# Co-ordination of a Macrocyclic Quadridentate Tertiary Amine Ligand in the *cis* Configuration: *X*-Ray Crystal Structure of *cis*-$[RuLCl_2]ClO_4$ (L = 1,4,7,10-tetramethyl-1,4,7,10-tetra-azacyclotridecane)*

**Chi-Ming Che, Wai-Tong Tang, Wing-Tak Wong, Hon-Wah Lam, and Ting-Fong Lai**
*Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong*

Reaction of $K_2[RuCl_5(H_2O)]$ with 1,4,7,10-tetramethyl-1,4,7,10-tetra-azacyclotridecane(L) in ethanol yielded *cis*-$[RuLCl_2]ClO_4$. The optical spectrum shows an intense $p_\pi(Cl) \longrightarrow d_\pi(Ru)$ charge-transfer transition at 378 nm. The *cis*-$[RuLCl_2]^+$ cation [space group $P2_1/n$, $a = 12.388(2)$, $b = 12.740(2)$, $c = 12.853(4)$ Å, $\beta = 96.68(2)°$, $Z = 4$; $R = 0.048$ for 1 897 observed Mo-$K_\alpha$ data] is distorted octahedral with two Ru–Cl bonds *cis* to each other. The measured Ru–Cl distances [2.406(3) and 2.370(4) Å] are unusually long for a ruthenium(III) system.

Since the first report on 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane by Barefield and Wagner[1] the co-ordination chemistry of macrocyclic tertiary amines has been an active area of research. This class of ligands, which are resistant towards oxidation and deprotonation upon co-ordination to a metal ion, has been found useful in stabilizing metal complexes in high and low oxidation states.[2] However, most of the reported tetra-azamacrocycles are mainly confined to those amines which co-ordinate to metal ions in the *trans* configuration. Since the presence of two *cis* vacant co-ordination sites is essential to a metal catalyst, we have initiated a programme aimed at the synthesis of *cis*-tetra-azametal complexes of macrocyclic tertiary amines.[3] In this contribution, the synthesis of 1,4,7,10-tetramethyl-1,4,7,10-tetra-azacyclotridecane (L) and the *X*-ray crystal structure determination of the ruthenium complex *cis*-$[RuLCl_2]ClO_4$ are described.

## Experimental

*Materials.*—Potassium aquapentachlororuthenate(III) $K_2[RuCl_5(H_2O)]$ was purchased from Johnson Matthey Chemicals Ltd. 1,4,7,10-Tetra-azacyclotridecane was prepared by the literature method.[4] All chemicals and solvents were of analytical grade.

*Physical Measurements and Instrumentation.*—N.m.r. spectra were run on a JOEL model FX 90Q (90 MHz) spectrometer. Chemical shifts (δ) were reported relative to tetramethylsilane. Conductivity measurements were obtained using a Radiometer model CDM2 conductivity meter with 0.1 mol $dm^{-3}$ KCl as calibrant.

*Ligand Synthesis.*—The ligand was synthesized by methylation of 1,4,7,10-tetra-azacyclotridecane. A mixture of the latter (5 g), formic acid (25 $cm^3$, 98—100%), and formaldehyde (25 $cm^3$, 37—41%) was refluxed at 90 °C with stirring for 24 h. The solution was cooled in an ice-bath. A saturated solution of sodium hydroxide was added with stirring until the solution became alkaline (pH 12). The resulting solution was extracted with chloroform and the organic extract collected and dried over anhydrous sodium sulphate. The organic solvent was rotatory evaporated to give a thick oil. Purification was carried out by distillation under reduced pressure (light colourless oil, b.p. ≈80 °C at 0.1 mmHg (*ca.* 13.3 Pa), yield ≈70%) (Found: C, 64.1; H, 12.5; N, 23.0. Calc. for $C_{13}H_{30}N_4$: C, 64.4; H, 12.5; N, 23.1%). $^1H$ N.m.r. in $CDCl_3$: δ 2.6—2.4 (m, 12 H), 2.23 (d, 12 H), and 1.8 (t, 2 H). I.r. spectrum: no absorption in the 3 000—3 500 $cm^{-1}$ region assignable to ν(N–H). Mass spectrum: parent molecular ion at *m*/*z* 242.

