Rhodium(III) Complexes of the Ambidentate Macrocycle 6,13-Diamino-6,13-dimethyl-1,4,8,11-tetra-azacyclotetradecane. Crystal Structure of the Sexidentate Complex†

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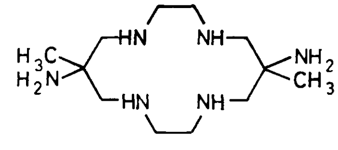
The diamino-substituted macrocyclic polyamine 6,13-diamino-6,13-dimethyl-1,4,8,11-tetra-azacyclotetradecane (L^1) may act as a quadri-, quinque-, or sexi-dentate ligand to rhodium(III), with *trans*-$[Rh(H_2L^1)Cl_2]^{3+}$, *cis*-$[Rh(HL^1)Cl]^{3+}$, and $[RhL^1]^{3+}$ ions all isolated as perchlorate salts and characterized spectroscopically. Unlike the cobalt(III) analogue, which forms a *trans* isomer with the ligand L^1 quinquedentate, only the *cis* isomer was observed with rhodium(III). The sexidentate complex adopts the common arrangement with the pendant primary amine groups in *trans* dispositions, confirmed by an *X*-ray crystal structure analysis: $[RhL^1][ClO_4]_3$ crystallizes in the space group $P2_1/c$, with a = 16.700(3), b = 8.776(2), c = 17.896(3) Å, and β = 114.58(1)°. The equatorial Rh–N bonds, 2.033—2.055 Å, are the shortest reported for a saturated hexa-amine complex of rhodium(III); axial bonds are only slightly longer (2.055 and 2.058 Å). This bond 'compression' is reflected in physical properties, with electronic maxima shifted to higher energy, and $E_{\frac{1}{2}}$ for Rh^{III}–Rh^{II} observed at a very negative potential. All complexes display irreversible one-electron reductions of the rhodium(III) centre in solution. Metal-centred reduction of the sexidentate complex with the aquated electron revealed a decay process which is rapid (k_d 4 × 10^4 s^{-1}), consistent with the voltammetric observations.

In a previous paper[1] we reported the synthesis and *X*-ray crystal structure determination of the sexidentate ligand 6,13-diamino-6,13-dimethyl-1,4,8,11-tetra-azacyclotetradecane (L^1) as its cobalt(III) complex. This complex displayed extreme electronic properties, *i.e.* high-energy electronic maxima and an exceptionally negative redox couple, as a result of short Co–N bonds. It is apparent that co-ordination of the pendant primary amines in the axial sites of the co-ordination sphere, in conjunction with binding of the secondary amines of the macrocycle, enforces an equatorial metal–nitrogen bond compression. It was of interest to see if the same bond compression occurred with the larger rhodium(III) ion, while retaining the same low-spin d^6 electronic configuration as in the cobalt(III) case.

Although L^1 may complex in a sexidentate manner, quinque- and quadri-dentate co-ordination of L^1 to cobalt(III) was also observed,[1] with both examples arising from protonation of one or both pendant primary amine groups, which precludes co-ordination of the nitrogens in the axial sites of the metal [(**1**), (**2**), and (**3**)]. All cobalt(III) complexes possessed a mirror-plane symmetry element bisecting the metal and both primary amine groups. The ligand may also 'fold' to give a *cis*-type configuration around a metal [(**4**) and (**5**)]. Inspection of molecular models clearly shows that the folded geometry forbids co-ordination of both primary amine groups simultaneously, thus only quinque- or quadri-dentate co-ordination of L^1 is feasible in the folded case.

In this paper, variable co-ordination of L^1 to rhodium(III) is examined. As well as a discussion of the spectroscopic and electrochemical properties of these compounds, the *X*-ray crystal structure of the sexidentate complex is reported.



