The Influence of Cavity Size on the Properties of Encapsulated Rhodium(III) Ions: Long-lived Metal-centred Emission in a Symmetric Expanded Cavity Rhodium Cage System

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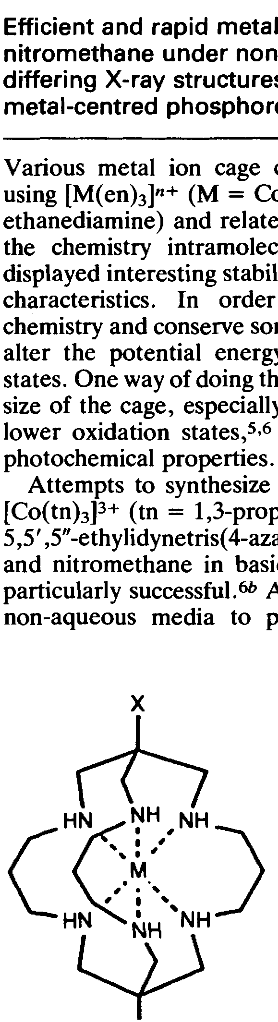
Efficient and rapid metal template reactions of rhodium(III) hexaamine complexes with paraformaldehyde and nitromethane under non-aqueous conditions lead to both optimal and expanded cavity cage complexes with widely differing X-ray structures and electronic properties; the larger cavity homologues feature a strongly enhanced metal-centred phosphorescence in water at 77 K.

Various metal ion cage complexes have been synthesized using $[M(en)_3]^{n+}$ (M = Co^{III}, Rh^{III}, Ir^{III} and Pt^{IV}, en = 1,2-ethanediamine) and related species as templates to organize the chemistry intramolecularly.[1–4] These complexes have displayed interesting stabilities, redox properties and spectral characteristics. In order to develop new chromophore chemistry and conserve some of the stability aspects one must alter the potential energy surfaces of the MN_6 electronic states. One way of doing this is to increase the preferred cavity size of the cage, especially to stabilize larger metal ions and lower oxidation states,[5,6] and to modify spectroscopic and photochemical properties.

Attempts to synthesize larger cages analogous to **1** using $[Co(tn)_3]^{3+}$ (tn = 1,3-propanediamine) or $[Co(stn)]^{3+}$ [stn = 5,5′,5″-ethylidynetris(4-azapentan-1-amine)], formaldehyde and nitromethane in basic conditions have not yet proved particularly successful.[6b] After carrying out such reactions in non-aqueous media to prevent rapid hydrolysis of some reaction intermediates, it became apparent that the capping process did not compete favourably with other synchronous condensation reactions. Dreiding models however indicated that longer M–N bond lengths would be more likely to promote the encapsulation relative to these reactions. It was therefore decided to use the larger $Rh^{III}N_6$ chromophore in the synthesis of molecules such as **1**.



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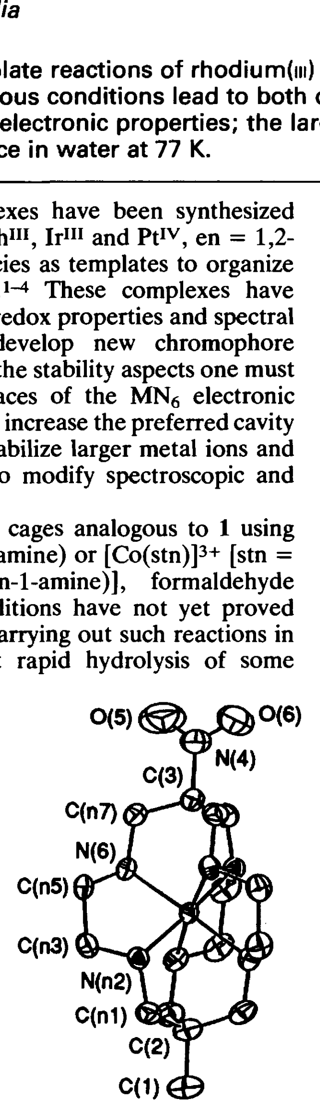