*cis*-$[RuLCl_2]ClO_4$.—An ethanolic solution of the ligand L (1.5 mmol in 200 $cm^3$) was added dropwise to a rigorously stirred ethanolic suspension of $K_2[RuCl_5(H_2O)]$ (0.5 g, 1.4 mmol) under reflux. The addition process took 3 h for completion and the mixture was further refluxed for 2 d, then filtered and evaporated to dryness. The yellow solid obtained was dissolved in hot HCl (2 mol $dm^{-3}$, 10 $cm^3$) and yellow *cis*-$[RuLCl_2]ClO_4$ was precipitated upon addition of excess of $NaClO_4$. It was recrystallized from either hot HCl (2 mol $dm^{-3}$, 60 °C) or $CH_3CN$–diethyl ether. Yield 0.2 g (45%) (Found: C, 30.5; H, 5.9; N, 10.8. Calc. for $[RuLCl_2]ClO_4$: C, 30.4; H, 5.8; N, 10.9%). U.v.–visible spectrum in acetonitrile: $\lambda_{max.}$ 378 nm ($\varepsilon_{max.}$ 2 100 $dm^3$ $mol^{-1}$ $cm^{-1}$).

X-*Ray Crystal Structure Determination of cis*-$[RuLCl_2]ClO_4$.—*X*-Ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda = 0.710\,73$ Å). The unit-cell dimensions were obtained from a least-squares fit of 25 reflections in the range of $19 < 2\theta < 27°$. Three check reflections monitored every 2 h showed no significant loss in intensity. The intensity data were corrected for Lorentz, polarization, and absorption effects. The empirical absorption correction was based on an azimuthal (ψ) scan of nine reflections with $80 < \chi < 90°$. The atomic scattering factors were taken from ref. 5. All computations were performed on a MICROVAX II computer using the Enraf-Nonius SDP programs.[6]

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically and allowed to ride on their parent carbon atoms with fixed isotropic thermal parameters. The thermal parameters for some of the carbon atoms in the ligand and for the oxygen atoms were rather large as a result of disorder. However, an attempt to refine the structure with two different conformations for the ligand failed to resolve the disorder.

Crystal and structure determination data and final agreement factors are given in Table 1, atomic co-ordinates of non-hydrogen atoms in Table 2, selected bond distances and angles in Table 3.

---

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

**Table 1.** Crystal data and summary of data collection and refinement for *cis*-$[RuLCl_2]ClO_4$

| | |
|---|---|
| $M$ | 513.84 |
| Space group | $P2_1/n$ |
| $a$/Å | 12.388(2) |
| $b$/Å | 12.740(2) |
| $c$/Å | 12.853(4) |
| $\beta$/° | 96.68(2) |
| $U$/Å$^3$ | 2 015(1) |
| $Z$ | 4 |
| $F$(000) | 1 052 |
| $D_c$/g cm$^{-3}$ | 1.694 |
| Crystal size/mm | 0.07 × 0.14 × 0.16 |
| $\mu$(Mo-$K_\alpha$)/cm$^{-1}$ | 11.9 |
| Scan type, speed/° min$^{-1}$ | $\omega$—2$\theta$, 1.2—5.5 |
| Scan width/° | 0.75 + 0.34tan$\theta$ |
| $T$/K | 295 ± 1 |
| Collection range | $2\theta_{max.} = 45°$, $\pm h\ k \pm l$ |
| Transmission factor | 0.975—0.999 |
| No. of reflections measured | 4 803 |
| No. of independent reflections | 2 774 |
| No. of reflections in calculations, $m$ | 1 897 [$F_o > 3\delta(F_o)$] |
| No. of parameters refined, $p$ | 226 |
| $R$[a] | 0.048 |
| $R'$[b] | 0.058 |
| $S$[c] | 1.79 |
| Residual extrema in final difference map/e Å$^{-3}$ | +0.73 to −0.44 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, with $w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$. [c] $S = [\Sigma w(|F_o| - |F_c|)^2/(m - p)]^{\frac{1}{2}}$.

