Studies on Ruthenium(II) Macrocyclic Amine Complexes. Synthesis and *X*-Ray Structure of the (*R*,*S*,*R*,*R*) Isomer of *trans*-[Ru^{II}(L)(N$_3$)(NCMe)]PF$_6$ (L = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)†

Chi-Ming Che,* Ting-Fong Lai, and Keung Lau
Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong
Thomas C. W. Mak*
Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

The reaction between K$_2$[RuCl$_5$(NO)] and L (L = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) in ethanol at reflux gave an intermediate product which, on treatment with N$_2$H$_4$·H$_2$O in acetonitrile yielded *trans*-[Ru^{II}(L)(N$_3$)(NCMe)]PF$_6$. This azide complex crystallizes in space group $P2_1/n$, with a = 14.775(3), b = 18.083(2), c = 18.167(2) Å, β = 90.26(1)°, and Z = 8. One of the two independent cations has a disordered ligand L, and the methyl groups in L of the ordered cation adopt a 'three-up, one-down' (*R*,*S*,*R*,*R*) configuration. The measured Ru–N(acetonitrile) bond lengths, 1.976(7) and 2.003(7) Å, are significantly shorter than the corresponding distance of 2.149(6) Å in the (*R*,*S*,*R*,*R*) isomer of *trans*-[Ru(L)O(NCMe)][PF$_6$]$_2$, attesting to a greater *trans* influence of the oxo ligand as compared to the azide ligand.

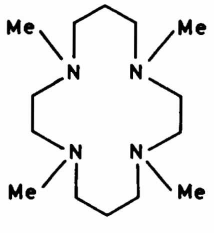
The chemistry of ruthenium complexes of the macrocyclic quadridentate amine, 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (L), and its analogues has recently been extensively explored in our laboratories. In addition to studies concerned with the high-valent oxo chemistry of these Ru–L systems,[1] their co-ordination by small molecules such as CO, NO$^+$, N$_2$, and R–C≡N has also been investigated. Despite the extensive work by Taube[2] on ruthenium(II) amine complexes containing π-acid ligands, as far as we are aware, analogous studies on ruthenium(II) macrocyclic amine complexes are rare. We describe here the first report on the preparation and structural characterization of a macrocyclic amine complex of ruthenium(II) containing axial azide and acetonitrile ligands. In this (*R*,*S*,*R*,*R*) isomer of *trans*-[Ru^{II}(L)(N$_3$)(NCMe)]PF$_6$ (**1**), the presence of strong π back-bonding is reflected by the low-frequency ν(C≡N) stretch at 2 200 cm^{-1} and the short Ru–N(acetonitrile) distances of 1.976(7) and 2.003(7) Å.

Experimental

Materials.—K$_2$[RuCl$_5$(NO)] and 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (L) were prepared by published methods.[2,3] All other reagents used were of analytical grade.

trans-[Ru^{II}(L)(N$_3$)(NCMe)]PF$_6$. An ethanolic solution of L (0.5 g in 200 cm^3) was added dropwise to a suspension of K$_2$[RuCl$_5$(NO)] in absolute ethanol (0.5 g in 100 cm^3) under reflux with vigorous stirring. This process took *ca.* 4 h and the reaction mixture was heated at reflux overnight (*ca.* 16—20 h). The solution was filtered while hot and the filtrate taken to dryness (rotary evaporator). The residue was dissolved in HCl (2 mol dm^{-3}, 20 cm^3) and filtered into a saturated solution of NaPF$_6$ (5 cm^3). A brownish yellow precipitate was collected and dried under vacuum overnight at room temperature.

