A Synthetic Route to Encapsulated Ru Compounds: Properties of the $[Ru(3,6,10,13,16,19\text{-hexa-azabicyclo}[6.6.6]\text{icosane})]^{2+/3+}$ Ions

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The synthesis of $Ru(sar)^{2+}$ (sar = 3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane) from $Ru(DMF)_6{}^{2+}$ (DMF = *N,N*-dimethylformamide) and sar is described along with its properties and oxidation to $Ru(sar)^{3+}$ and thence to a Ru^{II} monoimine complex.

Among the many complexes which have been obtained from the versatile $Ru(H_2O)_6{}^{2+}$ complex,[1] $Ru(DMF)_6{}^{2+}$ (DMF = *N,N*-dimethylformamide) is of special interest due to its synthetic potential. The orange salt $[Ru(DMF)_6](CF_3SO_3)_2$ (**1**) was prepared by treating $[Ru(H_2O)_6](CF_3SO_3)_2$ with pure DMF under argon and scavenging the water with triethylorthoformate, followed by concentration of the solution and crystallization at −20 °C (in >85% yield).† The yellow salt $[Ru(DMF)_6](CF_3SO_3)_3$ (**2**) was obtained by oxidizing (**1**) with

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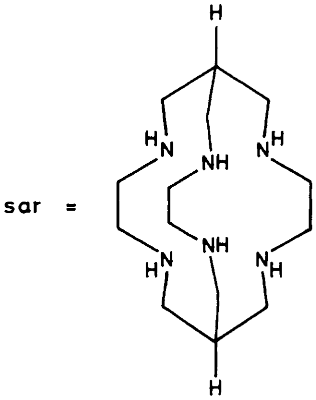
† Satisfactory elemental analyses (C,H,N,S,F) were obtained for all products. $\lambda_{max.}(\varepsilon_{max.})$ in DMF: (**1**), 492 (190), 314 nm (12 800). (**2**), 338 nm (5400). $E°[(\mathbf{2})/(\mathbf{1})]$ in 0.1 M Bu_4NClO_4/DMF (22 °C): −0.42 V *vs.* ferrocene.



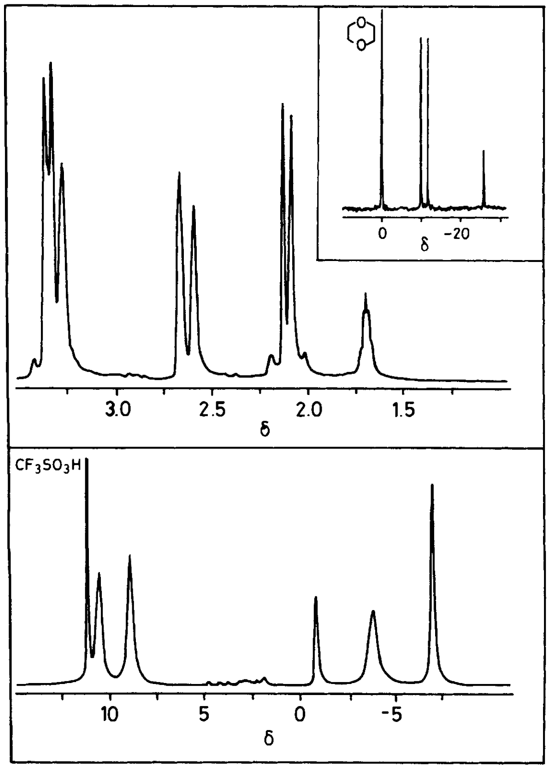


Figure 1. Upper part: 200 MHz ^{1}H and 50 MHz ^{13}C{^{1}H} n.m.r. spectra of Ru(sar)$^{2+}$ in D$_2$O *vs.* DSS (sodium 2-dimethyl-2-silapentane sulphonate) and 1,4-dioxane, respectively. Lower part: 200 MHz ^{1}H n.m.r. spectrum of Ru(sar)$^{3+}$ in CF$_3$SO$_3$D *vs.* DSS.