L^1

Experimental

Syntheses.—The ligand 6,13-diamino-6,13-dimethyl-1,4,8,11-tetra-azacyclotetradecane (L^1) was prepared as previously described.[1]

trans-*Dichloro*(6,13-*diammonio*-6,13-*dimethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*rhodium*(III) *perchlorate trihydrate, trans*-$[Rh(H_2L^1)Cl_2][ClO_4]_3{\cdot}3H_2O$. A solution of rhodium trichloride trihydrate (0.75 g) in water (150 cm^3) was heated to 80 °C. A separate solution of $L^1{\cdot}6HCl$ (1.5 g) in water (150 cm^3) was neutralized with dilute aqueous sodium hydroxide and added dropwise to the hot rhodium(III) solution with stirring. Heating was continued for 12 h. The mixture was then diluted to *ca.* 1 dm^3 and sorbed onto a column (20 × 4 cm) of Dowex-H^+ 50 × 2 cation-exchange resin. The eluate was monitored by its u.v. absorbance at 300 nm. Washing with 1 mol dm^{-3} aqueous HCl removed uncomplexed species which were discarded. The desired product was then eluted with 3 mol dm^{-3} acid. The eluate was evaporated to *ca.* 20 cm^3 and perchloric acid (3 cm^3, 5 mol dm^{-3}) was added to induce crystallization. On standing, yellow crystals formed which were collected, washed with ethanol and diethyl ether, then dried in a vacuum desiccator (0.1 g, 5%) (Found: C, 18.55, H, 4.8; N, 10.75. $C_{12}H_{38}Cl_5N_6O_{15}Rh$ requires C, 18.3; H, 4.6; N, 10.7%). Electronic spectrum (water): $\lambda_{max.}$ 401 (ε 83) and 241 nm (ε 2 200 dm^3 mol^{-1} cm^{-1}). N.m.r. spectra (D_2O): ^1H, δ 1.48 (s, 6 H) and 3.1 (m, 16 H); ^{13}C, δ 20.8, 54.6, 56.6, and 58.3 p.p.m.

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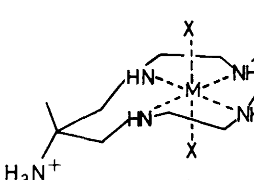
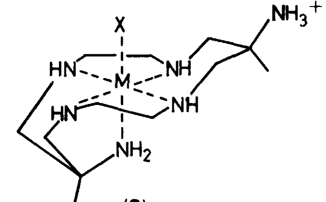
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



(1)



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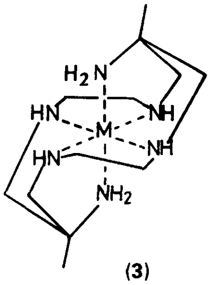

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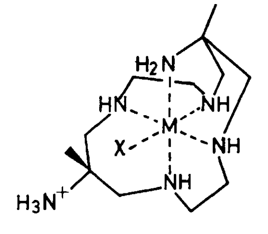

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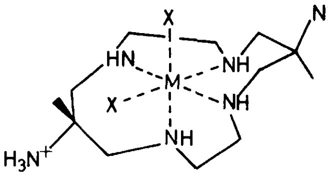

(5)

cis-(6-*Amino*-13-*ammonio*-6,13-*dimethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*chlororhodium*(III) *perchlorate dihydrate*, *cis*-$[Rh(HL^1)Cl][ClO_4]_3{\cdot}2H_2O$. In the above synthesis the band following the above compound was eluted (3 mol dm^{-3} aqueous HCl) then evaporated to *ca.* 50 cm^3. Perchloric acid (5 cm^3, 5 mol dm^{-3}) was added and precipitation of the pale yellow product occurred on standing. The crystals were collected, washed with ethanol and diethyl ether, then dried in a vacuum desiccator (0.8 g, 40%) (Found: C, 19.8; H, 4.9; N, 11.45. $C_{12}H_{35}Cl_4N_6O_{14}Rh$ requires C, 19.7; H, 4.8; N, 11.5%). Electronic spectrum (water): $\lambda_{max.}$ 342 (ε 270), 294 (ε 410), and 281 nm (ε 410 dm^3 mol^{-1} cm^{-1}). N.m.r. spectra (D_2O): ^1H, δ 1.37 (s, 3 H), 1.69 (s, 3 H), 3.1 (m, 8 H), and 3.5 (m, 8 H); ^{13}C, δ 21.0, 25.9, 54.0, 55.2, 55.9, 56.3, 57.1, 58.4, 65.3, and 69.8 p.p.m.