The crude product, in a minimum amount of MeCN, was treated with hydrazine hydrate (2 cm^3) and the resulting solution stirred overnight. A yellowish orange solid was deposited. This was purified by slow diffusion of diethyl ether into an acetonitrile solution of the crude solid (Found: C, 32.7; H, 6.0; N, 19.5; P, 5.7. Calc. for C$_{16}$H$_{35}$F$_6$N$_8$PRu: C, 32.8; H, 6.0; N, 19.5; P, 5.3%). I.r. (Nujol mull): ν(C≡N) at 2 200 cm^{-1} (sharp and strong); ν(N$_3$) at *ca.* 2 030 cm^{-1} (broad and strong).



L

X-*Ray Structural Determination of the* (R,S,R,R) *Isomer of trans*-[Ru(L)(N$_3$)(NCMe)]PF$_6$ (**1**).—*Crystal data.* C$_{16}$H$_{35}$F$_6$N$_8$PRu, yellow-brown prisms from MeCN, M = 585.55, monoclinic, space group $P2_1/n$, a = 14.775(3), b = 18.083(2), c = 18.167(2) Å, β = 90.26(1)°, U = 4 853.7(9) Å^3, D_m (flotation in CCl$_4$–BrCH$_2$CH$_2$Br) = 1.60 g cm^{-3}, Z = 8, D_c = 1.603 g cm^{-3}, F(000) = 2 399.5, μ(Mo-K_α) = 7.62 cm^{-1}. Crystal dimensions: 0.38 × 0.38 × 0.40 mm.

Intensities (h, k, $\pm l$; 8 551 unique data) were measured at 22 °C on a Nicolet R3m diffractometer using the ω—2θ variable-scan (2.02—8.37° min^{-1}) technique in the bisecting mode up to 2$\theta_{max.}$ = 50°. Azimuthal scans of 20 selected strong reflections over a range of 2θ values were used to define a pseudo-ellipsoid for the application of absorption corrections (μr = 0.21, transmission factors 0.542—0.562).[4]

Atomic co-ordinates for the two Ru atoms in the asymmetric unit were deduced from a sharpened Patterson function, and the other non-hydrogen atoms were located from subsequent difference-Fourier maps. The macrocyclic ring in one *trans*-[Ru(L)(N$_3$)(NCMe)]$^+$ cation (I) was found to be badly disordered; accordingly it was approximated by fractional N and C atoms with variable site occupancy factors. To facilitate refinement of the remaining well-ordered cation (II), its N–C(methylene), N–C(methyl), and C–C bond distances were treated as free variables (d_1, d_2, and d_3 respectively) by the method of observational equations.[5] Blocked-cascade least-

---

† Acetonitrile(azido)(1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)ruthenium(II) hexafluorophosphate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Atomic co-ordinates (× 10^5 for Ru; × 10^4 for other atoms) for **(1)** *

