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Gold(III) template synthesis of a pendant-arm macrocycle

Monica Rossignoli,[a] Paul V. Bernhardt,[b] Geoffrey A. Lawrance[a] and Marcel Maeder[a]

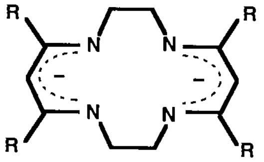
[a] *Department of Chemistry, The University of Newcastle, Callaghan 2308, Australia*
[b] *Department of Chemistry, The University of Queensland, Brisbane 4072, Australia*

Gold(III)-directed condensation of ethane-1,2-diamine with nitroethane and formaldehyde yielded the gold-coloured macrocyclic complex (*cis*-6,13-dimethyl-6,13-dinitro-1,4,8,11-tetraazacyclotetradecan-1-ido)gold(III) and the orange acyclic complex (1,9-diamino-5-methyl-5-nitro-3,7-diazanonan-3-ido)gold(III) in good yields. Dissolution in strongly acidic solution gave the colourless fully protonated complexes. The pendant nitro groups are disposed on the same side of the macrocycle in a *cis* geometry, as confirmed by crystal structure analysis. In both complexes the gold ion lies in a square-planar environment of four nitrogen donors, and the co-ordinate bond to the deprotonated amine is shorter than the remaining Au−N distances.

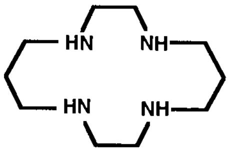
The metal-directed syntheses of a range of pendant-arm macromonocyclic polyamines formed using formaldehyde and the carbon acid nitroethane have been examined with copper(II) as the templating metal ion.[1–3] These reactions lead to ring closing at pairs of *cis*-disposed primary amines, resulting in molecules with C-pendant nitro and methyl groups, exemplified by the reaction of $[Cu(en)_2]^{2+}$ (en = ethane-1,2-diamine).[4] The metal-directed cyclisation chemistry relies dominantly on the presence of two *cis*-disposed primary amine donor groups. Beyond this requirement, it is not a demanding reaction and occurs with linear or branched multidentate ligands with terminal primary amine donors essentially independent of the type of internal donors.[5,6] It was also presumed that changing the templating metal ion need not necessarily reduce the facility of the reaction. However, examination of the chemistry with various templating metals has been restricted until recently to copper(II) and nickel(II) ions,[1–4,7] both of which can form relatively thermodynamically stable square-planar complexes. We anticipated that the chemistry could be extended at least to other stable square-planar complexes of polyamines. Recently, we have reported the success of the chemistry employing the second-row transition-metal ion palladium(II).[8] Here, we extend that by employing the third-row transition-metal ion gold(III).

There are few examples of gold(III)-templated complexes in the literature. A series of unsaturated, fourteen-membered complexes (L^1) have been reported based on the reaction between $[Au(en)_2]Cl_3$ and β-diketones.[9–12] The first saturated macrocyclic polyamine complexes of gold(III) were reported as recently as 1991, but were not prepared by template routes.[13] These included the complex of cyclam (L^2), prepared by treating cyclam with an equimolar amount of $Na[AuCl_4]\cdot H_2O$ in refluxing acetonitrile–ethanol; the crystal structure of this was reported 2 years later.[14] Notably, mixing of cyclam and $Na[AuCl_4]$ in aqueous 1 mol dm^{-3} HCl precipitates the 'gold-out' complex $[AuCl_2(H_2L^2)]^{3+}$ with the gold simply chelated to two secondary amines, and forcing conditions in the absence of acid are required for binding in the macrocycle cavity.[13] Other gold(III) macrocyclic complexes were prepared in a similar manner to that reported for cyclam, and include a phenol-pendant cyclam, a pyridyl-pendant cyclam, various monooxocyclams and an amino-pendant cyclam.[13,14]