(6,13-*Diamino*-6,13-*dimethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*rhodium*(III) *perchlorate*, $[RhL^1][ClO_4]_3$. To a solution of *cis*-$[Rh(HL^1)Cl][ClO_4]_3$ (0.2 g) in water (100 cm^3) was added dilute aqueous NaOH solution until a pH of 10 was reached. This solution was boiled under reflux for 24 h. Evaporation of this solution to *ca.* 40 cm^3, followed by addition of perchloric acid (1 cm^3, 5 mol dm^{-3}), afforded, upon standing, colourless crystals suitable for *X*-ray study (0.15 g, 82%) (Found: C, 21.6; H, 4.6; N, 12.45. $C_{12}H_{30}Cl_3N_6O_{12}Rh$ requires C, 21.85; H, 4.6; N, 12.75%). Electronic spectrum (water): $\lambda_{max.}$ 289 (ε 180) and 243 nm (ε 180 dm^3 mol^{-1} cm^{-1}). N.m.r. spectra (D_2O): ^1H, δ 1.36 (s, 6 H), 2.88, 3.51 (q, 8 H), and 2.96, 3.54 (q, 8 H); ^{13}C δ 20.1, 55.0, 61.2, and 66.7 p.p.m.

Physical Methods.—Electronic spectra were recorded on an Hitachi 150-20 spectrophotometer. Nuclear magnetic resonance spectra were recorded using a JEOL FX90Q Fourier-transform spectrometer employing sodium trimethylsilylpropionate and 1,4-dioxane as internal references for ^1H and ^{13}C spectra respectively, although resonances are cited *versus* tetramethylsilane. Infrared spectra of compounds, dispersed in potassium bromide discs, were measured on a Nicolet MX-1 FT-IR spectrometer. Cyclic voltammetry was performed with a BAS CV-27 controller employing a glassy carbon working electrode, silver–silver chloride reference electrode, and platinum counter electrode. All solutions contained 0.1 mol dm^{-3} $NaClO_4$ and were purged with nitrogen prior to measurement. D.c. polarography was conducted on an Amel Model 457 analyser in conjunction with a PAR model 303 dropping mercury electrode and counter and reference electrodes as above.

Pulse radiolysis experiments were performed with a van de Graaff electron accelerator that delivered electron pulses (1 μs) at *ca.* 1 MeV (eV = 1.60×10^{-19} J) through the thin wall of a cell (optical path 1 cm), as previously described.[2] Dosimetry was performed with an aerated solution of KSCN. A dose of approximately 100 Gy was observed. Experiments involving the aquated electron (e_{aq}) were conducted with 10^{-4} mol dm^{-3} aqueous solutions of complex with 0.1 mol dm^{-3} Bu^tOH added to scavenge OH radicals. Solutions were also purged with nitrogen before measurement. The formation rate constant was measured by monitoring the decay kinetics of e_{aq} (at 580 nm) for several concentrations of complex. The absorbance spectrum was constructed from averaged sets of optical density changes measured immediately after the electron pulse at 5—20 nm increments between 250 and 600 nm. The first-order decay constant of the transient was determined by a least-squares treatment of several averaged traces.

Structure Determination.—A unique data set was measured for $[RhL^1][ClO_4]_3$ at 294 K. Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4-F diffractometer. Data were collected to $2\theta_{max.} = 50°$, with monochromatic Mo-K_α radiation, $\lambda = 0.710\,69$ Å, a graphite monochromator, and the ω—θ scan mode. 4 626 Independent reflections were obtained, 2 864 with $I > 2.5\sigma(I)$ being considered observed and used for solution of the structure. Data were reduced and Lorentz, polarization, decomposition, and absorption corrections were applied using the Enraf-Nonius structure determination package. The structure was solved by heavy-atom methods and refined by full-matrix least-squares analysis with SHELX 76.[3] Anisotropic thermal parameters were refined for non-hydrogen atoms; $(x, y, z)_H$ were included and constrained at estimated values with group isotropic thermal parameters. The minor contributors to the disorder of the oxygen atoms of one perchlorate anion were refined with common isotropic thermal parameters. Residuals of $|F|$ at convergence are conventional $R = 0.036$, $R' = 0.045$, $w = g/[\sigma^2(F_o) + kF_o^2]$ where g and k are 1.38 and 5.1×10^{-4}. Scattering factors and anomalous dispersion corrections for Rh were taken from ref. 4, and for all other atoms the values supplied in SHELX 76 were used. Absorption correction was by numerical integration.[5] Non-hydrogen atom co-ordinates are listed in Table 1. The atomic nomenclature is defined in the Figure, drawn with ORTEP.[6] A list of non-hydrogen interatomic distances and angles appears in Table 2.

