1,4,7-Tris(2,2′-bipyridyl-5-ylmethyl)-1,4,7-triazacyclononane (L^1), a Powerful Tris(2,2′-bipyridyl) Chelating Macrocyclic Ligand. X-Ray Structure of $[Ru(L^1H)][PF_6]_3$, a Complex containing a Strongly Trapped Proton

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A new powerful tris(2,2′-bipyridyl) chelating ligand, 1,4,7-tris(2,2′-bipyridyl-5-ylmethyl)1,4,7-triazacyclononane (L^1), has been synthesised and characterised, and an X-ray structure of $[Ru(L^1H)]^{3+}$ obtained; in the complex all three bipyridyl groups are coordinated, with a fairly regular octahedral Ru^{II} geometry, and although the azamacrocyclic nitrogen-atoms are non-coordinating to Ru^{II}, in aqueous solution they trap a single proton in the cavity between the macrocycle and the Ru^{II}, and which cannot be removed even at high pH.

Polyazamacrocyclic ligands carrying up to six *N*-pendent 2,2′-bipyridyl (bipy) arms have been reported.[1–8] Since many metal ions (M^{n+}) form very stable six-coordinate complexes of the type $[M(bipy)_3]^{n+}$, ligands which possess three pendent bipy arms are especially interesting as having the potential to form a stable $[M(bipy)_3]^{n+}$ core structure. In this study a powerful hexadentate ligand of this type has been synthesised and investigated, based on the triazamacrocycle 1,4,7-triazacyclononane (9N3) carrying three *N*-pendent coordinating bipy-5-ylmethyl arms (L^1). A comparison of three closely related ligands of this type (L^1–L^3) has been made, using molecular modelling to establish the best point of attachment (at either the 4-, 5- or 6-positions of the 2,2′-bipyridyl groups) to ensure strong octahedral coordination by the three pendent arms. L^1 is found to be best for forming $[M(bipy)_3]^{2+}$ complexes, and an X-ray structure of $[Ru(L^1H)]^{3+}$ is also in good agreement with the geometry of $[Ru(L^1)]^{2+}$ predicted by the molecular modelling calculations.

Previous research indicates that ligands L^2 and L^4 are capable of forming a tris-chelate with Fe^{II}, although $[FeL^2]^{2+}$ is not found to be very stable, decomposing readily in aqueous solution with the precipitation of hydroxy–iron species.[1] In L^2 and L^4, the three 2,2′-bipyridyl arms are attached *via* a methylene link at the 6-position of each bipy unit. HYPERCHEM Version 3 was used to model the related complexes, $[ML]^{2+}$ (M = Fe, Ru; L = L^1–L^3), using MM+ with the Polak–Rubiere algorithm of HYPERCHEM. Molecular dynamics was also used (simulated heating to 3000 K) to ensure that the true energy minimum had been reached. Bond lengths and force constants were taken from literature values.[9,10] The modelling results show that the lowest energy is obtained by using L^1 rather than L^2, and that L^3 is especially poor for octahedral chelation.† A similar calculation was carried out for the uncomplexed ligands, and in Fig. 1 we show the relatively small conformational change L^1 must undergo to produce $[RuL^1]^{2+}$

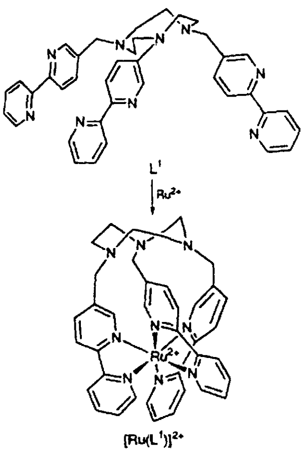


Fig. 1 Energy minimised structures of the free ligand L^1, and its complex $[RuL^1]^{2+}$, showing the relatively small conformational changes L^1 must undergo for octahedral coordination.