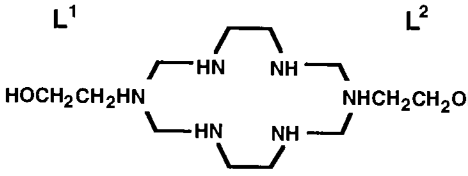
Given that $[Au(en)_2]^{3+}$ has been well characterised and is easily synthesized,[15] it is surprising that it has only had very limited use as the basis of metal template macrocyclisation reactions. During the course of this work a saturated macrocycle (L^3) was described by a template route between $[Au(en)_2]Cl_3$, ethanolamine and formaldehyde, although the ligand is not sufficiently robust to be recovered from the metal complex.[16] Here, we report the condensation chemistry between $[Au(en)_2]^{3+}$, nitroethane and formaldehyde in water at near neutral pH, resulting in both acyclic (L^4) and cyclic (L^5) saturated products of high stability.



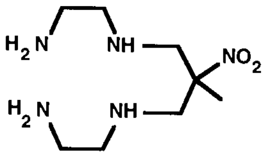
L^1



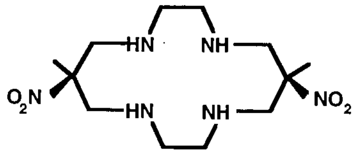
L^2



L^3



L^4



L^5

Experimental

Syntheses

The precursor complexes $[Au(en)_2]Cl_3$ and $[Au(en)_2][ClO_4]_3$ were prepared as described.[15]

(*cis*-6,13-Dimethyl-6,13-dinitro-1,4,8,11-tetraazacyclotetradecan-1-ido)gold(III) perchlorate hydrate, $[Au(L^5 - H)][ClO_4]_2\cdot H_2O$. A solution of $[Au(en)_2]Cl_3$ (0.65 g) and $[Au(en)_2][ClO_4]_3$ (0.15 g) in water (100 cm^3) was filtered, formaldehyde (1.2 cm^3) and nitroethane (0.6 cm^3) were added and the pH adjusted to 7.5 with 2.5 mol dm^{-3} NaOH. A dark orange colour developed rapidly as the solution was stirred. Stirring was continued at room temperature for 2 d, and during this time a gold mirror precipitated on the walls of the reaction vessel. The solution was filtered and, after dilution to 2 dm^3 with water, was sorbed onto a column of SP Sephadex C-25 cation-exchange resin

(25 × 4 cm). After washing with water (150 cm^3) the desired product was eluted with 0.2 mol dm^{-3} NaCl at pH 7. The eluate was reduced in volume and solid $NaClO_4$ added to aid precipitation of the product as a dark yellow powder. This was collected, washed with ethanol and diethyl ether and air dried (0.57 g). Three following very small bands were collected, but failed to produce precipitates and reduced to metallic Au on standing (Found: C, 19.7; H, 3.7; N, 11.2. Calc. for $C_{12}H_{27}AuCl_2N_6O_{13}$: C, 19.7; H, 3.7; N, 11.45%). Electronic spectrum (water, pH 6): λ_{max} 365 (ε 1670 dm^3 mol^{-1} cm^{-1}). Cyclic voltammetry (0.1 mol dm^{-3} aqueous $NaClO_4$, glassy C, 200 mV s^{-1} scan rate): $E_p(Au^{III/II})$ −0.68 (irreversible), $E_{pc}(NO_2)$ −0.92 V *vs.* Ag–AgCl. IR spectrum (KBr): 1553 and 1343 cm^{-1} (NO_2). NMR spectra: in D_2O, ^1H, δ 1.74 (s, 6 H), 3.0–3.3 (m, 16 H) and 3.6 (br s, 4 H); ^{13}C, δ 25.9, 58.9 (br), 93.5; in DCl, ^1H, δ 1.74 (s, 6 H), 3.4–3.6 (m, 8 H), 3.68 and 3.72 (AB q, *J* 14.8 Hz, 8 H); ^{13}C, δ 24.9, 56.8, 59.6 and 92.5.