Additional material available from The Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Crystal data. $[RhL^1][ClO_4]_3$, $C_{12}H_{30}Cl_3N_6O_{12}Rh$, M 659.67, monoclinic, space group $P2_1/c$, $a = 16.700(3)$, $b = 8.776(2)$, $c = 17.896(3)$ Å, $\beta = 114.58(1)°$, $U = 2\,385$ Å^3, $D_c = 1.837$ g cm^{-3}, $F(000) = 1\,332$, $Z = 4$, μ_{Mo} 10.6 cm^{-1}, $A^*_{max.,\,min.}$ 0.76, 0.51, range of hkl -18 to 18, 0—10, 0—19, merging $R = 0.02$.

Results and Discussion

Reactions of rhodium(III) with L^1 in aqueous solution yielded

Table 1. Positional parameters (× 10^4) for $[RhL^1](ClO_4)_3$

Atom	*x*	*y*	*z*
Rh(1)	0	0	0
N(11)	862(2)	1 133(4)	1 014(2)
N(12)	754(2)	722(4)	−583(2)
N(13)	751(2)	−1 810(4)	644(2)
C(11)	1 225(4)	38(4)	1 724(3)
C(12)	797(3)	−1 500(5)	1 482(2)
C(13)	188(3)	1 501(6)	−1 351(3)
C(14)	1 518(5)	1 857(9)	762(4)
C(15)	1 458(5)	1 613(11)	10(3)
C(16)	1 303(3)	−2 745(6)	2 093(3)
Rh(2)	5 000	5 000	0
N(21)	5 140(2)	7 228(4)	−231(3)
N(22)	3 668(2)	5 398(5)	−465(2)
N(23)	4 887(2)	5 259(4)	1 095(2)
C(21)	4 398(4)	2 704(6)	788(3)
C(22)	4 101(3)	4 270(6)	933(3)
C(23)	3 362(3)	4 958(6)	186(3)
C(24)	4 223(4)	−2 896(7)	4 375(6)
C(25)	3 535(4)	−2 050(8)	4 283(5)
C(26)	3 828(3)	4 184(7)	1 649(3)
Cl(1)	822(1)	8 800(1)	3 972(1)
O(11)	1 227(5)	9 871(5)	3 643(4)
O(12)	138(4)	−8 020(10)	3 324(3)
O(13)	500(7)	9 451(6)	4 516(4)
O(14)	1 446(3)	7 630(6)	4 383(3)
O(11′)	1 466(20)	8 959(37)	4 746(18)
O(12′)	577(26)	9 950(32)	3 309(22)
O(13′)	97(24)	9 163(42)	4 058(22)
O(14′)	729(25)	7 370(35)	3 738(23)
Cl(2)	3 617(1)	−1 183(2)	1 664(1)
O(21)	2 848(8)	−1 733(18)	1 073(7)
O(22)	3 582(8)	434(11)	1 772(10)
O(23)	3 802(8)	−1 780(15)	2 429(5)
O(24)	4 312(5)	−1 438(13)	1 406(7)
O(21′)	3 432(19)	−439(23)	942(14)
O(22′)	3 604(14)	−342(26)	2 283(11)
O(23′)	4 292(8)	−2 344(17)	1 940(10)
O(24′)	2 802(17)	−2 116(31)	1 413(19)
Cl(3)	2 764(1)	3 398(2)	3 339(1)
O(31)	2 337(7)	3 769(15)	2 531(5)
O(32)	2 552(8)	1 938(11)	3 434(8)
O(33)	3 730(5)	3 520(11)	3 619(5)
O(34)	2 510(11)	4 465(17)	3 823(9)
O(31′)	3 220(19)	2 078(37)	3 345(15)
O(32′)	1 823(13)	3 121(30)	2 968(21)
O(33′)	2 869(16)	4 617(18)	2 909(14)
O(34′)	2 913(26)	3 639(33)	4 096(15)