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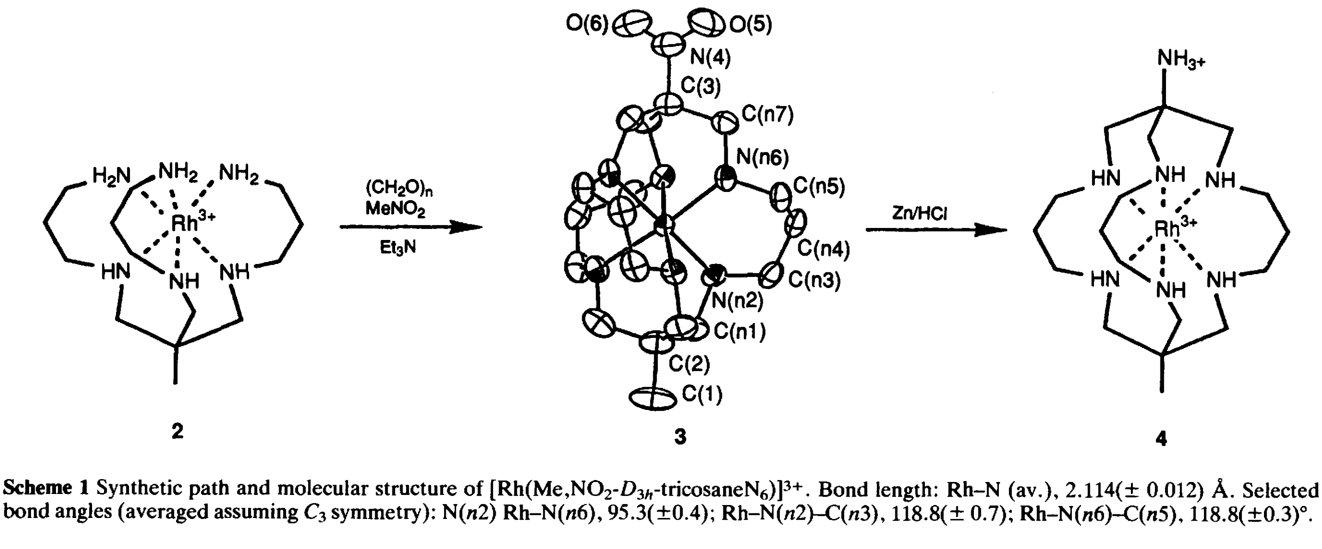
A new synthetic method[6b] for encapsulation in acetonitrile, using paraformaldehyde (10 equiv.), nitromethane (2 equiv.), the complex trifluoromethanesulfonate salt and triethylamine (2 equiv.) as base, was applied to the $[Rh(stn)]^{3+}$ ion **2** to give $[Rh(Me,NO_2\text{-}D_{3h}\text{-tricosaneN}_6)]^{3+}$ **3** (D_{3h}-tricosaneN_6 = 3,7,11,15,18,22-hexaazabicyclo[7.7.7]tricosane, derivatives substituted at 1,9 positions) (Scheme 1). The mixture was stirred at *ca.* 20 °C for 45 min, quenched with acetic acid and chromatographed on Dowex 50W–X2 cation exchange resin to isolate the $[Rh(Me,NO_2\text{-}D_{3h}\text{-tricosaneN}_6)]^{3+}$ complex (>70%). A similar procedure was used with $[Rh(tn)_3](CF_3SO_3)_3$ to give the more symmetric $[Rh\{(NO_2)_2\text{-}D_{3h}\text{-tricosaneN}_6\}]^{3+}$ (**1**, X = Y = NO_2). The $^{13}C\{^1H\}$ NMR spectrum of **3** was consistent with an average C_3 symmetry, with seven signals in D_2O at δ +20.2 ($C–NO_2$), −10.1, −12.0 (2 signals overlapped), −13.8 (CH_2–NH), −27.3 (C–Me), −42.95 (C–CH_2–C) and −44.9 (Me). The nitro group was reduced quantitatively in Zn/HCl or Sn/HCl to yield $[Rh(NH_3,Me\text{-}D_{3h}\text{-tricosaneN}_6)]^{4+}$ **4** with the ^{13}C NMR (D_2O) again indicating C_3 symmetry, and showing seven signals at δ −10.2, −11.8, −12.4, −13.8 (CH_2–NH), −27.6 (C–Me), −43.1 (C–CH_2–C) and −45.1 (Me). The average D_3 symmetry of $[Rh\{(NO_2)_2\text{-}D_{3h}\text{-tricosaneN}_6\}]^{3+}$ in solution is clearly apparent from its ^{13}C NMR spectrum which shows only four signals in D_2O at δ +20.1 ($C–NO_2$), −12.0, −13.9 (CH_2–NH) and −43.1 (C–CH_2–C). The nitro groups were reduced with Zn/HCl or Sn/HCl to give $[Rh\{(NH_3)_2\text{-}D_{3h}\text{-tricosaneN}_6\}]^{5+}$ with four ^{13}C NMR (D_2O) resonances at δ −11.7 ($C–NH_3$), −11.9, −13.9 (CH_2–NH) and −43.0 (C–CH_2–C),