(1,9-Diamino-5-methyl-5-nitro-3,7-diazanonan-3-ido)gold(III) perchlorate hydrate, $[Au(L^4-H)][ClO_4]_2\cdot H_2O$. The head of the main band from the chromatography in the above synthesis appeared paler in colour but complete separation was not achieved. Therefore the filtrate obtained upon isolation of the macrocycle (above) was diluted then sorbed on a column of SP Sephadex C-25 cation-exchange resin (25 × 4 cm). Elution with 0.1 mol dm^{-3} NaCl at pH 7 gave two closely running but distinct bands. Each was collected, reduced in volume and solid $NaClO_4$ added to aid in precipitation of the products. The first band proved to contain the macrocycle, the second produced, on prolonged standing, a small crop of orange crystals. These were collected, washed with ethanol and diethyl ether and air dried (0.1 g) (Found: C, 15.45; H, 3.0; N, 11.3. Calc. for $C_8H_{22}AuCl_2N_5O_{11}$: C, 15.65; H, 3.3; N, 11.4%). Electronic spectrum (water, pH 6): λ_{max} 364 (ε 1850 dm^3 mol^{-1} cm^{-1}). Cyclic voltammetry (0.1 mol dm^{-3} aqueous $NaClO_4$, glassy C, 200 mV s^{-1} scan rate): $E_p(Au^{III/II})$ −0.56 (irreversible), $E_{pc}(NO_2)$ −0.91 V *vs.* Ag–AgCl. IR spectrum (KBr): 1549, 1349 (NO_2) and 1583 cm^{-1} (NH_2). NMR spectra: in D_2O, ^1H δ 1.74 (s, 3 H) and 2.8–3.3 (m, 12 H); ^{13}C, δ 25.8, 48.0, 63.8 and 93.5; in DCl, ^1H, δ 1.81 (s, 3 H), 3.1–3.6 (m, 8 H), 3.62 and 3.75 (AB q, *J* 14.8 Hz, 4 H); ^{13}C, δ 25.4, 49.8, 57.4, 62.9 and 93.9.

Physical methods

Electronic spectra of compounds (in water, controlled pH) were recorded on a Hitachi 150-20 spectrophotometer, infrared spectra (as KBr discs) on a Bio-Rad FT7 Fourier-transform spectrometer. Cyclic voltammetry in nitrogen-purged aqueous 0.1 mol dm^{-3} $NaClO_4$ employed a BAS CV27 electrochemical controller with a glassy carbon working electrode, Ag–AgCl reference electrode and platinum-wire auxiliary electrode. The NMR spectra were recorded (D_2O solutions) using a Bruker Avance DPX300 spectrometer, with chemical shifts measured *versus* sodium 3-(trimethylsilyl)-(2,2,3,3-[$^2H_4$])propionate.

Crystallography

Room-temperature (293 K) cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections measured on an Enraf-Nonius CAD4 four-circle diffractometer employing graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å) and operating in the ω-scan mode. Data reduction was performed with the XTAL[17] package.

Absorption corrections were applied with the program DIFABS.[18] Both structures were solved by heavy-atom methods with SHELXS 86[19] and refined by full-matrix least-squares analysis on F^2 with SHELXL 93.[20] All non-H atoms were refined with anisotropic thermal parameters, and alkyl H atoms were included at estimated positions and their thermal parameters restrained to be 1.3 times that of their attached C atom. Amine H atoms were first located from difference maps then restrained as above. Pertinent results are collected in Table 1, and the atomic nomenclature is defined in Figs. 1 and 2 drawn with PLATON.[21] At convergence particularly large extrema close to the gold centre were observed in both structures, which could not be reduced further by empirical absorption correction.