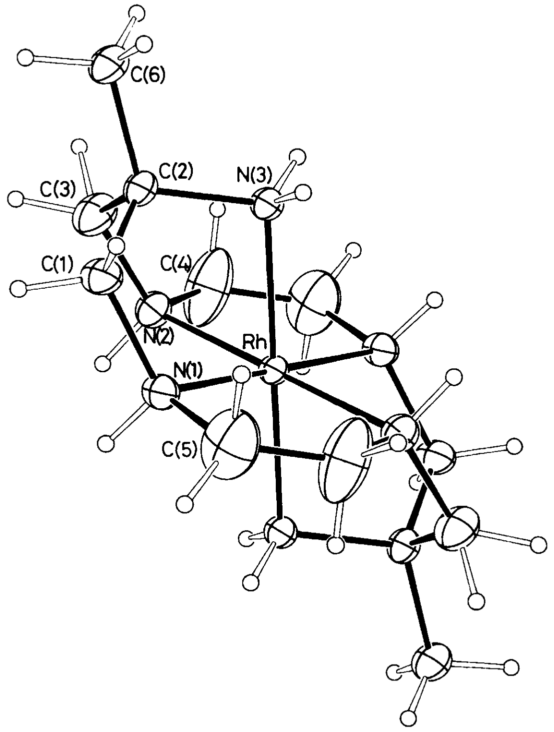

Figure. ORTEP drawing of the cation $[RhL^1]^{3+}$

complexes in a 1:1 ratio of metal to ligand. Of the five possible modes of co-ordination of L^1 to a metal ion preferring octahedral co-ordination with L^1 acting as at least a quadridentate ligand, we observed three. The symmetry of each complex was readily determined from its proton-decoupled ^{13}C n.m.r. spectrum. The ions *trans*-$[Rh(H_2L^1)Cl_2]^{3+}$ and $[RhL^1]^{3+}$ both possess C_{2h} symmetry about the metal centre. Consequently, there are only four types of magnetically distinct carbon atoms. The four carbons comprising the two ethylenediamine moieties of the ligand are equivalent, as are the four remaining methylenes situated in the two six-membered rings. The two pendant methyl groups are equivalent, as are the two tertiary carbons. The spectrum of the *cis*-$[Rh(HL^1)Cl]^{3+}$, however, displayed ten peaks; the C_1 symmetry of the ion renders all twelve carbons magnetically inequivalent, but accidental degeneracies prevent the observation of all resonances separately. The higher-symmetry *trans*-$[Rh(HL^1)Cl]^{3+}$, not isolated here, would yield a maximum of eight resonances in its proton-decoupled ^{13}C n.m.r. spectrum, a result of each methylene carbon having a magnetically equivalent partner reflected in the mirror plane bisecting the metal and both tertiary carbons. The i.r. spectra of the isolated complexes confirmed these assignments, with the higher-symmetry complexes displaying single peaks at 3 250 cm^{-1}, corresponding to N–H stretching in the secondary amine groups, whereas the low-symmetry complex displayed a doublet centred at 3 100 cm^{-1}.

The major product in the synthesis was the *cis*-$[Rh(H^1)Cl]^{3+}$ ion. While there does not appear to be a preference for *cis* as opposed to *trans* co-ordination of 1,4,8,11-tetra-azacyclotetradecane (cyclam) to rhodium(III),[7] the folded (*cis*) co-ordination of its substituted analogue L^1 to rhodium(III), a larger ion than cobalt(III), seems to be preferred, at least on a kinetic basis. Obviously the extra co-ordination of the pendant amine has an influence on the *cis*/*trans* ratio of products isolated. The synthesis of $[RhL^1]^{3+}$ from *cis*-$[Rh(HL^1)Cl]^{3+}$ involves a *cis* to *trans* isomerization of the cyclam core of the ligand. This has only previously been observed in sterically crowded systems, where two large *cis*-iodo ligands were believed to be the cause of *cis* to *trans* isomerization of the *cis*-$[Rh(cyclam)I_2]^+$ ion.[7] Clearly the basic conditions employed in the synthesis of $[RhL^1]^{3+}$ promote hydrolysis of the chloro ligand and permit deprotonation of secondary amine sites, allowing both rearrangement and six-co-ordination of L^1.

