Rhenium Complexes of Tetra-aza Macrocycles: The Synthesis and Single-crystal *X*-Ray Structure of *trans*-$[Re(O)_2(cyclam)]Cl\cdot2(BPh_3\cdot H_2O)$ †

Alexander J. Blake, John A. Greig, and Martin Schröder *
Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Reaction of $[ReOCl_3(PPh_3)_2]$ with 1,4,8,11-tetra-azacyclotetradecane (cyclam) in CH_2Cl_2 affords an intermediate '$ReOCl_3$(cyclam)' which hydrolyses readily to $[Re(O)_2(cyclam)]^+$ in solution. *trans*-$[Re(O)_2(cyclam)]Cl\cdot2(BPh_3\cdot H_2O)$ crystallises in the monoclinic space group $P2_1/n$, M = 974.26, a = 9.386 9(4), b = 13.550 4(7), c = 17.772 7(11) Å, β = 91.918(5)°, and Z = 2, implying that both the macrocyclic complex cation and the chloride counter ion lie on inversion centres. The single-crystal *X*-ray structure of the complex shows octahedral Re^V with the tetra-aza macrocyclic ligand bound in the equatorial plane adopting an *RRSS* (*trans*-III) configuration at the co-ordinated N donors, Re–N(1) 2.128(3), Re–N(11) 2.135(3) Å. The co-ordination shell is completed by mutually *trans* dioxo ligands, Re=O 1.756(3) Å. The Cl^- counter ion is not co-ordinated to the Re centre. Two molecules of the adduct $BPh_3\cdot H_2O$ are also observed in the crystal. Extensive hydrogen bonding is observed in the crystal between the oxo ligands, water molecules, chloride counter ions, and the amine protons of the macrocyclic ligand.

Very little work has been reported on the complexation of rhenium by macrocyclic ligands.[1] We were interested in investigating the macrocyclic chemistry of rhenium as an extension of our previous work on the platinum group metals.[2] The high-valent chemistry of rhenium is particularly well developed and, in view of the interest in the synthesis of ruthenium and osmium oxo complexes as redox catalysts for organic reactions,[3,4] we have undertaken a study of the complexation of rhenium by tetra-aza macrocyclic ligands.

We describe herein the synthesis of rhenium(v) mono-oxo and dioxo complexes of 1,4,8,11-tetra-azacyclotetradecane (cyclam), and the single-crystal *X*-ray structure of *trans*-$[Re(O)_2(cyclam)]Cl\cdot2(BPh_3\cdot H_2O)$.

Results and Discussion

Reaction of $[ReOCl_3(PPh_3)_2]$[5] with one molar equivalent of cyclam in dried CH_2Cl_2 for 2 h followed by addition of diethyl ether affords a pale brown product tentatively assigned as '$ReOCl_3$(cyclam)'. The i.r. spectrum of the complex shows, in addition to bands due to co-ordinated cyclam, a band at 915 cm^{-1} assigned to the Re=O stretching vibration, ν(Re=O), of a mono-oxo rhenium complex.[6] Repeated attempts to recrystallise this sensitive species in the presence of a variety of counter ions led to the isolation of a hydrolysed product, the fast atom bombardment mass spectrum of which showed a peak at M^+ = 419 corresponding to the molecular formula $[ReC_{10}H_{24}N_4O_2]^+$. Addition of $NaBPh_4$ to a solution of the product in $MeNO_2$ followed by addition of diethyl ether yielded a light brown product. The i.r. spectrum of the complex (KBr disc) shows a band at 825 cm^{-1} assigned to the asymmetric ν(O=Re=O) stretching vibration of a *trans*-dioxo O=Re=O species. Single crystals of this product were obtained from MeCN–Et_2O and a structural analysis was undertaken to confirm the co-ordination and stereochemistry of this isolated product.

The single-crystal *X*-ray structural analysis shows the product to be the dioxo rhenium(v) species $[Re(O)_2(cyclam)]Cl\cdot2(BPh_3\cdot H_2O)$. A view of the cation is shown in Figure 1 with a crystal packing diagram in Figure 2. The Re and Cl atoms lie on centres of inversion with the Re^V ion bound to all four N donors of the equatorially co-ordinated tetra-aza macrocycle, Re–N(1) 2.128(3), Re–N(11) 2.135(3) Å. *trans*-Dioxo ligands complete the octahedral co-ordination around the Re centre, Re=O 1.756(3) Å; O=Re–N(1) 89.51(13), O=Re–N(11) 89.29(13)°. The co-ordinated macrocyclic ligand shows a *RRSS* (*trans*-III)[7] conformation with two amine protons lying above, and the other two amine protons lying below the ReN_4 plane. The Cl is not bound to the Re centre. Extensive hydrogen bonding is observed in the crystal between the oxo ligands, water molecules, chloride counter ions, and the amine protons of the macrocyclic ligand (Figure 2). The presence of the previously unreported adduct $BPh_3\cdot H_2O$ in the crystal lattice is of interest, and is formed presumably *via* acid-catalysed hydrolysis of BPh_4^-. The formation of a *trans*-dioxo species formally by recrystallisation of a mono-oxo halide complex is intriguing, and reflects the high lability of the halide