Encouraged by the results of the molecular modelling calculations, we proceeded to prepare L^1 by reaction of the parent macrocycle, 1,4,7-triazacyclononane (9N3) in refluxing chlorobenzene with three mole equivalents of 5-(bromomethyl)-2,2′-bipyridine in the presence of a slight excess of triethylamine.[6] After removal of the precipitated $[Et_3NH]Br$, the solvent was evaporated and the product recrystallised from acetonitrile to give white needles of L^1 (66% yield). L^1 is characterised by its proton and ^{13}C NMR spectra, and a FAB MS. Reaction of L^1 with equimolar amounts of hydrated divalent metal (M^{2+}) salts of labile ions in methanol solution, followed by addition of excess ammonium hexafluorophosphate, led to the isolation of the divalent metal complexes of the monoprotonated ligand, $[M(L^1H)][PF_6]_3$ (M = Fe, Co, Ni, and Zn). $[Cu(L^1H)][ClO_4]_3$ was obtained in an analogous way from the reaction of a methanolic solution of L^1 with $[Cu(H_2O)_6][ClO_4]_2$. Unlike $[FeL^2]^{2+}$, the diamagnetic low-spin $[Fe(L^1H)]^{3+}$ ion is indefinitely stable in aqueous media, and has a VIS spectrum (λ_{max} 520 nm, ε 7140 $dm^3\,mol^{-1}\,cm^{-1}$) very similar to that of $[Fe(bipy)_3]^{2+}$ (λ_{max} 522 nm, ε 8650

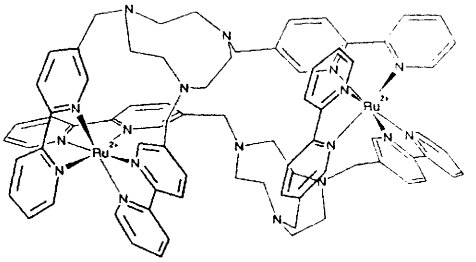


Fig. 2 Postulated molecular geometry of the unprotonated dimer ion $[Ru_2L^1{}_2]^{4+}$, based on the results of molecular modelling calculations.

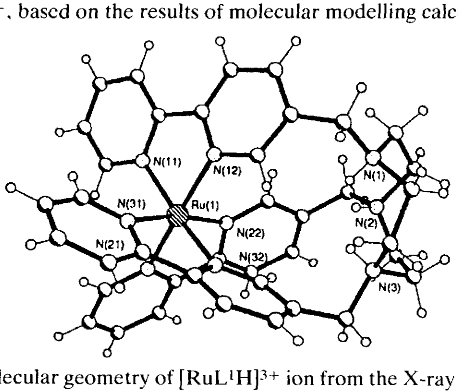
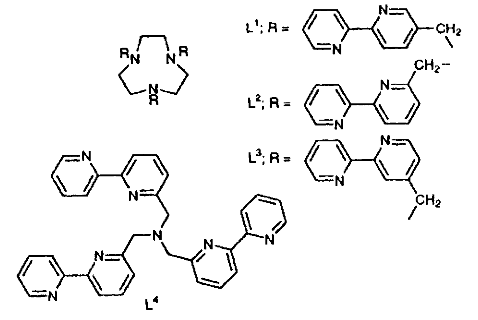


Fig. 3 Molecular geometry of $[RuL^1H]^{3+}$ ion from the X-ray structure determination, showing the atomic numbering. Selected bond lengths (Å) and angles (°) are as follows (values in [parentheses] are for $[Ru(bipy)_3]^{2+}$ for comparison; data from ref. 12): Ru–N(32) 2.035(6) [2.053(2)], Ru–N(21) 2.038(5), Ru–N(22) 2.039(6), Ru–N(11) 2.039(6), Ru–N(12) 2.050(5), Ru–N(31) 2.048(6), N(21)–Ru–N(32) 93.5(2) [89.4(2)], N(22)–Ru–N(32) 92.0(2) [95.7(1)], N(11)–Ru–N(32) 169.4(2) [172.6(2)], N(12)–Ru–N(32) 92.6(2) [95.7(1)], N(31)–Ru–N(32) 78.6(2) [78.6(2)], N(22)–Ru–N(21) 79.0(2), N(11)–Ru–N(21) 96.0(2), N(12)–Ru–N(21) 168.7(2), N(31)–Ru–N(21) 96.7(2), N(11)–Ru–N(22) 94.4(2), N(12)–Ru–N(22) 91.3(2), N(31)–Ru–N(22) 169.5(2), N(12)–Ru–N(11) 78.8(2), N(31)–Ru–N(11) 95.6(2), N(31)–Ru–N(12) 93.9(2).



