Stereospecific template synthesis of a new class of cage complexes: an example of self assembly

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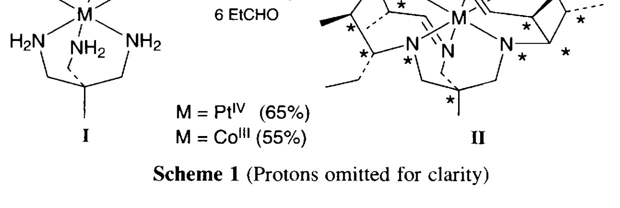
Reaction of $[M(tame)_2]^{n+}$ [tame = ethylidynetris(methanamine)], M = Pt^{IV}, Co^{III}, with propanal produces a new class of cage complex, with remarkable regio- and stereo-selectivity.

New classes of cage complexes with expanded cavities are being sought in order to influence the stabilities of metal oxidation states and to alter the spectroscopic, redox and electron-transfer behaviour of the encapsulated metal ion in a profound manner. Two such cage complexes, $[ML]^{n+}$ (Scheme 1; L = 18,22-diethyl-4,8,12,16,17,21-hexamethyl-2,6,10,14,19,23-hexaazatricyclo[10.4.4.4^{4,9}]tetracosa-6,14-diene), were formed in good yield in template syntheses by treating the chloride salts of $[M(tame)_2]^{n+}$ (M = Pt^{IV}, Co^{III}) in acetonitrile with an excess of propanal under basic conditions in the presence of anhydrous $NaClO_4$.

The products were separated from the reaction mixture by ion-exchange chromatography and X-ray crystallographic analyses were carried out on single crystals of $[Pt(L-H)][PF_6]_3\cdot5H_2O$ and $[CoL]Cl_3\cdot5H_2O$. They show that six propanal molecules have condensed with the $[M(tame)_2]^{n+}$ template to form cages with C_i symmetry. The ORTEP diagrams of both cations are depicted in Fig. 1. Both structures show that two pairs of propanal units have condensed with the $[M(tame)_2]^{n+}$ templates to form two six-membered chelate rings ('straps'), linking the two tame residues in a tetradentate structure such that the two remaining primary amine groups are *trans* to each other. Each strap is then linked to one of these *trans* primary amine sites by a propanal residue to form 'cross straps', which bear imines that are *trans* to each other. This process yields a rigid cage with fourteen chiral sites, ten associated with the carbon framework and four with the secondary nitrogen atoms. These are related in pairs by the centre of inversion. In one half of the complex, the carbon atoms C(2), C(6), C(9), C(11) and C(12) have (*S*), (*S*), (*S*), (*S*) and (*R*) configurations respectively, and the secondary nitrogen atoms N(1) and N(3) have the (*S*) configuration. The geometry about the metal ion is distorted slightly from octahedral, as a consequence of the steric constraints of the ligand. The three independent pairs of M–N bond lengths are given in the legend of Fig. 1. The M–N(1) bond distances are similar to those in analogous sarcophagine (3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane) cage complexes, the imine bond lengths [M–N(2)] are the shortest of the three, while the third pair [M–N(3)] are significantly longer and are among the longest reported for both Pt^{IV} and Co^{III} ions.



Scheme 1 (Protons omitted for clarity)

The NMR spectra of the reaction residues in each case showed that other complexes were present but no other major component was evident. This system therefore is an intriguing example of stereospecific self assembly in relatively high yield organised by the template complex with propanal and some analysis of the mechanism is therefore appropriate. As the configurations about the chiral centres for both complexes are identical, and the metal ions are significantly different, it is likely that the factors which govern their synthesis are the same (Scheme 2) and that the results are not simply a coincidence. A combination of inter- and intra-molecular Schiff-base and Mannich condensation reactions are involved and the observed regio- and stereo-specificity is attributed to a subtle combination of intraligand electronic and steric effects associated with the substituents and conformations of the six-membered chelate rings.