Electronic spectra of all the complexes were typical of rhodium(III) in its low-spin d^6 configuration. The $[RhL^1]^{3+}$ ion displayed maxima at 289 and 243 nm corresponding to transitions (from the $^1A_{1g}$ ground state) to the $^1T_{1g}$ and $^1T_{2g}$ states respectively. The energies of these transitions are higher than those of the respective transitions reported for all other hexa-amine rhodium(III) ions. A comparison of the physical

Table 2. Bond lengths (Å) and angles (°) for $[RhL^1][ClO_4]_3$

N(11)–Rh(1)	2.045(3)	N(21)–Rh(2)	2.033(4)	O(11)–Cl(1)	1.421(7)	O(11′)–Cl(1)	1.362(25)
N(12)–Rh(1)	2.042(4)	N(22)–Rh(2)	2.055(3)	O(12)–Cl(1)	1.419(6)	O(12′)–Cl(1)	1.480(34)
N(13)–Rh(1)	2.055(3)	N(23)–Rh(2)	2.058(4)	O(13)–Cl(1)	1.414(10)	O(13′)–Cl(1)	1.321(44)
C(11)–N(11)	1.505(5)	C(21)–N(21)	1.492(6)	O(14)–Cl(1)	1.430(5)	O(14′)–Cl(1)	1.311(32)
C(14)–N(11)	1.489(10)	C(24)–N(21)	1.514(9)	O(21)–Cl(2)	1.368(11)	O(21′)–Cl(2)	1.362(24)
C(13)–N(12)	1.474(5)	C(23)–N(22)	1.505(8)	O(22)–Cl(2)	1.437(10)	O(22′)–Cl(2)	1.338(22)
C(15)–N(12)	1.443(8)	C(25)–N(22)	1.508(8)	O(23)–Cl(2)	1.377(10)	O(23′)–Cl(2)	1.446(14)
C(12)–N(13)	1.494(6)	C(22)–N(23)	1.498(6)	O(24)–Cl(2)	1.434(10)	O(24′)–Cl(2)	1.489(27)
C(12)–C(11)	1.505(8)	C(22)–C(21)	1.519(8)	O(31)–Cl(3)	1.360(8)	O(31′)–Cl(3)	1.384(33)
C(15)–C(14)	1.324(10)*	C(25)–C(24)	1.319(10)*	O(32)–Cl(3)	1.359(10)	O(32′)–Cl(3)	1.450(20)
C(16)–C(12)	1.528(6)	C(26)–C(22)	1.530(9)	O(33)–Cl(3)	1.480(8)	O(33′)–Cl(3)	1.371(22)
C(13)–C(12)	1.562(6)	C(23)–C(22)	1.517(6)	O(34)–Cl(3)	1.453(19)	O(34′)–Cl(3)	1.289(28)

N(12)–Rh(1)–N(11)	86.9(1)	N(22)–Rh(2)–N(21)	87.2(2)	C(12)–C(13)–N(12)	111.4(4)	C(22)–C(23)–N(22)	111.8(4)
N(13)–Rh(1)–N(11)	80.7(1)	N(23)–Rh(2)–N(21)	98.8(2)	C(16)–C(12)–N(13)	111.7(4)	C(26)–C(22)–N(23)	114.1(4)
N(13)–Rh(1)–N(12)	99.5(1)	N(23)–Rh(2)–N(22)	81.6(1)	C(16)–C(12)–C(11)	112.4(3)	C(26)–C(22)–C(21)	109.3(5)
C(11)–N(11)–Rh(1)	109.0(2)	C(21)–N(21)–Rh(2)	108.0(2)	C(15)–C(14)–N(11)	119.0(6)	C(25)–C(24)–N(21)	120.0(7)
C(14)–N(11)–Rh(1)	105.9(3)	C(24)–N(21)–Rh(2)	106.7(2)	C(14)–C(15)–N(12)	122.0(7)	C(24)–C(25)–N(22)	119.4(6)
C(14)–N(11)–C(11)	116.1(4)	C(24)–N(21)–C(21)	112.3(4)	C(13)–C(12)–C(11)	112.8(4)	C(23)–C(22)–C(21)	114.4(4)
N(11)–Rh(1)–N(11)	180.0	N(21)–Rh(2)–N(21)	180.0	C(16)–C(12)–C(13)	109.9(4)	C(26)–C(22)–C(23)	109.9(5)
C(13)–N(12)–Rh(1)	109.2(3)	C(23)–N(22)–Rh(2)	107.5(2)	O(12)–Cl(1)–O(11)	109.9(4)	O(13)–Cl(1)–O(11)	113.6(4)
C(15)–N(12)–Rh(1)	106.2(4)	C(25)–N(22)–Rh(2)	106.5(3)	O(13)–Cl(1)–O(12)	110.5(5)	O(14)–Cl(1)–O(11)	108.5(4)
C(15)–N(12)–C(13)	116.4(4)	C(25)–N(22)–C(23)	115.1(4)	O(14)–Cl(1)–O(12)	104.0(4)	O(14)–Cl(1)–O(13)	109.9(4)
N(12)–Rh(1)–N(12)	180.0	N(22)–Rh(2)–N(22)	180.0	O(22)–Cl(2)–O(21)	112.0(8)	O(23)–Cl(2)–O(21)	112.6(8)
C(12)–N(13)–Rh(1)	100.8(2)	C(22)–N(23)–Rh(2)	99.9(3)	O(23)–Cl(2)–O(22)	104.3(9)	O(24)–Cl(2)–O(21)	108.8(9)
N(13)–Rh(1)–N(13)	180.0	N(23)–Rh(2)–N(23)	180.0	O(24)–Cl(2)–O(22)	106.3(9)	O(24)–Cl(2)–O(23)	112.5(9)
C(12)–C(11)–N(11)	110.7(3)	C(22)–C(21)–N(21)	111.9(4)	O(32)–Cl(3)–O(31)	108.1(7)	O(33)–Cl(3)–O(31)	111.0(6)
C(11)–C(12)–N(13)	105.8(4)	C(21)–C(22)–N(23)	103.6(4)	O(33)–Cl(3)–O(32)	109.3(7)	O(34)–Cl(3)–O(31)	109.0(8)
C(13)–C(12)–N(13)	103.8(4)	C(23)–C(22)–N(23)	105.4(4)	O(34)–Cl(3)–O(32)	112.1(10)	O(34)–Cl(3)–O(33)	107.4(7)