**Table 2.** Fractional atomic co-ordinates for non-hydrogen atoms in $[RuLCl_2]ClO_4$ with estimated standard deviations in parentheses

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Ru | 0.236 92(5) | 0.313 64(5) | 0.052 41(5) |
| Cl(1) | 0.371 9(2) | 0.378 0(2) | 0.187 0(2) |
| Cl(2) | 0.115 0(3) | 0.420 9(3) | 0.133 9(3) |
| N(1) | 0.266 4(7) | 0.432 1(6) | −0.059 3(6) |
| N(2) | 0.109 6(6) | 0.262 0(6) | −0.058 6(5) |
| N(3) | 0.201 5(6) | 0.176 5(6) | 0.136 1(5) |
| N(4) | 0.373 4(6) | 0.225 1(6) | −0.016 7(6) |
| C(1) | 0.427(1) | 0.161 3(9) | 0.074(1) |
| C(2) | 0.356(2) | 0.083(1) | 0.106(1) |
| C(3) | 0.286(1) | 0.109(1) | 0.175(1) |
| C(4) | 0.154(2) | 0.202(1) | 0.234(1) |
| C(5) | 0.109 6(8) | 0.120 0(8) | 0.068(1) |
| C(6) | 0.107 7(9) | 0.148 3(8) | −0.048 2(9) |
| C(7) | −0.003 8(8) | 0.301 1(9) | −0.045 8(9) |
| C(8) | 0.138 8(9) | 0.303(1) | −0.158 8(7) |
| C(9) | 0.175(1) | 0.420(1) | −0.145 1(8) |
| C(10) | 0.281(2) | 0.534(1) | −0.017(1) |
| C(11) | 0.378(1) | 0.401(1) | −0.107 9(8) |
| C(12) | 0.446 9(8) | 0.314(1) | −0.037 1(9) |
| C(13) | 0.364(1) | 0.155 8(9) | −0.111 2(8) |
| Cl | 0.265 5(2) | 0.337 3(2) | 0.574 9(2) |
| O(1) | 0.302(1) | 0.258 3(7) | 0.638 8(6) |
| O(2) | 0.248(1) | 0.308(1) | 0.476 2(6) |
| O(3) | 0.181 1(8) | 0.395(1) | 0.605 9(8) |
| O(4) | 0.341 4(9) | 0.411(1) | 0.584(1) |

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

## Results and Discussion

The ligand was prepared by N-methylation of 1,4,7,10-tetraazacyclotridecane, as for other macrocyclic tertiary amines.[1,7]

**Table 3.** Selected bond distances (Å) and angles (°) in *cis*-$[RuLCl_2]^+$

| | | | |
|---|---|---|---|
| Ru–Cl(1) | 2.406(3) | Ru–N(2) | 2.105(7) |
| Ru–Cl(2) | 2.370(4) | Ru–N(3) | 2.124(7) |
| Ru–N(1) | 2.143(8) | Ru–N(4) | 2.296(8) |
| Cl(1)–Ru–Cl(2) | 84.9(1) | Cl(2)–Ru–N(3) | 94.1(2) |
| Cl(1)–Ru–N(1) | 94.8(2) | N(1)–Ru–N(2) | 86.5(3) |
| Cl(1)–Ru–N(3) | 94.8(2) | N(1)–Ru–N(4) | 84.1(4) |
| Cl(1)–Ru–N(4) | 87.9(2) | N(2)–Ru–N(3) | 84.5(3) |
| Cl(2)–Ru–N(1) | 93.3(3) | N(2)–Ru–N(4) | 96.4(3) |
| Cl(2)–Ru–N(2) | 90.9(2) | N(3)–Ru–N(4) | 89.9(3) |