The synthesis is initiated by the deprotonated $[M(tame)_2]^{n+}$ template (**A**) which condenses with propanal, to form the propanimine species **B** and a rational route to products is given in Scheme 2. This route takes account of steric and electronic factors involved and intermolecular attack of a carbanion at a coordinated imine followed by rapid intramolecular chelation is a proposed order of events to accommodate these results and others.[1] The first relatively stable imine formed influences the relative acidities of the remaining primary amines and the differences appear to be related to whether the amines are *cis* or *trans* to a coordinated imine and also on which tame residue the

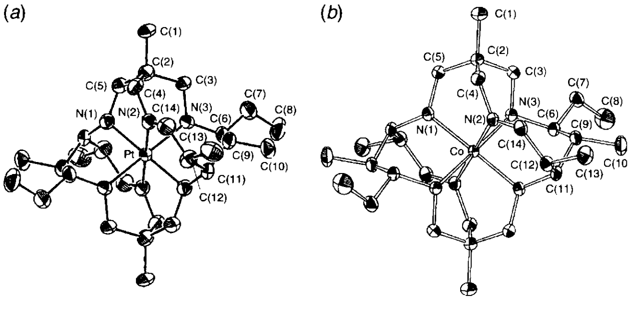
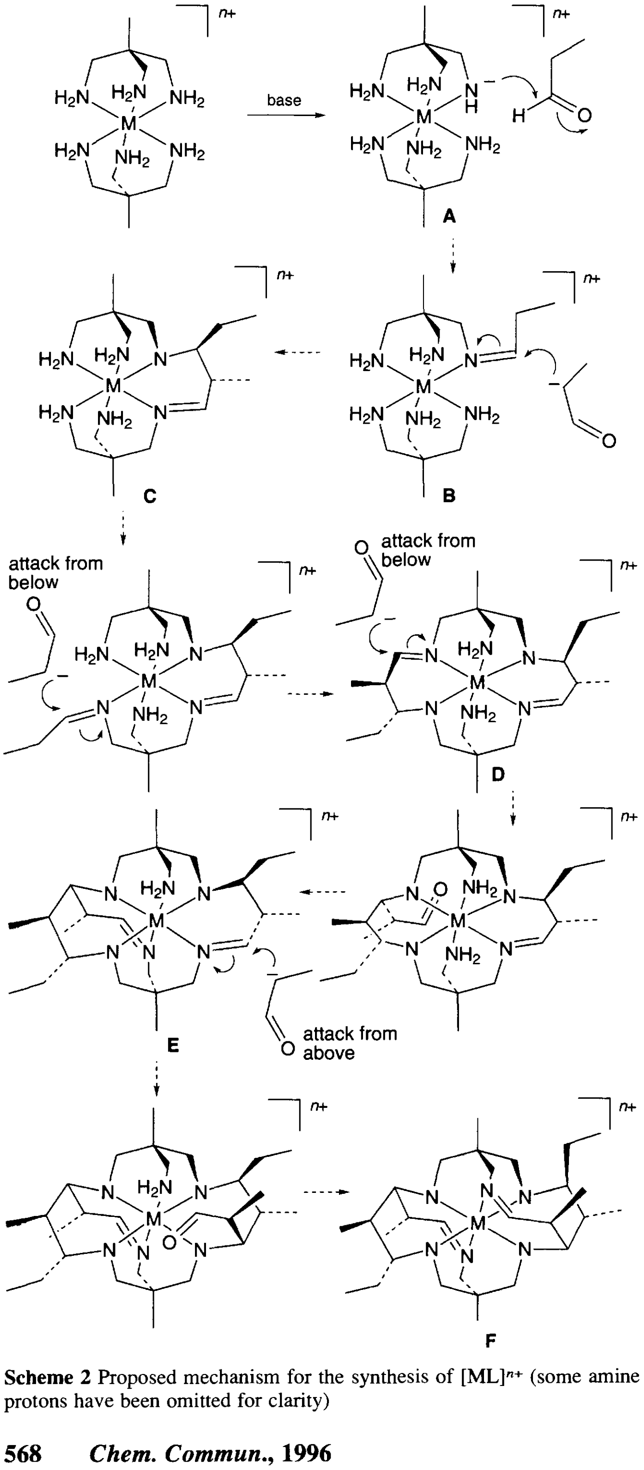