Scheme 1 Synthetic path and molecular structure of $[Rh(Me,NO_2\text{-}D_{3h}\text{-tricosaneN}_6)]^{3+}$. Bond length: Rh–N (av.), 2.114(± 0.012) Å. Selected bond angles (averaged assuming C_3 symmetry): N(*n*2) Rh–N(*n*6), 95.3(±0.4); Rh–N(*n*2)–C(*n*3), 118.8(± 0.7); Rh–N(*n*6)–C(*n*5), 118.8(±0.3)°.

again consistent with an average D_3 symmetry. All chemical shifts were measured relative to that of internal 1,4-dioxane.

The homologous smaller cage complexes $[Rh(Me,NO_2\text{-}sar)]^{3+}$ **5** (sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane, derivatives substituted at 1,8 positions) and $[Rh(NH_3,Me\text{-}sar)]^{4+}$ were obtained from $[Rh(sen)](CF_3SO_3)_3$ (sen = 4,4′,4″-ethylidynetris(3-azabutan-1-amine)) by similar methods.

The structures of $[Rh(Me,NO_2\text{-}D_{3h}\text{-}tricosaneN_6)]^{3+}$ **3** and $[Rh(Me,NO_2\text{-}sar)]^{3+}$ **5** (Fig. 1) have been established by single crystal X-ray analyses of their $(ZnCl_4)Cl$ salts.† The configurations of both complex ions are essentially C_3 symmetric. For the D_{3h}-tricosaneN$_6$ complex, the Rh–tn rings adopt chair conformations and the caps have $R + S$ skewed forms relative to the C_3 axis. The Rh–N distances which vary from 2.102(3) to 2.123(3) Å are about 0.05 Å longer than those found for $[Rh(en)_3]^{3+}$ (2.06(1) Å)[7], *lel*$_3$-$[Rh(bn)_3]^{3+}$ [2.055(4) Å, bn = 2,3-butanediamine][8] and $[Rh(Me,NO_2\text{-}sar)]^{3+}$ **5** [2.056(3) −2.077(3)] Å. The latter three structures contain three five-membered chelate rings with the C–C bonds approximately parallel to the C_3 axes of the complex ions and are therefore structural analogues able to sustain the rhodium(III) ion in a near optimal cavity (2.06 Å). The results in total demonstrate the chromophore expansion potential of the bicyclic hexaazatricosane cage **1** and reflect its larger preferred cavity size. The two cage structures also display quite different trigonal twists of the upper and lower N_3 planes in the chromophores. The twist angles (ϕ) determined by the torsion angles N(*n*2)···C(2)···C(3)···N(*n*6) [where N(*n*2) and N(*n*6) belong to the same bicyclic bridge and *n* = 1–3] are 66 (±0.7)° for **3**, compared with 52 (±0.7)° for the smaller sar cage complex. The magnitudes of these angles lie either side of the octahedral twist angle of 60° and imply that the structural preference of the ligand plays an important if not decisive part in the determination of the chromophore configuration, despite the relatively large ligand field stabilisation energy of the low-spin octahedral $Rh^{III}N_6{}^{3+}$ system.