Crystal data. $[Au(L^4-H)][ClO_4]_2$; $C_8H_{20}AuCl_2N_5O_{10}$, $M = 614.2$, triclinic, space group $P1$, $a = 8.037(1)$, $b = 8.466(1)$, $c = 13.672(5)$ Å, $\alpha = 90.93(2)$, $\beta = 104.50(2)$, $\gamma = 106.17(1)°$, $U = 861.3(3)$ Å^3, D_c $(Z = 2) = 2.368$ g cm^{-3}, μ(Mo-Kα) = 89.1 cm^{-1}, $F(000) = 592$. Specimen: yellow prism 0.27 × 0.27 × 0.20 mm; $N = 3021$, $N_o = 2755$ $[|F_o| > 2\sigma(|F_o|)$, $2 < \theta < 25°]$, h 0–9, k −9 to 9, l −15 to 15. Final $R1 = 0.0396$, $wR2 = 0.1067$, $w^{-1} = \sigma(F_o)^2 + (0.0853P)^2 + 0.19P$ where $P = (F_o^2 + 2F_c^2)/3$. Residual extrema +2.2 and −2.0 e Å^{-3}.

$[Au(L^5-H)][ClO_4]_2$; $C_{12}H_{25}AuCl_2N_6O_{12}$, $M = 713.3$, monoclinic, space group $P2_1$, $a = 8.303(4)$, $b = 16.926(2)$, $c = 8.530(4)$ Å, $\beta = 117.48(2)°$, $U = 1063.5(7)$ Å^3, D_c $(Z = 2) = 2.227$ g cm^{-3}, μ(Mo-Kα) = 72.4 cm^{-1}, $F(000) = 696$. Specimen: yellow prism 0.50 × 0.30 × 0.20 mm; $N = 1935$, $N_o = 1710$, $[|F_o| > 2\sigma(|F_o|)$, $2 < \theta < 25°]$, h −8 to 8, k 0–20, l 0–10. Final $R1 = 0.0620$, $wR2 = 0.1698$, $w^{-1} = \sigma(F_o)^2 + (0.1463P)^2$ where $P = (F_o^2 + 2F_c^2)/3$. Residual extrema +2.6 and −4.2 e Å^{-3}.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/332.

Results and Discussion

Condensation reactions employing formaldehyde and nitroethane with the square-planar gold(III) complex of ethane-1,2-diamine, $[Au(en)_2]^{3+}$, proceed readily at pH 7.5 to yield both a macrocyclic and a 'half-capped' acyclic product, and parallel chemistry described with copper(II) and palladium(II) as templates where similar products are obtained.[4,8] Careful control of pH is necessary, since the precursor and products are susceptible to redox-based decomposition at elevated pH which yields metallic gold. The condensations around copper(II) and palladium(II) can be performed successfully at more elevated pH, these complexes being less susceptible to base-promoted decomposition reactions. Evidently, the condensation chemistry between the pair of *cis*-disposed primary amine groups, formaldehyde and the carbon acid nitroethane proceeds readily at the pH employed, presumably because the acidity of both the carbon acid and the co-ordinated primary amines generates sufficient concentrations of carbanion and amido N atom for condensation reactions with formaldehyde to proceed at a reasonable rate. The present and earlier work has established that $[M(en)_2]^{n+}$ complexes with metal ions from each row of the d block of the Periodic Table may direct the condensation chemistry, provided the precursor complex is of sufficient stability.

