Synthesis of the First Closed Cage Ruthenium(II) Complex with Tris(di-imine) Ligand Sphere

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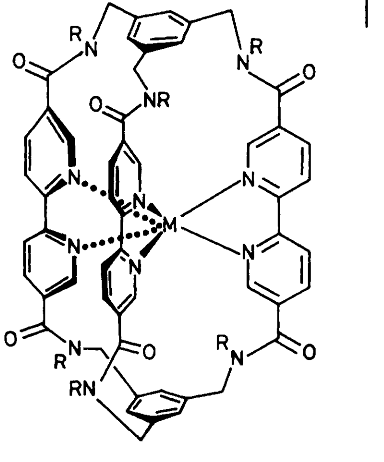
The synthesis of a closed cage tris(di-imine) ruthenium(II) complex *via* a template reaction is described, along with some of its light absorption and emission properties.

The synthesis of caged metal ion complexes containing the 2,2′-bipyridine fragment has been recently reported.[1,2] Despite the numerous complexes of Ru^{II} containing di-imine ligands,[3] no cage compound of this type has previously been described. The oxidation of the only known Ru-cage,[4] $Ru(sar)^{2+}$ (sar = 3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane) yields a hexaimine complex, where the –C=N– double bonds are oriented towards the cap of the cage (*exo*). Vögtle *et al.*[5] reported the preparation of an Fe^{II} complex of type (**1**) from the tris(macrocyclic) ligand, by incorporation of Fe^{2+} from solution.

With ruthenium(II) as the central metal, direct incorporation into the caged ligand structure is much more difficult due to slow ligand substitution reactions. In the present communication we report the synthesis of the ruthenium complex (**1**), starting from the ruthenium–tris(diethyl 2,2′-bipyridine-5,5′-dicarboxylate) complex (**2**)[6] as its chloride salt. The cage structure is achieved by a template reaction using the acid chloride derivative (**3**) prepared from complex (**2**) and 1,3,5-tris[*N*-benzyl(aminomethyl)]benzene (**4**).[7]

The caged ruthenium complex (**1**) was synthesised according to Scheme 1.† The clearest evidence for the closed cage structure is provided by the ^{1}H-n.m.r. spectrum of the PF_6^- salt of (**1**) dissolved in dimethylformamide (DMF) (Figure 1). The pattern clearly indicates D_3 symmetry of the species. The analogous open cage complex,[8] being capped on only one side by a tris(amide), moiety shows a very different ^{1}H n.m.r. spectrum with C_3 symmetry.

The u.v.–vis. absorbance spectrum shows one long-wavelength absorption [metal to ligand charge transfer (MLCT)] at λ 455 nm (ε 10 300), which is very close to that of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine), but significantly different from that of (**2**), λ 500 nm (ε 10 000). In the latter the –C=O groups are expected to influence strongly the signal, but this effect is reduced in the cage complex by their orthogonal orientation with respect to the aromatic rings of bpy. This orthogonal orientation was deduced from molecular models, which demonstrate the strong rigidity of the cage, which is also mirrored in the emission intensity ($\lambda_{max.}$ 612 nm, aerated