dm^3 mol^{-1} cm^{-1}). Reaction of equimolar amounts of [Ru($Me_2SO)_4Cl_2$] and L^1 for 12 h in refluxing water gave an orange solution, and upon cooling and addition of excess saturated ammonium hexafluorophosphate gave a complex which analysed as the monoprotonated dimer $[Ru_2(L^1)_2H][PF_6]_5 \cdot 2H_2O$. The ^{1}H and ^{13}C NMR spectra of this dimer are consistent with the postulated structure shown in Fig. 2.‡ Curiously, when crystals were grown by allowing diethyl ether to slowly diffuse into a saturated solution of this dimer in nitromethane, the crystalline product obtained was that of the monomer, $[Ru(L^1H)][PF_6]_3$. Elemental analysis, a FAB MS and ^{1}H and ^{13}C NMR spectra confirmed this formulation.§ For $[Ru(L^1H)]^{3+}$, a single broad proton resonance is observed at δ 7.58 in the ^{1}H NMR spectrum in $(CD_3)_2SO$ (integral 1H), and this proton was found to be strongly attached to the three azamacrocyclic N atoms. This was established from the symmetric nature of the complex (all three bipy arms are equivalent), and the coupling pattern produced by the interaction of this NH$^+$ proton with the two protons of each of the linking methylene groups of the pendent arms (a single split AB quartet with ^2J −13.7 Hz, centred at δ 3.95. The single N–H$^+$ proton shows a strong '*trans*' ^3J coupling to one of each of the CH$_2$ group protons (^3J 3.19 Hz), and a weaker '*cis*' coupling to each of the other CH$_2$ protons (^3J 0.47 Hz) as expected from the Karplus relationship. To confirm these findings, and for comparison with the molecular modelling calculations, a single crystal of the ruthenium(II) complex was subjected to X-ray analysis.¶ The molecular geometry (Fig. 3) was found to be in excellent agreement with that predicted by the molecular modelling calculations, and the three uncomplexed $[PF_6]^-$ groups were located in the lattice confirming the analytical data and the presence of a protonated ligand complex. It can be seen that anchoring the three bipy groups to 9N3 results in a geometry about Ru^{II} which is not significantly different to that found in $[Ru(bipy)_3]^{2+}$ ion, although in water the visible spectrum of $[Ru(bipy)_3]^{2+}$ (λ_{max} = 452 nm, ε = 14 600 dm^3 mol^{-1} cm^{-1}([13] is somewhat different to that of $[Ru(L^1H)]^{3+}$ (λ_{max} = 468 nm, ε = 9500 dm^3 mol^{-1} cm^{-1}). From the crystal structure, although the trapped NH$^+$ proton was not located in the refinement it is calculated to be 4.8–4.9 Å from the metal centre, and is therefore too far away to be in a position to form a ruthenium hydride bond.

Attempts were made to deprotonate $[Ru(L^1H)]^{3+}$ in aqueous solution at high pH. However, in an NMR study carried out in 0.1 mol dm^{-3} $NaOD/D_2O$ at 70 °C for 1 h, there was no evidence for loss of the NH$^+$ proton, or for H–D exchange. The hydrophobic pocket produced by coordination of the three bipy arms, and the favourable disposition of the three azamacrocyclic lone-pairs, are undoubtedly the major causes of this strong proton chelation.

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Footnotes

† For $[RuL^1]^{2+}$, the following bond lengths (Å) and angles (°) were found after energy minimisation with HYPERCHEM (atomic numbering scheme in Fig. 3): Ru–N(32) 2.101, Ru–N(21) 2.095, Ru–N(22) 2.101, Ru–N(11) 2.095, Ru–N(12) 2.101, Ru–N(31) 2.095, N(21)–Ru–N(32) 94.7, N(22)–Ru–N(32) 94.2, N(11)–Ru–N(32) 164.9, N(12)–Ru–N(32) 94.2, N(31)–Ru–N(32) 72.9, N(22)–Ru–N(21) 72.9, N(11)–Ru–N(21) 99.6, N(12)–Ru–N(21) 164.9, N(31)–Ru–N(21) 99.6, N(11)–Ru–N(22) 94.7, N(12)–Ru–N(22) 94.2, N(31)–Ru–N(22) 164.9, N(12)–Ru–N(11) 72.9, N(31)–Ru–N(11) 99.6, N(31)–Ru–N(12) 94.7.