The condensation around $[Au(en)_2]^{3+}$ yields more of the macrocycle L^5 (50%) than the acycle L^4 (7%), although the relative yields may be varied by controlling the amounts of reactants employed, as established for the copper(II) analogue.[4] The macrocycle is readily identified from its infrared spectrum, with the most distinct features being the presence of nitro group frequencies (1553, 1343 cm^{-1}) and the absence of primary amine bands. It is easily distinguished from the open-chain product, as the latter contains both NO_2 and NH_2 resonances. Both L^4 and L^5 complexes have been isolated in their N-deprotonated amido forms. This has not been reported previously for a saturated tetraaza macrocyclic gold(III) complex. The intense yellow colour of the amido complexes is convenient for chromatographic separation, with the acyclic complex preceding the macrocycle upon elution on a Sephadex cation-exchange resin; separation is not complete, but fractional crystallisation isolates the less-soluble macrocycle effectively. The amido complexes characteristically[22] show a ligand-to-metal charge-transfer absorption band at 364 (L^4) and 365 nm (L^5) at pH *ca.* 6. This band occurs at 360 nm for the deprotonated cyclam complex and at 369 nm for the $[Au(dien - H)Cl]^+$ complex (dien = 3-azapentane-1,5-diamine). The dissociation of a proton from a secondary amine has not been observed in the corresponding palladium(II) complexes at such low pH values, and attests to the acidity of the gold(III) complex ions. The gold(III) complexes of L^4 and L^5 exhibit irreversible Au^{III}–Au^{I} couples at −0.56 and −0.68 V *versus* Ag–AgCl respectively; an oxidation wave is seen for each reduced complex at −0.03 and −0.07 V respectively, distant from the reduction wave and consistent with significant ligand dissociation or rearrangement upon reduction. Further reduction to Au^0 is not observed prior to the solvent limit. The presence of the nitro pendants is clearly defined by a multielectron reduction near −0.9 V.

The acidity of the gold(III) ion is greater than met in copper(II) or even palladium(II) complexes, and was characterised for $[AuL^2]^{3+}$ by a pH titration with base, which demonstrated ready removal of a proton from one secondary amine (pK_a 5.4).[13] Reprotonation can be achieved, although the complex is unstable in neutral and basic solution and decomposes to precipitate gold metal.[13] Similarly, deprotonation can be observed for $[Au(NH_3)_4]^{3+}$ (pK_a 7.5),[23] $[Au(en)_2]^{3+}$ (pK_a 6.3)[22] and $[Au(dien)Cl]^{2+}$ (pK_a 4.0),[22] with a clear trend from NH_3 to primary to secondary amine observed. No such behaviour was reported for $[AuL^3]^{3+}$,[16] although the electronic spectrum of the complex suggests that deprotonation also occurs in this case. Moreover, in the absence of added acid this complex is unstable in water.[16] The present macrocyclic complex, $[AuL^5]^{2+}$, is a relatively strong acid and exhibits a pK_a of *ca.* 1.5 (determined by a spectrophotometric titration), the difference from the value of 5.4 reported for cyclam being assigned to the electronic effects of the nitro substituents. The complex is stable for long periods provided the pH is below 7, decomposition occurring slowly above that pH. The additional stability compared with L^2 and L^3 may result from stabilisation of the amido form by the presence of the electron-withdrawing nitro group.

The NMR spectra of the $[Au(L^4 - H)]^{2+}$ and $[Au(L^5 - H)]^{2+}$ complexes in D_2O undergo clear changes on conversion from amido into amine forms, achieved by the addition of DCl. The acyclic complex, excluding deprotonation behaviour, contains only one mirror plane passing through the tertiary carbon, the pendant groups and the gold atom, with five magnetically distinct carbon atoms anticipated and observed in the proton-decoupled ^{13}C NMR spectrum. In addition to single resonances for the methyl and tertiary carbon atoms, three separate resonances at δ 49.8, 57.4 and 62.9 are observed for the three non-equivalent methylenes in strong acid, whereas at higher pH the amide yields a number of signals centred on δ 48.0 and 63.8. An AB quartet centred at δ 3.69 in the ^1H spectrum of the protonated complex defines the geminal coupling of the methylenic hydrogen atoms on the introduced ‘cap’, downfield from a complicated pattern of quartets resulting from geminal and vicinal coupling of methylene hydrogen atoms in the ethane-1,2-diamine residue.