* Bond length artificially reduced as a result of disorder (see text).

Table 3. Physical properties of selected rhodium(III) hexa-amine complexes

Complex[a]	Electronic maxima (nm)	E (Rh^{III}–Rh^{II}) (V *vs.* Ag–AgCl)	Rh–N bond length (Å)	Ref.
$[Rh(NH_3)_6]^{3+}$	305, 255	−0.98	2.069	*b*
$[Rh(en)_3]^{3+}$	301, 255	−0.70	2.067, 2.056	11, *c*
$[RhL^2{}_3]^{3+}$	302, 255	—	2.075, 2.067	*d*
$[RhL^3]^{3+}$	299, 251	−1.40	—	*e*
$[RhL^1]^{3+}$	289, 243	−1.24	2.044, 2.056	This work

[a] L^2 = Cyclohexane-1,2-diamine; L^3 = 3,6,10,13,16,19-hexa-azabicyclo[6.6.6]eicosane-1,8-diamine. [b] N. J. Curtis, G. A. Lawrance, and A. M. Sargeson, *Aust. J. Chem.*, 1983, **36**, 1327; J. K. Beattie and T. W. Hambley, unpublished work. [c] C. K. Jørgensen, *Adv. Chem. Phys.*, 1963, **5**, 33; P. A. Lay, Doctoral Dissertation, Australian National University, 1981. [d] F. Galsbøl, P. Steenbøl, and B. S. Sørensen, *Acta Chem. Scand.*, 1972, **26**, 3405; H. Miyame, S. Sato, and Y. Saito, *Acta Crystallogr., Sect. B*, 1977, **33**, 3391. [e] J. M. Harrowfield, A. J. Herlt, P. A. Lay, A. M. Sargeson, A. M. Bond, W. A. Mulac, and J. C. Sullivan, *J. Am. Chem. Soc.*, 1983, **105**, 5503.

properties of some rhodium(III) hexa-amines is given in Table 3. The spectrum of *cis*-$[Rh(HL^1)Cl]^{3+}$ displayed three maxima at 342, 294, and 281 nm. The lower-energy pair arise as a result of a splitting of the $^1T_1$ state to a $^1A_2$ and ^1E pair under the influence of the low-symmetry ligand field. The spectrum of *trans*-$[Rh(H_2L^1)Cl_2]^{3+}$ displayed a broad band at 401 nm, the transiton to the $^1T_{1g}$ state broadened by the axial symmetry of the ion, whereas the second *d–d* transition was obscured by a charge-transfer band at 241 nm.