Fig. 1 ORTEP diagrams of the cations in (*a*) $[Pt(L-H)][PF_6]_3\cdot5H_2O$† and (*b*) $[CoL]Cl_3\cdot5H_2O$‡ (H atoms omitted). Selected bond lengths (Å) and angles (°) for (*a*): Pt–N(1) 2.087(7), Pt–N(2) 2.035(6), Pt–N(3) 2.109(7), N(1)–Pt–N(2) 86.3(3), N(1)–Pt–N(3) 93.7(3), N(2)–Pt–N(3) 82.5(3), Pt–N(1)–C(5) 114.5(5), Pt–N(2)–C(4) 115.3(3), Pt–N(3)–C(3) 113.2(2), Pt–N(1)–C(11′) 114.4(5), Pt–N(2)–C(14) 126.5(6), Pt–N(3)–C(6) 115.6(5) (primes indicate atoms generated by the symmetry operation $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$). ^{13}C NMR (0.1 mol dm^{-3} DCl) δ (in ppm relative to 1,4-dioxane at δ 67.3) 14.1, 15.8, 21.2, 22.3, 24.7, 35.3, 41.6, 42.2, 50.2, 64.0, 64.2, 197. Selected bond lengths and angles for (*b*): Co–N(1) 1.979(2), Co–N(2) 1.961(2), Co–N(3) 2.029(2), N(1)–Co–N(2) 87.0(1), N(1)–Co–N(3) 92.7(1), N(2)–Co–N(3) 84.1(1), Co–N(1)–C(5) 116.7(1), Co–N(2)–C(4) 116.6(1), Co–N(3)–C(3) 115.1(1), Co–N(1)–C(11′) 116.5(1), Co–N(2)–C(14) 127.2(1), Co–N(3)–C(6) 117.1(1) (primes indicate atoms generated by the symmetry operation $1-x, 1-y, 1-z$). ^{13}C NMR (D_2O) 13.7, 15.3, 20.3, 21.6, 24.8, 33.6, 37.4, 38.4, 48.9, 53.4, 61.8, 62.6, 65.4, 193.4.

imine resides. There is evidence that the amines *cis* to a coordinated imine are more acidic than those *trans* in amine complexes of Pt^{IV}[2,3] and also in other condensation reactions of related platinum(IV) amine complexes.[4] Therefore, it is likely that the third propanal molecule condenses preferentially with an amine *cis* to the imine in complex **C**, on the same tame residue. The fourth propanal unit approaches the propanimine moiety in **C** from its least sterically hindered side in the same manner as the first chelate strap was made. Dreiding models also indicate that rotation of the pendant carbonyl group is restricted and that it is now favourably poised for condensation with the amine in the opposite tame cap, so forming the second strap, as shown in **D**. This leads to the configurations of the three chiral centres generated in the second strap being catoptric to the corresponding sites in the first strap. The imines are located *trans* to each other, as are the remaining primary amines, and the latter cannot therefore be linked in the same manner. Sequential condensation of each of the imines with the fifth and sixth propanal carbanions forms the cross-straps, resulting in firstly, **E**, then the fully encapsulated complex, **F**. Dreiding models indicate that each propanal carbanion should attack the least hindered face of the relevant imine (as shown), with the methyl group pointing away from the complex and the carbonyl group oriented toward the opposite tame residue. Each pendant carbonyl group is then oriented very favourably for attack by the deprotonated primary amine on the opposite tame residue, to form imines at these sites, which are *trans* to each other. Three chiral centres are generated by addition of each of these propanal units, one at the methine derived from the carbanion and the other two arising from the imines in the original straps.



Scheme 2 Proposed mechanism for the synthesis of $[ML]^{n+}$ (some amine protons have been omitted for clarity)

Clearly, the formation of mainly one isomer out of many possible is extraordinary for both the Pt^{IV} and Co^{III} templates. The synthesis must be governed by some common factors such as the electronic effects imparted by the imines formed on the template and steric effects in the vicinity of the reacting species, alluded to in the above rationalisation. Also, the fact that there is no other major component indicates that the template and steric effects steer the complicated synthesis. It is possible, of course, that there is a degree of reversibility in the condensation reactions and that thermodynamic stabilities of some intermediates are influential. However, it is very unlikely that it is governed overall by thermodynamics given the enormous number of possibilities available for various condensation paths.