The ^1H NMR spectrum of the protonated macrocycle displays an AB quartet for the ‘cap’ methylenes and a complicated multiplet for the ethane-1,2-diamine residues; these signals are more complex for the deprotonated complex. This is strongly suggestive of the *cis* complex, as the four ethane-1,2-diamine residue protons become non-equivalent if the complex adopts the preferred *RRSS* configuration of N-donors. By contrast, a symmetrical AA′BB′ coupling pattern is expected for the *trans* isomer. The two non-equivalent methylene signals in the ^{13}C NMR spectrum (δ 56.8, 59.6) are similar in position to those reported for the analogous cyclam complex (δ 53.2, 59.1),[13] the shift in the first signal for the former complex being associated with electronic effects of the adjacent pendant groups. There is sufficient evidence from the NMR spectra to show that the crystallised macrocyclic complex is isomerically pure. However, the last crop of solid isolated gave a more complex NMR spectrum, consistent with the presence of a second minor product, presumably the other (*trans*) geometric isomer. Stereoselective rather than stereospecific reaction was anticipated, as found with other template metal ions, and this observation is consistent with this expectation.

The crystal structure of the $[Au(L^5 - H)]^{2+}$ ion identified the presence of a fourteen-membered macrocycle with pairs of nitro and methyl substituents. The structure of the macrocyclic complex cation is best defined as square planar, with perchlorate anions making only weak contacts in the axial co-ordination sites [Au · · · O(1C) 2.91, Au · · · O(2B) 3.19 Å]. The *cis* disposition of the two pendant nitro groups is a notable feature, and this represents the first crystal structure of a complex of L^5, although there exist several structurally characterised complexes of the hexaamine derivative formed by reduction of the nitro groups to primary amines.[24–26] Including the lone pair on N(1) in stereochemical considerations, the macrocycle adopts an *RRSS* configuration at the co-ordinated nitrogen atoms, in common with the analogous palladium macrocycle,[14] and regardless of differing nitro group orientations in the two. This is the common configuration for a fourteen-membered tetraaza macrocycle.

The acyclic $[Au(L^4 - H)]^{2+}$ ion also contains a N_4 donor set, but carries only one six-membered chelate ring and accompanying pendant methyl and nitro groups and consequently two secondary and two primary amine centres. In common with the macrocyclic complex, only weak intermolecular contacts were observed between the perchorate anion and the metal centre [Au · · · O(1B) 3.11, Au · · · O(2C) 3.30 Å]. The ligand is deprotonated at N(2), and the Au–N(2) bond length is significantly shorter than the remaining co-ordinate bonds. Notably, the Au–N(4) bond length is significantly longer than the other Au–N bonds, which reflects the *trans* influence of the co-ordinated amido group. The nitro group occupies an axial position with respect to the six-membered chelate ring to which it is bound. This particular N-based diastereomer is commonly referred to as an α isomer.