AgCF$_3$SO$_3$ in DMF and was crystallized as described above (in >85% yield).† Overall rate constants‡ for reaction (1) for the complexes in 0.1 M CF$_3$SO$_3$H (25 °C) are $k = 2.5 \times 10^{-3}$ s^{-1} (**1**) and $k = 2 \times 10^{-7}$ s^{-1} (**2**) which are only an order of magnitude smaller than the water exchange rate constants for the hexa-aqua ions respectively.[2]

$$\mathrm{Ru(DMF)_6}^{n+} + 6\mathrm{H_2O} \xrightarrow{k} \mathrm{Ru(H_2O)_6}^{n+} + 6\mathrm{DMF} \quad (1)$$

The potential for use of Ru(DMF)$_6$$^{2+}$ in reactions with strongly basic ligands§ is demonstrated by the reaction of Ru(DMF)$_6$$^{2+}$ with sar (sar = 3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane):[3] stoicheiometric amounts of (**1**) and sar in dry ethanol (*ca.* 0.1 M solution) were refluxed for 2 days in a strictly O$_2$-free atmosphere. Upon cooling to 0 °C the compound [Ru(sar)](CF$_3$SO$_3$)$_2$ (**3**) precipitated. It was re-crystallized from 1 M CF$_3$SO$_3$H (in *ca.* 60% yield).† The pale-yellow compound is extremely sensitive towards oxidants. This synthetic route circumvents the difficulties encountered on attempting to cap the Ru(en)$_3$$^{3+}$ (en = 1,2-diaminoethane) ion.

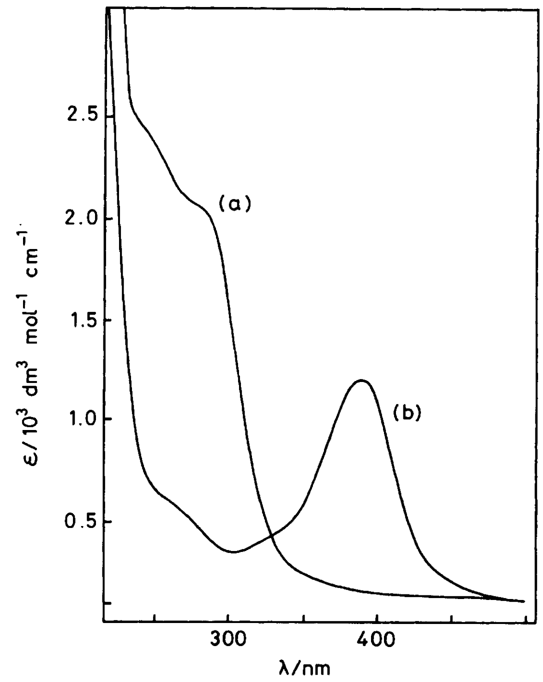


Figure 2. Optical spectra of (a) Ru(sar)$^{2+}$ and (b) Ru$^{\mathrm{II}}$ monoimine complex in 0.1 M CF$_3$SO$_3$H.

[Ru(DMF)$_6$](CF$_3$SO$_3$)$_n$
(**1**); $n = 2$
(**2**); $n = 3$

[Ru(sar)](CF$_3$SO$_3$)$_2$
(**3**)

The ^{1}H n.m.r. spectrum of the Ru(sar)$^{2+}$ complex exhibits essentially two AB patterns [–CH$_2$– groups (en and cap)] one of which (δ 2.6 and 3.3) is weakly coupled (J ~ 2 Hz) to the cap ⋛C–H group (δ 1.7) and is therefore assigned to the –CH$_2$– groups of the cage cap. The ^{13}C{^{1}H} n.m.r. spectrum exhibits two intense signals and a weaker one which are assigned correspondingly. The spectra (Figure 1, upper part) clearly point to the D_3 symmetry of the ion. The ^{1}H n.m.r. spectrum of the paramagnetic Ru(sar)$^{3+}$ complex which was obtained by oxidizing (**3**) in neat CF$_3$SO$_3$D with AgCF$_3$SO$_3$ exhibits five broad signals with relative intensities of 3 : 3 : 1 : 3 : 3 (Figure 1, lower part). With the exception of the cap ⋛C–H group (δ −0.9) no assignments to the four different protons of the –CH$_2$– groups can be made from this spectrum at this stage.

The electronic spectrum of Ru(sar)$^{2+}$ in 0.1 M CF$_3$SO$_3$H is shown in Figure 2(a). A weak shoulder at 387 nm (ε ~ 35 dm^3

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‡ Strictly speaking, the reaction involves a number of different rate constants; but the decrease of the absorptions at 492 nm (**1**) and 338 nm (**2**) in the electronic spectra showed a single first order decay.