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	
Ru	75 493(5)	9 175(4)	40 826(4)	C(16)	7 045(7)	2 617(5)	2 243(6)	
Ru′	31 035(5)	40 885(5)	38 580(4)	N(6)	7 792(8)	275(6)	5 031(5)	
P(1)	4 938(2)	1 447(2)	1 334(2)	N(7)	7 777(10)	−227(5)	5 352(6)	
F(1)	5 892(5)	1 096(5)	1 448(5)	N(8)	7 735(26)	−704(9)	5 685(10)	
F(2)	4 521(6)	788(4)	1 775(5)	N(1)d	3 159(10)	3 603(9)	2 808(8)	[0.64(3)]
F(3)	4 796(10)	944(7)	682(5)	N(2)d	3 164(10)	5 166(8)	3 302(8)	[0.65(3)]
F(4)	5 376(6)	2 078(7)	913(8)	N(3)d	2 897(16)	4 733(18)	5 016(13)	[0.74(5)]
F(5)	5 090(6)	1 848(5)	2 088(5)	N(4)d	2 987(14)	2 979(11)	4 448(14)	[0.94(5)]
F(6)	3 971(5)	1 793(5)	1 268(6)	N(5)d	3 169(44)	3 069(37)	3 415(38)	[0.23(3)]
P(1′)	−17(2)	2 696(2)	1 971(2)	N(6)d	3 123(23)	5 392(18)	4 064(22)	[0.44(6)]
F(1′)	−503(4)	2 878(4)	1 222(4)	N(7)d	3 125(18)	4 028(15)	5 056(18)	[0.51(6)]
F(2′)	401(4)	3 482(4)	1 979(4)	C(1)d	3 003(22)	4 353(23)	2 361(17)	[1.00]
F(3′)	−837(4)	2 982(5)	2 411(4)	C(2)d	2 716(19)	5 073(16)	2 728(16)	[1.00]
F(4′)	−484(7)	1 917(4)	1 992(4)	C(3)d	2 794(18)	5 720(14)	3 742(15)	[0.60(5)]
F(5′)	820(6)	2 402(6)	1 570(5)	C(4)d	3 625(44)	5 540(26)	4 629(27)	[0.83(8)]
F(6′)	456(5)	2 545(4)	2 741(4)	C(5)d	2 804(39)	5 402(28)	4 693(29)	[0.85(9)]
N(1)	8 062(7)	1 918(4)	4 621(4)	C(6)d	2 674(15)	3 180(16)	5 170(14)	[1.00]
N(2)	6 289(6)	1 259(3)	4 547(3)	C(7)d	2 621(14)	2 686(11)	3 956(12)	[0.69(4)]
N(3)	7 015(4)	19(4)	3 491(4)	C(8)d	2 933(16)	2 531(13)	3 183(12)	[1.00]
N(4)	8 832(4)	574(3)	3 670(5)	C(9)d	2 604(17)	3 035(14)	2 655(14)	[0.79(3)]
C(1)	7 369(5)	2 061(8)	5 210(6)	C(10)d	3 810(28)	4 295(20)	5 472(20)	[0.95(5)]
C(2)	6 484(5)	2 013(4)	4 856(7)	C(11)d	1 988(27)	2 571(22)	4 102(22)	[0.54(3)]
C(3)	5 577(6)	1 229(4)	3 959(5)	C(12)d	4 328(26)	5 519(22)	3 903(21)	[0.56(4)]
C(4)	5 477(9)	502(6)	3 630(8)	C(13)d	2 345(22)	4 503(18)	2 225(17)	[0.91(4)]
C(5)	6 165(6)	262(7)	3 110(5)	C(14)d	2 449(27)	3 786(26)	2 320(19)	[0.60(5)]
C(6)	7 741(11)	−165(8)	2 933(10)	C(15)d	2 896(34)	3 783(37)	5 531(40)	[0.81(9)]
C(7)	8 539(9)	312(7)	2 922(6)	C(11′)	4 075(12)	3 491(9)	2 464(9)	
C(8)	9 473(8)	1 218(6)	3 648(3)	C(12′)	4 059(16)	5 358(13)	3 028(14)	
C(9)	9 613(7)	1 539(10)	4 372(5)	C(13′)	2 080(14)	4 947(12)	5 190(11)	
C(10)	8 937(7)	1 648(9)	4 940(6)	C(14′)	3 964(19)	2 698(15)	4 565(15)	
C(11)	8 198(11)	2 639(5)	4 242(7)	N(5′)	1 749(5)	4 122(4)	3 828(4)	
C(12)	5 908(10)	796(7)	5 149(7)	C(15′)	982(6)	4 123(5)	3 820(5)	
C(13)	6 817(11)	−673(5)	3 911(7)	C(16′)	−1(6)	4 107(6)	3 824(6)	
C(14)	9 315(9)	−16(7)	4 087(8)	N(6′)	4 516(7)	4 073(8)	3 951(7)	
N(5)	7 358(5)	1 601(4)	3 247(4)	N(7′)	5 221(6)	3 877(6)	3 749(5)	
C(15)	7 229(6)	2 029(5)	2 795(5)	N(8′)	5 911(8)	3 722(7)	3 578(8)	

* Site occupancy factors of the disordered atoms (d) are given in square brackets.

squares refinement[6] proceeded with anisotropic thermal parameters for all non-hydrogen atoms except those belonging to the disordered macrocyclic ring, methylene H atoms in the ordered cation (II) being generated geometrically and allowed to ride on their respective parent C atoms.