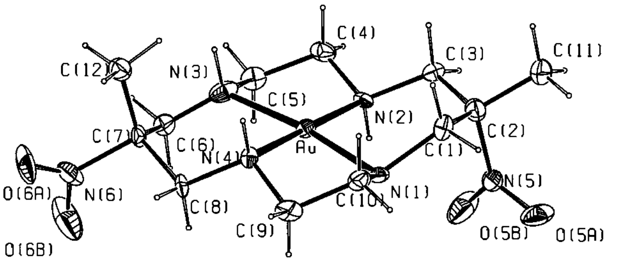


Fig. 1 View of the $[Au(L^5 - H)]^{2+}$ cation, showing the atom numbering

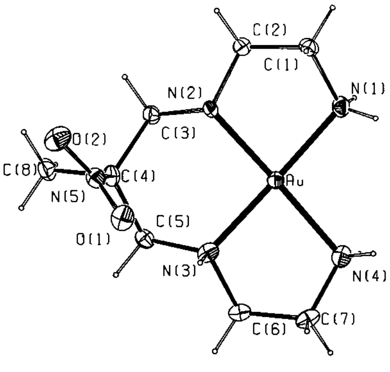


Fig. 2 View of the $[Au(L^4 - H)]^{2+}$ cation, showing the atom numbering

Table 1 Gold environment in acyclic $[Au(L^4 - H)]^{2+}$ and cyclic $[Au(L^5 - H)]^{2+}$ [*r* is the gold–donor atom distance (Å); the other entries are angles (°) subtended at the gold ion by the relevant atoms at the head of the row and column]

	$[Au(L^4 - H)]^{2+}$				$[Au(L^5 - H)]^{2+}$			
Atom	*r*	N(1)	N(2)	N(3)	*r*	N(1)	N(2)	N(3)
N(4)	2.091(8)	97.4(3)	177.2(3)	83.9(3)	2.02(2)	81.1(8)	179.2(6)	93.6(12)
N(3)	2.039(8)	178.5(2)	94.2(3)		2.08(2)	172(2)	86.6(12)	
N(2)	2.004(7)	84.5(3)			2.06(2)	98.7(9)		
N(1)	2.016(8)				2.02(3)			

In both complexes the gold lies in the same plane as the co-ordinated heteroatoms, although the variation in bond lengths leads to a slightly distorted square plane, also reflected in non-ideal N−Au−N angles (Table 1). Fitting of a least-squares plane to the gold and nitrogen atoms yielded a root-mean-square deviation of fitted atoms of 0.012 Å in the case of $[Au(L^4 - H)]^{2+}$ and 0.043 Å for $[Au(L^5 - H)]^{+}$. A smaller distortion in the complex of the more flexible acyclic ligand is not unreasonable. The $[Au(L^4 - H)]^{2+}$ ion can be considered as a 'half-built' macrocycle intermediate, as also observed earlier for the analogous copper(II) and palladium(II) systems.[4,8] The distortions identified in the structure of $[Au(L^4 - H)]^{2+}$ relate to the shortening of Au−N(2) and lengthening of Au−N(4) in the structure. For this well defined acyclic complex, the gold–amide [2.004(7) Å], –amine(secondary) [2.016(8) Å] and –amine(primary) distances [2.039(8), 2.091(8) Å] differ as a result of both *trans* effects and the inherent non-equivalence of donor groups. The observed Au−N bond lengths in $[Au(L^5 - H)]^{2+}$ are consistent with observations in the acyclic complex, although the difference between the Au−N (amido) and its *trans* Au−N (amine) bond lengths relative to their standard deviation is not great. Nevertheless, the results are, overall, consistent with the *trans* influence of an amido group being greater than that of an amine, a characteristic observed earlier in $[Au(dien)Cl]^{2+}$ and $[Au(dien - H)Cl]^{+}$,[27] where the Au−Cl bond elongates from 2.237(8) in the former to 2.33(1) Å in the latter.

A recent report of the metal-directed reaction leading to $[Au(L^3)Cl_2]^{+}$ described the complex as being tetragonally elongated, with weak bonds to axial chloride ligands.[16] However, the equatorial Au−N bond lengths in the structures of $[Au(L^4 - H)]^{2+}$, $[Au(L^5 - H)]^{2+}$ and $[Au(L^3)Cl_2]^{+}$ are similar (≈2.05 Å), as are the axial contacts to their anions (≈3.1 Å). There appears to be little point in describing these structures as tetragonally elongated given the magnitude of the distortion, particularly given the fact that all complexes possess low-spin electronic ground states as expected for a square-planar d^8 complex. It is notable that the closely related d^8 complexes of Pd^{II} and Pt^{II} of the tetradentate hexaamine derivative of the *trans* isomer of L^5 exhibit weak axial interactions (≈3.2 Å) to perchlorate ions, but there is no suggestion that these complexes are anything but square planar.[28]