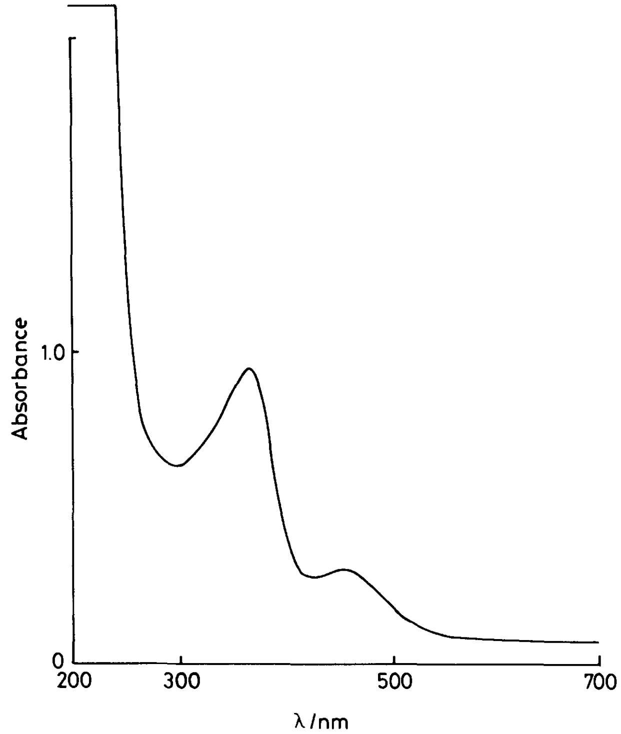

**Figure 1.** U.v.–visible spectrum of *cis*-$[RuLCl_2]^+$ in acetonitrile

Unlike 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane which is crystalline solid,[1] 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclotridecane (L) is a colourless oil at room temperature, and this is probably due to its unsymmetrical nature. As expected, its i.r. spectrum shows the absence of a ν(N–H) stretch in the region 3 500—3 000 cm$^{-1}$. Previous work showed that the reaction of $K_2[RuCl_5(H_2O)]$ with macrocyclic quadridentate amines in refluxing ethanol yielded *trans*-[Ru(amine)$Cl_2]^+$.[8] In this work, insertion of ruthenium into the ligand is also brought about by a similar method but unlike previous cases only the *cis* isomer was obtained. This is due to the small ring size of the ligand, which would be too small to accommodate the ruthenium atom for an equatorial arrangement of four N lone pairs. In fact, the use of a quadridentate amine ligand having a small cavity size for the synthesis of a *cis*-dichlororuthenium(III) complex has recently been described.[9]

Figure 1 shows the u.v.–visible spectrum of *cis*-$[RuLCl_2]^+$ in acetonitrile, which is virtually identical to that for the analogous complex *cis*-dichloro(*N*,*N*,*N*′,*N*′,3,6-hexamethyl-3,6-diazaoctane-1,8-diamine)ruthenium(III) (**1**).[9] Once again only one intense ligand-to-metal charge-transfer (l.m.c.t.) transition [$p_\pi(Cl) \longrightarrow d_\pi(Ru)$] at 378 nm is observed, in contrast to the report by Verdonck and Vanquickenborne[10] who suggested two l.m.c.t. transitions with similar intensities for the *cis*-