All computations were performed on a Data General Nova 3/12 minicomputer with the SHELXTL system of programs.[7] Analytical expressions of neutral-atom scattering factors incorporating the real and imaginary components of anomalous dispersion were employed.[8] Convergence for 6 147 observed data ($|F_o| > 3\sigma|F_o|$) and 540 variables was reached at $R = 0.085$ and $R' = 0.113$, the weighting scheme being $w = [\sigma^2(|F_o|) + 0.002|F_o|^2]^{-1}$. The final difference-Fourier map showed residual extrema in the range +0.96 to −0.83 e Å^{-3}, with the three highest peaks lying in the neighbourhood of the disordered atoms. The free variables d_1, d_2, and d_3 refined to 1.502(3), 1.490(4), and 1.455(4) Å, respectively. Final atomic co-ordinates of non-hydrogen atoms are given in Table 1.

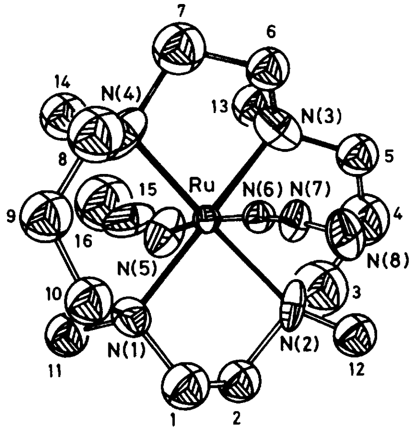


Figure. Perspective view of the ordered cation (II) of **(1)** with the atom labelling (carbon atomic symbols not given)

Results and Discussion

Reactions between $K_2[RuCl_5(NO)]$ and L in ethanol yielded a brownish yellow solid with an intense i.r. band at 1 860 cm^{-1} characteristic of the $\nu(NO^+)$ stretching frequency.[9] This species is possibly a Ru–L–NO complex, the nature of which is uncertain at present. As found previously for ruthenium nitrosyl complexes,[10,11] the Ru–NO group in this brownish yellow complex is electrophilic and susceptible to nucleophilic attack as indicated by its reaction with $N_2H_4{\cdot}H_2O$ to form complex **(1)**. Similar reactions with $[Ru(pdma)_2(NO)Cl]^{2+}$ [pdma = *o*-phenylenebis(dimethylarsine)] have previously been reported by Feltham and co-workers.[12] Complex **(1)** has also been characterized by *X*-ray crystallography.

A perspective view of the well-ordered cation (II) of **(1)** with atom labelling is shown in the Figure. Selected bond distances and angles are given in Table 2. The axial ligands in cation (I)

Table 2. Selected bond distances (Å), bond angles (°), and torsion angles (°, e.s.d.s *ca.* 0.5°) for *trans*-$[Ru^{II}(L)(N_3)(NCMe)]PF_6$

Cation (II)