It is notable that the amido group can be considered to be located at a single site in both structures reported here as well as others reported for gold(III).[27] For the observed α isomer of $[Au(L^4 - H)]^{2+}$ the pendant methyl group is in an equatorial position and the nitro group is necessarily axial, but has rotated about the N(5)−C(4) bond such that one of the oxygen atoms O(1) closely approached the hydrogen [H(3)] of the secondary amine N(3) [O(1) · · · H(3)−N(3) 2.14 Å]. It is likely that the presence of this hydrogen bond 'freezing' the nitro group in this conformation has enabled the deprotonated amide to be identified conclusively crystallographically. In solution the negative charge appears to be partitioned between at least both secondary nitrogen sites as a consequence of rapid proton exchange, as can be inferred from NMR spectroscopy. The nitro group closest to the deprotonated N(1) in $[Au(L^5 - H)]^{2+}$ also forms a hydrogen bond to the adjacent amine [O(5B) · · · H(2)−N(2) 2.34 Å]. To enable this approach the six-membered chelate ring bearing the N(5) nitro group has adopted a chair conformation with the nitro group axial and rotated about the C(2)−N(5) bond. The remaining six-membered chelate ring is in a boat conformation with the N(6) nitro group equatorial, and incapable of intramolecular interactions, the adjacent secondary amine hydrogens residing on the opposite side of the N_4 plane from the N(6) nitro group. Disorder of the sites of deprotonation has been observed in the structure of a vanadium(IV) macrobicyclic diamido polyamine,[29] where no strong intramolecular hydrogen-bonding interactions to a particular site can exist.

The Au−N distances for $[Au(L^5 - H)]^{2+}$ [2.02(2)–2.08(2) Å] are similar to those in $[AuL^2]^{3+}$ [1.93(1)–2.11(1) Å][14] and $[AuL^3]^{3+}$ [2.043(6)–2.055(6) Å].[16] The general expansion of the co-ordination sphere in these saturated systems compared with the tetramethyl-substituted form of $[AuL^1]^{+}$ (average Au−N 1.98 Å)[11] is presumably associated with the presence of four amido N-donors and unsaturation in the latter macrocycle.

The angle subtended on the open face of the $[Au(L^4 - H)]^{2+}$ molecule, N(1)−Au−N(4) is slightly larger [97.4(3)°] than that of the capped face [N(2)−Au−N(3) 94.2(3)°], indicating the strain in bridging the primary amines of $[Au(en)_2]^{3+}$. In a copper(II) analogue the equivalent 'internal' and 'external' angles vary less [95.2(2) *versus* 95.6(2)° respectively].[30] The variation in free-ion size from copper(II) (0.72 Å) to palladium(II) (0.80 Å) to gold(III) (0.85 Å) suggests different strains resulting from the capping reaction. Whether there is a structurally defined limit to successful condensation is difficult to assess. Very large metal ions often form such thermodynamically unstable complexes with the precursor ethane-1,2-diamine ligand that condensation clearly fails for other reasons. The kinetic stability of second- and third-row complexes compared with first-row certainly assists, and this effect may offset other influences.

The validity of the cyclisation reactions well established for polyamine systems[1,2] but previously examined only for first- and second-row d^8 or d^9 metal ions has been confirmed in this study as also applicable for synthesis of macrocyclic systems employing a third-row d^8 metal ion as template. Moreover, a preference for the pendant groups attached directly to the ring to adopt *cis* rather than *trans* geometry in the latter case is noted. Potentially, *cis* and *trans* isomers may exist, and weak axial co-ordination of the nitro group during cyclisation has been proposed as responsible for directing the stereochemistry dominantly to the *anti* isomer in the case of reactions around copper(II),[24] and is supported by molecular mechanics calculations.[31] The greater tendency towards square-planar character generally found for gold(III), where axial interactions are not anticipated, would limit this behaviour.

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