(**1**) M = Fe, Ru
R = CH_2Ph

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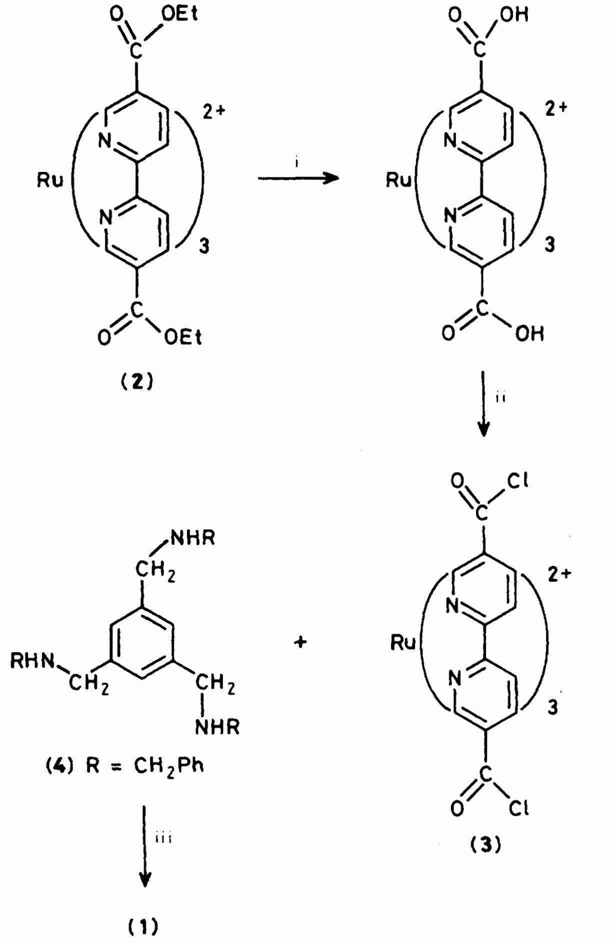
† The last step in the synthesis must be carried out in very dilute solution with rigorous exclusion of water.



Scheme 1. *Reagents*: i, KOH–H_2O; ii, $SOCl_2$; iii, $MeNO_2$–tetrahydrofuran (THF), NEt_3.

solution) at room temperature. In fact the closed cage ruthenium(II) complex has an emission intensity twice that of the $Ru(bpy)_3{}^{2+}$ complex.

In view of the interesting properties of $Ru(bpy)_3{}^{2+}$ and related complexes, the rigid caged complex (**1**) is very promising as light absorption sensitizer (LAS) and light emission sensitizer (LES) for electron-transfer reactions.[3,9]

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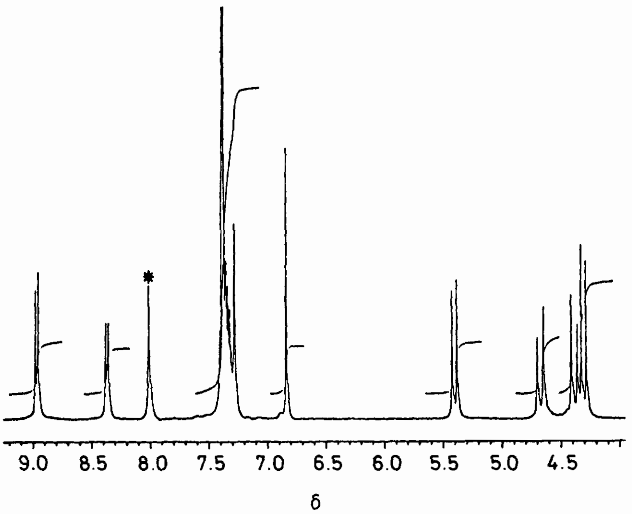

Figure 1. 360 MHz ^1H N.m.r. spectrum in $[^2H_7]$ DMF (* = solvent peak).

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References

1 J. C. Rodriguez-Ubis, B. Alpha, D. Plancherel, and J.-M. Lehn, *Helv. Chim. Acta*, 1984, **67**, 2264.
2 B. Alpha, J.-M. Lehn, and G. Mathis, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 266.
3 A. Juris, F. Barigelletti, S. Campagna, V. Balzani, P. Belser, and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.
4 P. Bernhard and A. M. Sargeson, *J. Chem. Soc., Chem. Commun.*, 1985, 1516.
5 S. Grammenudi and F. Vögtle, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 1122.
6 M. J. Cook, A. P. Lewis, G. S. G. McAuliffe, V. Skarda, A. J. Thomson, J. L. Glasper, and D. J. Robbins, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1293.
7 S. Grammenudi, M. Franke, F. Vögtle, and E. Steckhan, *J. Incl. Phenom.*, 1987, **5**, 695.
8 P. Belser, L. De Cola, A. von Zelewsky, V. Balzani, F. Barigelletti, F. Vögtle, and F. Ebmeyer, unpublished results.
9 V. Balzani, F. Bolletta, M. Ciano, and M. Maestri, *J. Chem. Ed.*, 1983, **60**, 447.