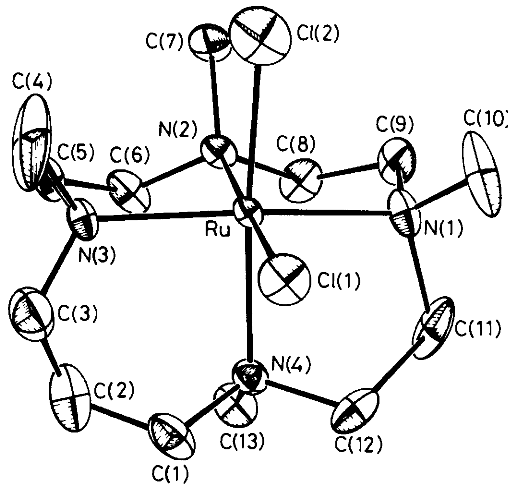

**Figure 2.** ORTEP drawing and atomic numbering scheme for *cis*-$[RuLCl_2]^+$ cation (15% probability ellipsoids).

dichlorotetra-amineruthenium(III) system. The structure of *cis*-$[RuLCl_2]ClO_4$ has been established by *X*-ray crystallography. Figure 2 shows an ORTEP plot of the *cis*-$[RuLCl_2]^+$ cation with the atomic numbering scheme. The most interesting structural feature is the *cis*-configuration of the metal complex. As for complex (**1**), the co-ordination geometry about the ruthenium atom is distorted octahedral with two chloride ligands *cis* to each other. The ligand is in a folded conformation with N(2)–Ru–N(4) being 96.4(3)°. The four N-methyl groups adopt the 'three up one down' configuration in which three are *syn* to one chloro group [Cl(2)]. The Ru–N(1), Ru–N(2), and Ru–N(3) distances of 2.105—2.143(8) Å are normal and comparable to those values found in other *cis*- and *trans*-dichlororuthenium(III) complexes of quadridentate amines.[9,11,12] However, the Ru–N(4) distance of 2.296(8) Å is very long; it is *ca.* 0.1 Å longer than the other Ru–N bonds. This may be due to the steric constraint of the ligand.

An important structural feature of *cis*-$[RuLCl_2]^+$ is also the long Ru–Cl bonds. The measured distances of 2.406 and 2.370 Å are even 0.06 Å longer than that for (**1**),[9] which is isostructural and isoelectronic. Therefore one would expect that the chloro groups in *cis*-$[RuLCl_2]^+$ should be very labile, which is indeed the case. The molar conductivity of the complex in water is about 300 S cm$^2$ mol$^{-1}$, indicating rapid hydrolysis.

In conclusion, we find that the 1,4,7,10-tetramethyl-1,4,7,10-tetra-azacyclotridecane ligand, because of its small ring size, co-ordinates to ruthenium in the *cis* configuration. The presence of two vacant co-ordination sites should facilitate substrate binding, which is important in homogeneous catalysis. The synthesis of high-valent ruthenium oxo complexes of this ligand is currently under investigation.

## Acknowledgements

We acknowledge financial support from the University of Hong Kong, the University and Polytechnic Granting Committee, and the Croucher Foundation. H-W. L. and W-T. W. acknowledge the receipt of Croucher Studentships, administered by the Croucher Foundation.

## References

1 E. K. Barefield and F. Wagner, *Inorg. Chem.*, 1973, **12**, 2435.
2 See, for example, C. M. Che, T. F. Lai, and K. Y. Wong, *Inorg. Chem.*, 1972, **26**, 2289; A. J. Blake, R. O. Gould, T. I. Hyde, and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1987, 431; A. J. Blake, T. I. Hyde, R. S. E. Smith, and M. Schröder, *ibid.*, 1986, 334; M. Schröder, *Pure Appl. Chem.*, 1988, **60**, 517; N. Jubran, G. Ginzburg, H. Cohen, Y. Koresh, and D. Meyerstein, *Inorg. Chem.*, 1985, **24**, 251; N. Jubran, H. Cohen, Y. Koresh, and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 1984, 1683.
3 See also, G. A. Kalligeros and E. L. Blinn, *Inorg. Chem.*, 1972, **11**, 1145.
4 Y. Hung, *Inorg. Synth.*, 1980, **20**, 106.
5 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
6 Enraf-Nonius Structure Determination Packages, SDP, Enraf-Nonius, Delft, 1985.
7 See, for example, N. W. Alcock, L. H. Curzon, P. Moore, and C. Pierpoint, *J. Chem. Soc., Dalton Trans.*, 1984, 605.
8 C. K. Poon and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1984, 495; C. M. Che, S. S. Kwong, and C. K. Poon, *Inorg. Chem.*, 1985, **24**, 1601.
9 C. M. Che, W-T. Tang, M. H-W. Lam, and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1988, 2885.
10 E. Verdonck and L. G. Vanguickenborne, *Inorg. Chem.*, 1974, **13**, 762.
11 C. M. Che, S. S. Kwong, C. K. Poon, T. F. Lai, and T. C. W. Mak, *Inorg. Chem.*, 1985, **24**, 1359.
12 D. D. Walker and H. Taube, *Inorg. Chem.*, 1981, **20**, 2828.

*Received* 15*th September* 1989; *Paper* 9/05207K