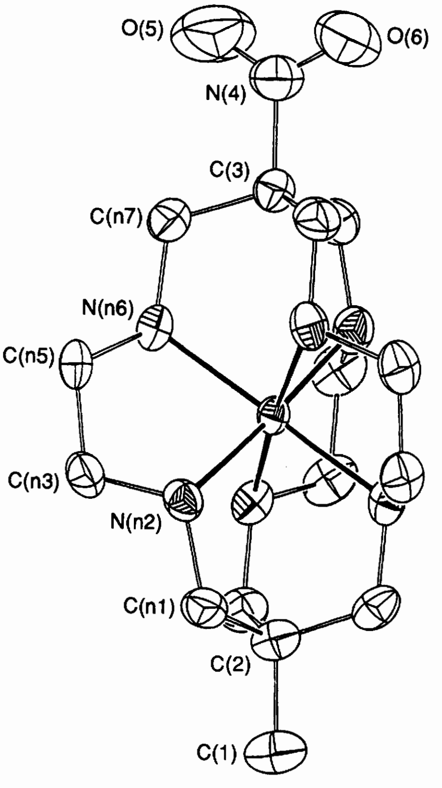


Fig. 1 Molecular structure of $[Rh(MeNO_2\text{-}sar)]^{3+}$ **5**. Bond length: Rh-N (av.), 2.069(±0.013) Å. Selected bond angles (averaged assuming C_3 symmetry): N(*n*2)-Rh-N(*n*6), 85.0(±0.6); Rh-N(*n*2)-C(*n*3), 105.5(±0.4); Rh-N(*n*6)-C(*n*5), 107.3(±0.5)°.

The electronic spectrum of $[Rh(NH_3,Me\text{-}D_{3h}\text{-}tricosaneN_6)]^{4+}$ in 0.1 mol dm^{-3} HCl shows bands at λ_{max} (ε_{max}) 315 nm (250 dm^3 mol^{-1} cm^{-1}) (of $^1A_{1g} \rightarrow {}^1T_{1g}$ parentage) and 265 nm (251 dm^3 mol^{-1} cm^{-1}) (of $^1A_{1g} \rightarrow {}^1T_{2g}$ parentage). These are substantially shifted from 297 nm (461 dm^3 mol^{-1} cm^{-1}) and 251 nm (308 dm^3 mol^{-1} cm^{-1}) for the smaller homologue $[Rh(NH_3,Me\text{-}sar)]^{4+}$. This reflects the increase from 2.069(8) to 2.114(7) Å in the average Rh–N bond length between the $[Rh(Me,NO_2\text{-}sar)]^{3+}$ **5** and the larger $[Rh(Me,NO_2\text{-}D_{3h}\text{-}tricosaneN_6)]^{3+}$ **3** structures.