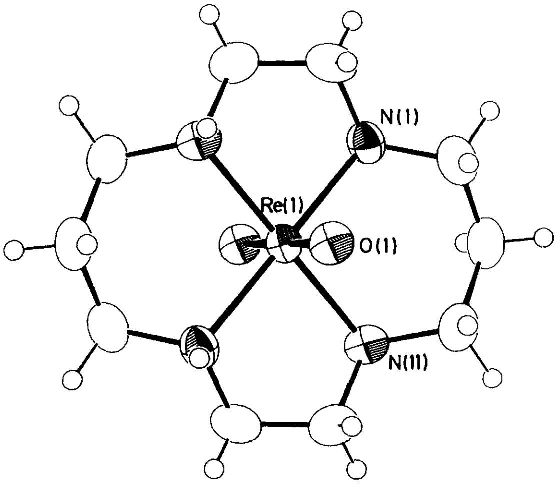

Figure 1. Single-crystal *X*-ray structure of the *trans*-$[Re(O)_2(cyclam)]^+$ cation with numbering scheme adopted

---

† *trans*-Dioxo(1,4,8,11-tetra-azacyclotetradecane)rhenium(v) chloride–(triphenylborane monohydrate) (1/2).

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

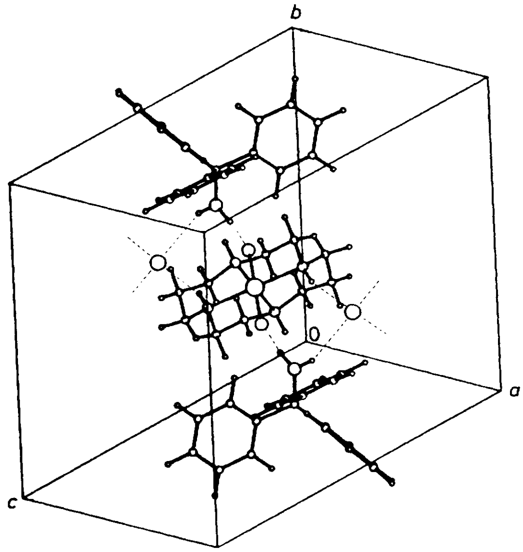

Figure 2. A view of part of the hydrogen-bonding network in *trans*-[Re(O)$_2$(cyclam)]Cl·2(BPh$_3$·H$_2$O). Hydrogen bonds, shown as dashed lines, link the Re-bound oxygen atoms, the water molecules, the chloride anions and two of the N-bound hydrogen atoms on each co-ordinated cyclam. The chlorides link to other [Re(O)$_2$-(cyclam)]$^+$·2(BPh$_3$·H$_2$O) units

Table 1. Bond lengths (Å) with estimated standard deviations in parentheses

Re(1)–O(1)	1.756(3)	N(1)–C(2)	1.498(6)
Re(1)–N(11)	2.135(3)	C(2)–C(3)	1.523(6)
Re(1)–N(1)	2.128(3)	B(1)–O(1W)	1.602(6)
N(11)–C(12)	1.484(6)	B(1)–C(21)	1.654(5)
C(12)–C(13)	1.524(7)	B(1)–C(31)	1.650(5)
C(13)–C(14)	1.541(7)	B(1)–C(41)	1.636(6)
C(14)–N(1)	1.489(6)		

Table 2. Bond angles (°) with estimated standard deviations in parentheses

O(1)–Re(1)–N(11)	89.29(13)	C(12)–N(11)–C(10)	115.0(3)
O(1)–Re(1)–N(1)	89.51(13)	O(1W)–B(1)–C(21)	107.2(3)
N(11)–Re(1)–N(1)	97.31(13)	O(1W)–B(1)–C(31)	104.6(3)
Re(1)–N(11)–C(12)	111.7(3)	O(1W)–B(1)–C(41)	105.2(3)
N(11)–C(12)–C(13)	112.3(4)	C(21)–B(1)–C(31)	114.3(3)
C(12)–C(13)–C(14)	117.7(4)	C(21)–B(1)–C(41)	113.6(3)
C(13)–C(14)–N(1)	111.4(4)	C(31)–B(1)–C(41)	111.0(3)
Re(1)–N(1)–C(14)	112.9(3)	B(1)–C(21)–C(22)	119.29(25)
Re(1)–N(1)–C(2)	107.6(3)	B(1)–C(21)–C(26)	120.68(25)
C(14)–N(1)–C(2)	113.7(3)	B(1)–C(31)–C(32)	118.40(24)
N(1)–C(2)–C(3)	106.6(4)	B(1)–C(31)–C(36)	121.45(25)
C(2)–C(3)–N(4)	108.9(4)	B(1)–C(41)–C(42)	122.9(3)
Re(1)–N(11)–C(10)	106.07(25)	B(1)–C(41)–C(46)	117.0(3)