The structure of $[RhL^1][ClO_4]_3$ consists of two rhodium atoms located on centres of symmetry and three perchlorate anions at general sites. All perchlorates displayed some disorder in their oxygen atoms. The equatorial Rh–N bond lengths of 2.033, 2.042, 2.045, and 2.055 Å are exceptionally short, the shortest reported in a rhodium hexa-amine structure (Table 3). The axial Rh–N bonds, 2.055 and 2.058 Å, are slightly longer, an observation common to other octahedral complexes of L^1 and attributed to steric strain in the ligand.[1,8,9] There is also a considerable trigonal distortion in the complex. This is seen in the ideally square N–Rh–N angles, N(11)–Rh–N(13) 80.7° and N(12)–Rh–N(13) 99.5°. There is also strain in the ligand, especially in the ethylenediamine moieties. It is evident from the large thermal motion of atoms C(14) and C(15) perpendicular to the five-membered ring and the near planarity of this ring [θ = 2.8(8)°] that the refined geometry is in fact the average of two skew conformations. Attempts to locate individual sites for these atoms were unsuccessful. Comparison with the structures of the cobalt(III),[1] chromium(III),[8] and iron(III)[9] analogues shows that as the M–N bond length increases (Co–N, 1.94; Fe–N, 1.97; Rh–N, 2.04; Cr–N, 2.05 Å) this ring flattens and disorder of the ring becomes increasingly facile. This distortion is not general for chelating amines. For example, the N–C–C angles in $[Rh(en)_3]^{3+}$ and $[Cr(en)_3]^{3+}$ (en = ethylenediamine) are all approximately 109°, so large metal ions do not necessarily cause flattening of the five-membered chelate rings.[10,11] Thus the observed distortions in the L^1 complexes are indeed characteristic. It is apparent that the short metal–nitrogen bond lengths observed in all of the L^1 structures are the result of a minimization of intramolecular strain in the ligand. As can be seen from the series of structures, when the M–N bond lengths are increased the ligand undergoes considerable distortion. To counter this, the M–N bond lengths are minimized by the ligand so as to reduce strain in the ligand. The resultant short M–N bond lengths observed to date in all structures are consistent with this.

Electrochemistry of all rhodium(III) complexes identified irreversible Rh^{III}–Rh^{II} couples in each case. Aqueous d.c. polarography (scan rate 10 $mV\ s^{-1}$) of the *trans*-$[Rh(H_2L^1)Cl_2]^{3+}$ ion yielded an $E_{\frac{1}{2}}$ of -0.70 V (*versus* Ag–AgCl) and for *cis*-$[Rh(HL^1)Cl]^{3+}$ an $E_{\frac{1}{2}}$ of -1.15 V was obtained. The irreversible nature of these couples was determined by cyclic voltammetry where no anodic back wave was observed in either case (at scan rates up to 500 $mV\ s^{-1}$). Polarography of $[RhL^1]^{3+}$ yielded an $E_{\frac{1}{2}}$ of -1.24 V which was also found to be irreversible. Comparison with $E_{\frac{1}{2}}$ values of other hexa-amines is made in Table 3. Cyclic voltammetry of $[RhL^1]^{3+}$ in acetonitrile allowed the observation of two irreversible waves at -1.29 and -1.84 V. These may be assigned, from their relative wave heights, as being due to Rh^{III}–Rh^{II} and Rh^{II}–Rh^{0} couples. Pulse radiolysis of $[RhL^1]^{3+}$ allowed an investigation of the stability of the putative $[RhL^1]^{2+}$ ion. Reaction of $[RhL^1]^{3+}$ with e_{aq} generated a species (k_f 8×10^{10} $dm^3\ mol^{-1}\ s^{-1}$) displaying an intense maximum at 290 nm (ε 2 200 $dm^3\ mol^{-1}\ cm^{-1}$) which decayed (k_d 4×10^4 s^{-1}) to a shoulder at the same wavelength (ε 760 $dm^3\ mol^{-1}\ cm^{-1}$). The instability of the initially formed rhodium(II) monomer species is apparent. Whether the final product is still a rhodium(II) complex is not certain. Generally rhodium(II) is unstable in monomeric complexes and in this case both radiolytic and voltammetric measurements indicate that dissociation or significant rearrangement occurs on reduction to rhodium(II) rapidly (half-life $\ll$ 1 ms). This is not unreasonable, since the larger rhodium(II) ion would not be easily accommodated in the contracted co-ordination sphere imposed by the sexidentate ligand, this effect acting to reduce the stability of the lower-oxidation-state complex. We are proceeding with studies of L^1 complexed to other transition-metal ions.

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