Photoexcitation (PE) and emission (E) spectra and phosphorescence lifetimes (τ_p) were measured at 77 K for the complexes **3** [λ_{max} (PE) 302 nm, λ_{max} (E) 535 nm, τ_p 160 μs], **4** (305 nm, 544 nm, 165 μs) and $[Rh\{(NH_3)_2\text{-}D_{3h}\text{-}tricosaneN_6\}]^{5+}$, (310 nm, 544 nm, 205 μs) in water (*ca.* 10^{-4} mol dm^{-3}), and for crystals of the chloride salts of **3** (308 nm, 553 nm, 165 μs) and **4** (300 nm, 540 nm, 170 μs). No emission was observed at 77 K for the smaller cage complex $[Rh(NH_3,CH_3\text{-}sar)]^{4+}$ in water nor in crystals of its chloride salt. As τ_p was not measurable for periods less than 0.01 μs, these results show that either the intersystem crossing process is much less efficient for the smaller cage, or that the phosphorescence lifetimes for the expanded cavity complexes are increased by more than 10^4-fold. At 77 K where conformational motility is restricted for both systems, it seems unlikely that differences in radiative or non-radiative decay rate constants would lead to such a large difference in excited state lifetimes. It is more probable that the intersystem crossing parameters are significantly different for the two systems because of the variance in their preferred cavity sizes. In other complexes with $Rh^{III}N_6$ chromophores such as $[Rh(en)_3]^{3+}$ and $[Rh(dmbpy)_3]^{3+}$ (dmbpy = 3,3′-dimethyl-2,2′-bipyridine), metal-centred emissions were observed at 77 K with excited state lifetimes of 21[9] and 75 μs,[10] somewhat shorter than those found for the expanded cavity molecules. However, there is a more fundamental difference between the emission characteristics of the $[Rh(X,Y\text{-}D_{3h}\text{-}tricosaneN_6]^{n+}$ (X,Y = NH_3,Me,NO_2) cages and the analogous electronically saturated $[Rh(en)_3]^{3+}$ complex. The emission for the latter species, which has a maximum at 588 nm[9] and is red-shifted from those of the larger cages by 40 to 50 nm, has been assigned[9] as $^3T_{1g} \rightarrow {}^1A_{1g}$ (in O_h symmetry). This implies that, because of their weaker preferred ligand fields, the emissions for the expanded molecules do not originate from the lowest energy $^3T_{1g}$ state but rather from the higher energy $^3T_{2g}$.

The one electron $Rh^{III/II}$ reduction potential in acetone is raised by +0.4 V (equivalent to a free energy difference of 38.6 kJ mol^{-1}) on going from $[Rh(NH_3,Me\text{-}sar)]^{4+/3+}$ to the larger cavity $[Rh(NH_3,Me\text{-}D_{3h}\text{-}tricosaneN_6)]^{4+/3+}$ ions. Cyclic voltammograms of both cages show reversible III → II reductions, even at low scan rates, in non-aqueous solvents. The reduction potentials observed in acetone at a glassy carbon electrode were −2.12 V (*vs.* ferrocene) (0.1 mol dm^{-3} $NEt_4CF_3SO_3$, 500 mV s^{-1}) for $[Rh(NH_3,Me\text{-}sar)]^{4+}$ and −1.74 V for $[Rh(NH_3,Me\text{-}D_{3h}\text{-}tricosaneN_6)]^{4+}$. The increase in the stability of the Rh^{II} state clearly correlates with the increased cavity size observed in the structure of $[Rh(Me,NO_2\text{-}D_{3h}\text{-}tricosaneN_6)]^{3+}$.

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† *Crystal data* for **3**: $C_{18}H_{39}N_7O_2RhZnCl_4Cl{\cdot}3H_2O$, monoclinic, $P2_1/c$, a = 11.190(1), b = 10.114(1), c = 26.702(3) Å, β = 90.87(1)°, V = 3021.7 Å^3, D_c= 1.726 g cm^{-3} for Z = 4, μ = 100.5 cm^{-1}, 4440

reflections with $I > 3\sigma(I)$, $2\theta_{max} = 125°$, final $R = 0.044$. For **5**: $C_{15}H_{33}N_7O_2RhZnCl_4Cl \cdot 3H_2O$, monoclinic $P2_1/c$, $a = 11.088(1)$, $b = 9.878(1)$, $c = 25.654(2)$ Å, $\beta = 93.13(1)°$, $V = 2805.6$ Å^3, $D_c = 1.759$ g cm^{-3} for $Z = 4$, $\mu = 107.9$ cm^{-1}, 4560 reflections with $I > 3\sigma(I)$, $2\theta_{max} = 130°$, final $R = 0.043$. Intensity data were collected on a Picker FACS-I diffractometer using graphite-monochromated Cu-Kα radiation. The structures were solved by direct methods and difference Fourier techniques, and refined by full-matrix least-squares analysis. Hydrogen atoms were included at calculated positions (non-methyl H atoms of cations) and not refined. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallography Centre. See Information for Authors, Issue No. 1.

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