Ru–N(1)	2.191(8)	N(5)–C(15)	1.14(1)	Ru–N(4)	2.134(6)	C(15)–C(16)	1.49(1)
Ru–N(3)	2.100(7)	N(6)–N(7)	1.08(1)	Ru–N(6)	2.107(10)	N(7)–N(8)	1.06(2)
Ru–N(5)	1.976(7)	Ru–N(2)	2.139(8)				
N(1)–Ru–N(2)	83.4(3)	N(6)–Ru–N(3)	93.1(4)	N(2)–Ru–N(3)	95.7(2)	N(6)–Ru–N(2)	88.9(3)
N(3)–Ru–N(4)	85.8(2)	N(5)–Ru–N(6)	174.7(4)	N(4)–Ru–N(1)	95.2(3)	N(6)–Ru–N(4)	88.8(4)
N(5)–Ru–N(1)	82.8(3)	N(5)–C(15)–C(16)	177(1)	N(5)–Ru–N(2)	90.1(3)	Ru–N(5)–C(15)	175.7(7)
N(5)–Ru–N(3)	92.2(3)	N(6)–N(7)–N(8)	177(2)	N(5)–Ru–N(4)	92.1(3)	Ru–N(6)–N(7)	154(1)
N(6)–Ru–N(1)	91.9(4)						
N(1)–C(1)–C(2)–N(2)	62.8	N(4)–C(8)–C(9)–C(10)	−39.2	N(2)–C(3)–C(3)–C(5)	−75.6	C(8)–C(9)–C(10)–N(1)	−41.2
C(2)–N(2)–C(3)–C(4)	174.3	C(9)–C(10)–N(1)–C(1)	−177.7	C(4)–C(5)–N(3)–C(6)	−175.2	C(10)–N(1)–C(1)–C(2)	−156.6
C(3)–C(4)–C(5)–N(3)	77.1	C(11)–N(1)–C(1)–C(2)	83.3	N(3)–C(6)–C(7)–N(4)	36.5	C(12)–N(2)–C(2)–C(1)	85.5
C(5)–N(3)–C(6)–C(7)	113.9	C(13)–N(3)–C(6)–C(7)	−128.1	C(7)–N(4)–C(8)–C(9)	169.7	C(14)–N(4)–C(7)–C(6)	76.8
C(6)–C(7)–N(4)–C(8)	−163.9	C(1)–C(2)–N(2)–C(3)	−159.0				

Cation (I) (containing the disordered macrocyclic ligand)

Ru′–N(5′)	2.003(7)	Ru′–N(6′)	2.093(10)	N(5′)–Ru′–N(6′)	176.8(4)	Ru′–N(5′)–C(15′)	178.1(7)
N(5′)–C(15′)	1.13(1)	C(15′)–C(16′)	1.45(1)	N(5′)–C(15′)–C(16′)	179(1)	Ru′–N(6′)–N(7′)	151(1)
N(6′)–N(7′)	1.16(1)	N(7′)–N(8′)	1.10(2)	N(6′)–N(7′)–N(8′)	176(1)		

are little affected by the orientational disorder of its equatorial L ligand. In both cations (I) and (II), the approximate linear bonding in the axial direction is interrupted by a bend at the coordinating N atom of the azide group, the relevant mean bond angle being 153(1)°. The Ru–N(L) bond lengths are similar to those observed for *trans*-$[Ru(cyclam)Cl_2]^+$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane), 2.083(3) Å,[13] *trans*-$[Ru^{IV}(L)O(NCMe)]^{2+}$ (**2**), 2.085(5)—2.125(7) Å,[1a] and *trans*-$[Ru^{IV}(L)O(Cl)]^+$ (**3**), 2.07(2)—2.16(2) Å,[14] despite the differences in axial ligands and metal oxidation states. The Ru–N(acetonitrile) bond distances are significantly shorter than the corresponding distance of 2.149(6) Å in (**2**),[1a] attesting both to the stronger *trans* influence of the oxo ligand as compared to the azide ligand and the metal $[d_\pi(Ru)]$ to ligand $[\pi^*(NCMe)]$ π back-bonding effect as manifested by the observed decrease in ν(C≡N) stretching frequency (2 200 cm^{-1}). The N-methyl groups in the ligand L in (**1**) and (**3**) adopt the unusual 'three-up, one-down' (*R,S,R,R*) configuration,* as opposed to the 'all-four-down' (*R,S,R,S*)[15,16] and 'two-up, two-down' (*R,S,S,R*) configurations commonly found in other structurally characterized metal-L complexes.[17,18] The (*R,S,R,R*) isomer of $[Ni(L)]^{2+}$ [19] has previously been characterized only by ^1H and ^{13}C n.m.r. spectroscopy. In complex (**1**), three of the four N-methyl groups are *cis* to the acetonitrile ligand, and the torsion angles around the macrocyclic ring closely match those in (**3**). In fact, the disposition of the N-methyl groups in complexes (**1**)—(**3**) can be rationalized in terms of the steric bulk of the axial ligands, which follows the trends $Cl^- > O^{2-} >$ NCMe and $N_3^- >$ NCMe.