‡ For $[Ru_2(L^1)_2H]^{5+}$, ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 8.79 (d, 4H), 8.76 (d, 4H), 8.66 (d, 2H), 8.57 (s, 2H), 8.36 (d, 4H), 8.22 (m, 12H), 7.93 (t, 2H), 7.75 (m, 6H), 7.65 (s, br, 1H), 7.44 (m, 2H), 6.93 (s, 4H), 4.10 (d, 4H), 4.03 (AB quartet, 8H), 3.38 (t, 4H), 3.24–2.88 (m, 16H), 2.79–2.76 (m, 4H). ^{13}C NMR (100.62 MHz, $(CD_3)_2SO$): δ (relative populations in parentheses) 156.6 (4), 156.5 (4), 155.1 (2), 154.6 (2), 151.7 (4), 151.4 (4), 150.1 (2), 149.0 (2), 139.1 (4), 138.3 (2), 137.9 (4), 137.1 (2), 136.6 (4), 130.9 (2), 128.0 (4), 124.7 (4), 124.3 (4), 124.1 (2), 120.5 (2), 120.3 (2), 56.3 (4), 55.9 (2), 49.3 (4), 49.1 (4), 48.5 (4). Attempts to obtain an FAB MS were unsuccessful.

§ For $[Ru(L^1H)]^{3+}$, ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 8.81 (t, 6H), 8.20 (m, 9H), 7.73 (t, 3H), 7.58 (s, br, 1H), 6.90 (s, 3H), 4.02 (AB quartet, 6H), 3.35 (m, 3H), 2.97–2.86 (m, 9H). ^{13}C NMR (100.62 MHz, $(CD_3)_2SO$): δ (relative populations in parentheses) 156.71 (3), 156.68 (3), 151.9 (3), 151.6 (3), 139.3 (3), 138.2 (3), 136.9 (3), 128.3 (3), 125.0 (3), 124.5 (3), 56.3 (3), 49.5 (3), 48.6 (3). FAB (NBA) MS: *m/z* 1026 (calc. for $[Ru(L^1H)(PF_6)_2]^+$, 1026).

¶ *Crystal data*: $[C_{39}H_{40}N_9Ru][PF_6]_3 \cdot (MeNO_2)_3$, M = 1353.91, monoclinic, a = 12.596(13), b = 25.81(2), c = 17.417(14) Å, β = 110.65(7)°, U = 5299(8) Å^3, D_c = 1.697 g cm^{-3}, T = 220(2) K, Mo-Kα radiation, λ = 0.71073 Å, space group $P2_1/n$, Z = 4, μ = 0.509 mm^{-1}, $F(000)$ = 2736, crystal size 0.49 × 0.34 × 0.28 mm. Data were collected with a Siemens P3R3 four-circle diffractometer in the ω-2θ mode to a maximum 2θ of 45°. An analytical absorption correction was applied and resulted in transmission factors ranging from 0.89 to 0.85. The number of reflections collected was 7320, of which 6954 (R_{int} = 0.0421) were unique. Refinement was upon F^2 using SHELXL-93;[11] the final cycle involved 6941 reflections and 761 parameters. A disordered model was used for one of the $[PF_6]^-$ groups and also for one of the nitromethane solvent molecules. Hydrogen atoms were inserted at calculated positions; the proton trapped by N(1), N(2) and N(3) was given a site occupation factor of 1/3. The final R factors were $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ = 0.059 [for $I > 2\sigma(I)$] and $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{\frac{1}{2}}$ = 0.1733 [for all data]. The maximum and minimum peaks on a final difference Fourier map corresponded to 0.684 and −0.636 e Å^{-3}.

The weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0472\,P)^2 + 26.39P]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$ was shown to be satisfactory. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallograpic Data Centre. See Information for Authors, Issue No. 1.

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