The redox, spectral and electron-transfer properties of the cobalt(III) complex and the electrochemical behaviour of the platinum(IV) complexes are currently being investigated. Preliminary results show that the imines in the ligand framework may be reduced using BH_4^- at high pH for both complexes. Both the diimine and the saturated cobalt(III)–L complexes have surprisingly negative reduction potentials (−0.2 V *vs*. NHE) for the large cage skeleton but the electron self-exchange rate constant of the saturated form is now ≈ 200 dm^3 mol^{-1} s^{-1} at 25 °C (I = 0.2 mol dm^{-3}). This is $\approx$ 100-fold greater than those of the Co^{III}–Co^{II} couples of the sarcophagine type.[6] The platinum(IV) complex undergoes a complex irreversible two-electron reduction involving substantial rearrangements at the metal centre and the ligand, which are being unravelled. Finally, it may be possible to extrude the Co^{II} ion from the saturated cage complex to yield the free cage ligand, into which other metal ions may be introduced. It is anticipated that their properties will be markedly different from their sarcophagine and tricosaneN_6 analogues.[5]

Footnotes

† *Crystal data* for $C_{28}H_{63}F_{18}N_6O_5P_3Pt$: M = 1193.82, monoclinic, space group *C2/c*, a = 17.203(3), b = 14.999(1), c = 17.273(2) Å, β = 92.41(2)°, U = 4453.0(9) Å^3, Z = 4, D_c = 1.781 g cm^{-3}, μ(Cu-Kα) = 80.9 cm^{-1}. Data comprising 2365 reflections with $I > 3\sigma(I)$ to 2θ = 120° were collected on a Rigaku AFC-6R diffractometer with graphite-monochromated Cu-Kα radiation and data was corrected for absorption. The structure was solved by Patterson and difference Fourier techniques. All non-hydrogen atoms were located and refined with anisotropic displacement factors. Hydrogen atoms attached to carbon atoms of the cation were placed at calculated positions (tetrahedral at the carbon atom, terminal methyl groups assumed to be in the staggered conformation) and not refined, but were periodically recalculated. Chemical evidence had indicated that three of the four nitrogen donors in each cation would be protonated. As the cation possesses a centre of symmetry in the solid state, this would lead to disorder, the protons either being equally delocalised over the two crystallographic sites (both with occupancy 0.75) or preferring one site over the other (one site with occupancy 1.0, the other 0.5). The former scheme has been adopted here. Some of the fluorine atom displacement factors are very large. Attempts were made to model this motion by disorder, but were not successful. The anions appear rather free to rotate and the anisotropic model has been retained. Refinement was continued until all shift/error ratios were < 0.07. Final R factor 0.042, R_w 0.064.

‡ *Crystal data* for $C_{28}H_{64}Cl_3CoN_6O_5$: M = 730.15, monoclinic, space group $P2_1/n$; a = 11.605(3), b = 12.152(3), c = 12.409(3) Å; β = 98.46(2)°; U = 1731.0(6) Å^3; Z = 2; D_c = 1.401 g cm^{-3}; μ(Mo-Kα) = 7.67 cm^{-1}. Data comprising 3351 reflections with $I > 2.5\sigma(I)$ to $2\theta = 50°$ were collected on a Enraf-Nonius CAD-4F four-circle diffractometer employing graphite-monochromated Mo-Kα radiation and were corrected for absorption. The structure was solved by direct methods and difference Fourier techniques. A common site is equally occupied by Cl and O. Hydrogen atoms were refined with isotropic thermal parameters and all other atoms were refined anisotropically. Final R factor 0.033, R_w 0.039.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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5 The properties of the sarcophagine cage complexes with metal ions other than Co^{III} have been reviewed.[6,7] The properties of [M(Me)$_5$-D_{3h}-tricosaneN$_6$)]$^{n+}$ complexes are currently being examined (M = Co^{III}, Rh^{III}, Cr^{III}, Ni^{II}, Cu^{II},. Zn^{II}, Cd^{II}, Hg^{II}, Mn^{II}, Ag^{I}, Pb^{II}).[8–10]

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