Both independent PF_6 groups in (**1**) are ordered and approximately octahedral, with measured bond lengths in the range 1.51—1.59(1) Å.

Acknowledgements

Support from the Committee of Research and Conference Grants of University of Hong Kong (to C-M. C.) is acknowledged.

References

1 (*a*) C. M. Che, K. Y. Wong, and T. C. W. Mak, *J. Chem. Soc., Chem. Commun.*, 1985, 546; (*b*) p. 986; (*c*) C. M. Che and K. Y. Wong, *ibid.*, 1986, 229; (*d*) C. M. Che, K. Y. Wong, and C. K. Poon, *Inorg. Chem.*, 1985, **24**, 1797.

2 H. Taube, *Coord. Chem. Rev.*, 1978, **26**, 33.

3 E. K. Barefield and F. Wagner, *Inorg. Chem.*, 1973, **12**, 2435.

4 G. Kopfmann and R. Huber, *Acta Crystallogr., Sect. A*, 1968, **24**, 348; A. C. T. North, D. C. Phillips, and F. S. Mathews, *ibid.*, p. 351.

5 J. S. Rollett, in 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1980, p. 167.

6 J. W. Schilling, in 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970, p. 201.

7 G. M. Sheldrick, in 'Computational Crystallography,' ed. D. Sayre, Oxford University Press, New York, 1982, p. 506.

8 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99, 149.

9 F. Bottomley, *Coord. Chem. Rev.*, 1978, **26**, 7; *Acc. Chem. Res.*, 1978, **11**, 158.

10 R. W. Adams, J. Chatt, N. E. Hooper, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1974, 1075.

11 F. Bottomley and E. M. R. Kiremire, *J. Chem. Soc., Dalton Trans.*, 1977, 1125.

12 P. G. Douglas, R. D. Feltham, and H. G. Metzger, *J. Am. Chem. Soc.*, 1971, **93**, 84.

13 D. D. Walker and H. Taube, *Inorg. Chem.*, 1981, **20**, 2828.

14 C. M. Che, K. Y. Wong, and T. C. W. Mak, *J. Chem. Soc., Chem. Commun.*, 1985, 988.

15 K. D. Hodges, R. G. Wollmann, S. L. Kessel, D. N. Hendrickson, D. G. Van Derveer, and E. K. Barefield, *J. Am. Chem. Soc.*, 1979, **101**, 906.

16 M. J. D. Aniello, jun., M. T. Mocella, F. Wagner, E. K. Barefield, and I. C. Paul, *J. Am. Chem. Soc.*, 1975, **97**, 192.

17 P. Moore, J. Sachinidis, and G. R. Willey, *J. Chem. Soc., Dalton Trans.*, 1984, 1323.

18 E. K. Barefield, G. M. Freeman, and D. G. V. Derveer, *Inorg. Chem.*, 1986, **25**, 552.

19 S. F. Lincoln, J. H. Coates, D. A. Hadi, and D. L. Pisaniello, *Inorg. Chim. Acta*, 1984, **81**, L9.

Received 26th January 1987; *Paper* 7/022

---

* The terminology is used with a N-methyl group *cis* to the NCMe ligand arbitrarily designated as 'up'; see also N. W. Alcock, E. H. Curzon, P. Moore, and C. Pierpont, *J. Chem. Soc., Dalton Trans.*, 1984, 605.