§ Reaction of Ru(H$_2$O)$_6$$^{2+}$ with strongly basic ligands leads to decomposition (presumably disproportionation of the divalent oxidation state under formation of Ru metal and polymeric oxo- and hydroxo-species).

mol^{-1} cm^{-1}) is assigned to the spin allowed transition $^1A_1 \rightarrow {}^1T_1$ whereas the high intensity of the band at 282 nm (ε ~ 2000 dm^3 mol^{-1} cm^{-1}) implies charge transfer character thus obscuring further d–d transitions; in fact, similar intense bands in $Ru(NH_3)_6{}^{2+}$ [$\lambda_{max.}$ ($\varepsilon_{max.}$): 275 nm (640 dm^3 mol^{-1} cm^{-1})] and $Ru(en)_3{}^{2+}$ [302 nm (1020 dm^3 mol^{-1} cm^{-1})] have been interpreted in terms of a charge transfer to the solvent (c.t.t.s.) on the basis of their solvent dependence and the photochemical properties of these complexes.[4]

The reversible reduction potential for the $Ru(sar)^{3+/2+}$ couple, established by cyclic voltammetry in 1.0 M CF_3SO_3H (scan rate: 0.5 V s^{-1}) was 0.290 ± 0.005 V *vs.* normal hydrogen electrode (NHE) (25.0 °C), slightly higher than for $Ru(en)_3{}^{3+/2+}$ and $Ru(NH_3)_6{}^{3+/2+}$.[4,5] Even in strongly acidic aqueous solutions $Ru(sar)^{3+}$ appeared to be stable only on the voltammetric timescale and oxidized rapidly to give a Ru^{II} monoimine species. This reactivity obviated the direct measurement of the electron self exchange rate.¶ However, from the rates of oxidation of $Ru(sar)^{2+}$ by the complexes $(NH_3)_5RuL^{3+}$ (L = pyridine, nicotinamide, isonicotinamide)[6] a value of *ca.* 10^5 dm^3 mol^{-1} s^{-1} (25.0 °C, 1.0 M CF_3SO_3H) for the $Ru(sar)^{3+/2+}$ self exchange was obtained using the Marcus–Hush cross relationship. The rate is thus faster than those for $Ru(NH_3)_6{}^{3+/2+}$ and $Ru(en)_3{}^{3+/2+}$ [7] which is consistent in general with the observed increases of the self exchange rates for the encapsulated cobalt complexes.

The Ru^{II} monoimine complex exhibits a visible band at 392 nm [Figure 2(b)] which is assigned to a t_{2g} (M) → π* (L) charge transfer. The ^1H and ^{13}C n.m.r. data indicate that the imine group is in the cap rather than in the ethanediamine portion of the ligand. In 1 M CF_3SO_3H, further oxidation of the ligand was achieved electrochemically but these species have not yet been characterised.

We are grateful to the A.N.U. Microanalytical Services Unit for analyses.

Received, 16th July 1985; Com. 1036

References

1 P. Bernhard, H. B. Bürgi, J. Hauser, H. Lehmann, and A. Ludi, *Inorg. Chem.*, 1982, **21**, 3936.
2 I. Rapaport, L. Helm, P. Bernhard, A. Ludi, and A. Merbach, *J. Chem. Soc., Chem. Commun.*, 1984, 302.
3 A. M. Sargeson, *Pure Appl. Chem.*, 1984, **56**, 1603.
4 T. Matsubara, S. Efrima, H. I. Metiu, and P. C. Ford, *J. Chem. Soc., Faraday Trans. 2*, 1979, **75**, 390.
5 H. S. Lim, D. J. Barcley, and F. C. Anson, *Inorg. Chem.*, 1972, **11**, 1460.
6 G. M. Brown, H. J. Krentzien, M. Abe, and H. Taube, *Inorg. Chem.*, 1979, **18**, 3374.
7 N. Sutin, *Prog. Inorg. Chem.*, 1982, **30**, 441 and references therein.

¶ For the same reason a reproducible electronic spectrum of $Ru(sar)^{3+}$ has not been obtained so far.