{III} LMCT band. However, the most notable feature of the $\mathbf{4}^{5+}$ absorption spectrum is an intense, structured band in the NIR region with an absorbance maximum at 2085 nm ($\varepsilon = 8400\ \mathrm{mol^{-1}\,dm^3\,cm^{-1}}$). The final oxidation to give $\mathbf{4}^{6+}$ results in the collapse of all bands in the NIR region (which confirms their assignment as IVCT processes) and further growth of the S→Ru^{III} LMCT band.

The energies of the bands in the NIR region observed for the mixed-valence [Ru^{II}/Ru^{II}/Ru^{III}] $\mathbf{4}^{4+}$ and [Ru^{II}/Ru^{III}/Ru^{III}] $\mathbf{4}^{5+}$ states are consistent with previous reports of IVCT that indicate electron transfer between Ru^{II} and Ru^{III} sites.[11] However, the differing intensities and structures of these bands imply very different electron-transfer properties. The NIR spectral region for $\mathbf{4}^{4+}$ contains a structured, low-intensity, and extremely broad band that seems to be comprised of several overlapping transitions. Similar structured IVCTs were previously observed in oligonuclear Ru- and Os-based mixed-valence systems[12] and arise as a result of a combination of low-symmetry, extensive orbital mixing and spin–orbit coupling, which split the $d\pi^5$ states into Kramer doublets. The relatively low intensity of these transitions and the low K_c value of 760 indicate that $\mathbf{4}^{4+}$ is a valence-localized structure. In contrast, the band for $\mathbf{4}^{5+}$ in the NIR region is intense and clearly consists of at least three overlapping transitions. The intensity of these transitions and their sharpness suggest that the $\mathbf{4}^{5+}$ state is a valence-delocalized system.

Further evidence for these conclusions can be drawn from the application of the Hush theory[13] to the lowest energy IVCTs of the $\mathbf{4}^{4+}$ and $\mathbf{4}^{5+}$ states. If the bands are assumed to be Gaussian-shaped, the low-energy shoulder for the IVCT of $\mathbf{4}^{4+}$ can be used to estimate $\Delta\tilde{\nu}_{1/2}$ for this transition.[12c] In this case, $\Delta\tilde{\nu}_{1/2} \approx 3500\ \mathrm{cm^{-1}}$, which is relatively close to $\Delta\tilde{\nu}_{1/2}(\mathrm{calcd}) = 4100\ \mathrm{cm^{-1}}$. Taken together, the data for $\mathbf{4}^{4+}$ indicates that it is a Robin and Day[14] class II (valence-localized/solvent-coupled) system, or perhaps a class II/III (valence-localized/solvent-decoupled) system.[12c,15]

In contrast, the same calculation carried out on the lowest energy band for $\mathbf{4}^{5+}$ reveals that $\Delta\tilde{\nu}_{1/2}(\mathrm{experimental}) = 900\ \mathrm{cm^{-1}}$ is much narrower than $\Delta\tilde{\nu}_{1/2}(\mathrm{calcd}) = 3325\ \mathrm{cm^{-1}}$. Given this very narrow bandwidth, the large K_c, and the exceptionally high intensity of this IVCT ($\varepsilon_{max} = 8500\ \mathrm{mol^{-1}\,dm^3\,cm^{-1}}$), it is clear that $\mathbf{4}^{5+}$ is a fully valence-delocalized, solvent-decoupled class III system.

In summary, the triangular metallamacrocyclic complex $\mathbf{4}^{6+}$ is kinetically stable in all oxidation states and takes part in a reversible four-membered redox chain in which, remarkably, one mixed-valence state is a class II and the second is a class III system. Further investigations of this phenomenon and the host–guest chemistry of the complex in its different oxidation states are in progress.

Experimental Section

3$(CF_3SO_3)_2$: Crystal data for $C_{16}H_{25}F_6N_5O_7RuS_6$ ($M = 806.84$); which crystallizes from ethanol as yellow blocks, were measured on a Bruker Smart CCD area detector with an Oxford Cryosystems low-temperature system. Cell parameters were refined from the setting angles of 2900 reflections (θ range $1.66 < 28.29°$). Crystal dimensions $0.21 \times 0.10 \times 0.10\ \mathrm{mm^3}$, triclinic, $a = 10.9018(15)$, $b = 11.9162(16)$, $c = 12.8948(18)$ Å, $\alpha = 73.636(3)°$, $\beta = 81.112(3)°$, $\gamma = 83.179(3)°$, $U = 1583.0(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.693\ \mathrm{Mg\,m^{-3}}$, space group $P\bar{1}$ ($C^{1,i}$, no. 2), $Mo_{K\alpha}$ radiation ($\lambda,^{-} = 0.71073$ Å), $\mu(Mo_{K\alpha}) = 0.969\ \mathrm{mm^{-1}}$, $F(000) = 812$. Of the 10213 reflections measured, all of which were corrected for Lorentz and polarization effects and for absorption by semiempirical methods based on symmetry-equivalent and repeated reflections (minimum and maximum transmission coefficients 0.8225 and 0.9094), 3878 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. Refinement converged at a final $R = 0.0744$ ($WR_2 = 0.2049$, for all 7221 data, 369 parameters, mean and maximum δ/σ0.000) with allowance for the thermal anisotropy of all non-hydrogen atoms.CCDC 233715 contains the supplementary crystallographic data for this paper. These data (excluding structure factors) can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data

Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Received: March 17, 2004 [Z460022]

Keywords: electrochemistry · electron transfer · mixed-valent compounds · ruthenium · self-assembly

---

[1] a) G. F. Swiegers, T. J. Malefetse, *Chem. Rev.* **2000**, *100*, 3483; b) G. F. Swiegers, T. J. Malefetse, *Coord. Chem. Rev.* **2002**, *225*, 91; c) M. Fujita, *Chem. Soc. Rev.* **1998**, *27*, 417; d) S. Leninger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853; e) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa, K. Biradha, *Chem. Commun.* **2002**, 509; f) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972.

[2] a) P. H. Dinolfo, J. T. Hupp, *Chem. Mater.* **2001**, *13*, 3113; b) M. H. Keefe, K. D. Benkstein, J. T. Hupp, *Coord. Chem. Rev.* **2002**, *225*, 91.

[3] a) D. P. Smith, E. Baralt, B. Morales, M. M. Olmstead, M. F. Maestre, R. H. Fish, *J. Am. Chem. Soc.* **1992**, *114*, 10647; b) H. Chen, S. Ogo, R. H. Fish, *J. Am. Chem. Soc.* **1995**, *117*, 3631; c) H. Chen, S. Ogo, R. H. Fish, *J. Am. Chem. Soc.* **1996**, *118*, 4993; d) R. H. Fish, *Coord. Chem. Rev.* **1999**, *185–186*, 569.

[4] a) K. Yamanari, S. Yamamoto, R. Ito, Y. Kushi, A. Fuyuhiro, N. Kubota, T. Fukuo, R. Arakawa, *Angew. Chem.* **2001**, *113*, 2328; *Angew. Chem. Int. Ed.* **2001**, *40*, 2268; b) K. Yamanari, R. Ito, S. Yamamoto, T. Konno, A. Fuyuhiro, K. Fujioka, R. Arakawa, *Inorg. Chem.* **2002**, *41*, 6824.

[5] a) S. Korn, W. S. Sheldrick, *J. Chem. Soc. Dalton Trans.* **1997**, 2191; b) P. Annen, S. Schildberg, W. S. Sheldrick, *Inorg. Chim. Acta* **2000**, *307*, 115.

[6] a) T. Habereder, M. Warchhold, H. Nöth, K. Severin, *Angew. Chem.* **1999**, *111*, 3422; *Angew. Chem. Int. Ed.* **1999**, *38*, 3225; b) H. Piotrowski, K. Polborn, G. Hilt, K. Severin, *J. Am. Chem. Soc.* **2001**, *123*, 2699; c) H. Piotrowski, G. Hilt, A. Schulz, P. Mayer, K. Polborn, K. Severin, *Chem. Eur. J.* **2001**, *7*, 3196; d) K. Severin, *Coord. Chem. Rev.* **2003**, *245*, 3.

[7] Z. Grote, R. Scopelliti, K. Severin, *Angew. Chem.* **2003**, *115*, 3951; *Angew. Chem. Int. Ed.* **2003**, *42*, 3821.

[8] a) S. Roche, L. J. Yellowlees, J. A. Thomas, *Chem. Commun.* **1998**, 1429; b) C. S. Araújo, M. G. B. Drew, V. Félix, L. Jack, J. Madureira, M. Newell, S. Roche, T. M. Santos, J. A. Thomas, L. Yellowlees, *Inorg. Chem.* **2002**, *41*, 2260.

[9] S. Roche, C. Haslam, H. Adams, S. L. Heath, J. A. Thomas, *Chem. Commun.* **1998**, 1429.

[10] C. Landgrafe, W. S. Sheldrick, *J. Chem. Soc. Dalton Trans.* **1994**, 1885.

[11] a) C. Creutz, *Prog. Inorg. Chem.* **1983**, *30*, 1; b) R. J. Crutchley, *Adv. Inorg. Chem.* **1994**, *41*, 273.

[12] a) V. Kasack, W. Kaim, J. H. Binder, J. Jordanov, E. Rothl, *Inorg. Chem.* **1995**, *34*, 1924; b) M. Moscherosch, E. Waldhör, H. Binder, W. Kaim, J. Fiedler, *Inorg. Chem.* **1995**, *34*, 4326; c) K. D. Demadis, C. M. Hartshorn, T. J. Meyer, *Chem. Rev.* **2001**, *101*, 2655, and references therein.

[13] a) N. S. Hush, *Prog. Inorg. Chem.* **1967**, *8*, 391; b) N. S. Hush, *Electrochim. Acta* **1968**, *13*, 1005.

[14] M. B. Robin, P. Day, *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

[15] B. S. Brunschwig, C. Creutz, N. Sutin, *Chem. Soc. Rev.* **2002**, *31*, 168.