trans to the oxo ligand in the initially formed [ReOCl-(cyclam)]$^{2+}$ cation or related species. Presumably, this species can hydrate to [Re(O)(H$_2$O)(cyclam)]$^{3+}$, which readily deprotonates to afford the dioxo product. The formation of the *trans*-dioxo species [Re(O)$_2$(cyclam)]$^+$ in organic media is probably linked to the relatively high acidity of the water co-ordinated to the highly electropositive Re^{V} centre (Scheme).

Synthesis of [Re(O)$_2$(cyclam)]$^{2+}$.—[Re(O)Cl$_3$(PPh$_3$)$_2$] (0.2 g, 0.24 mmol) was treated with cyclam (0.05 g, 0.25 mmol) in CH$_2$Cl$_2$ (30 cm^3) for 2 h under reflux under N$_2$. The solvent was removed by rotary evaporation, and the residue dissolved in CH$_3$NO$_2$. Addition of NaBPh$_4$ (0.17 g, 0.49 mmol) followed by Et$_2$O yielded the light brown tetraphenylborate salt in low yield, 0.06 g (26%).

$$\begin{tikzcd}
{[\mathrm{ReOCl_3(PPh_3)_2}] + \text{cyclam}} \arrow[r] & {[\mathrm{Re(O)Cl(cyclam)}]^{2+}} \arrow[r, "+\mathrm{H_2O}", "-\mathrm{Cl^-}"'] & {[\mathrm{Re(O)(H_2O)(cyclam)}]^{3+}} \arrow[d, "-\mathrm{H^+}"] \\
 & {[\mathrm{Re(O)_2(cyclam)}]^{+}} & {[\mathrm{Re(O)(OH)(cyclam)}]^{2+}} \arrow[l, "-\mathrm{H^+}"']
\end{tikzcd}$$

Scheme.

Related tetra-aza macrocyclic species incorporating the mono-oxo, [Ru(O)(L)]$^{x+}$,[3,8] and dioxo, [Ru(O)$_2$(L)]$^{x+}$,[9] moieties are known, and several kinetically inert amide complexes containing the [Tc(O)]$^{3+}$ unit have been unequivocally defined.[10,11] The single-crystal *X*-ray structure of *trans*-[Tc(O)$_2$(cyclam)]$^+$ shows Tc=O 1.751(4), Tc–N 2.125(11) Å.[10]

Clearly, complicated interconversions of mono-oxo and dioxo Re^{V} species are occurring in solution, and current work is aimed at elucidating the nature of these processes.

Experimental

Infrared spectra were measured as Nujol mulls and KBr discs using a Perkin-Elmer 598 spectrometer over the range 200—4 000 cm^{-1}. Microanalyses were performed by the Edinburgh University Chemistry Department microanalytical service. Mass spectra were run by electron impact on a Kratos MS 902 and by fast atom bombardment on a Kratos MS 50TC spectrometer.

Crystal Structure Determination of trans-[Re(O)$_2$-(cyclam)]Cl·2(BPh$_3$·H$_2$O).—Pale brown crystals of *trans*-[Re(O)$_2$(cyclam)]Cl·2(BPh$_3$·H$_2$O) were grown from MeCN–Et$_2$O and a columnar crystal of dimensions 0.62 × 0.23 × 0.17 mm was selected for data collection on a Stoe-Siemens AED2 four-circle diffractometer.

Crystal data. $C_{10}H_{24}N_4O_2Re^+Cl^-\cdot 2(C_{18}H_{15}B\cdot H_2O)$, M = 974.26, monoclinic, space group $P2_1/n$, a = 9.386 9(4), b = 13.550 4(7), c = 17.772 7(11) Å, β = 91.918(5)°, U = 2 259.35 Å^3 (from 2θ values of 58 reflections measured at $\pm\omega$, $30 < 2\theta < 32°$), D_c = 1.432 g cm^{-3}, Z = 2 (implying that both the macrocyclic complex cation and the chloride counter ion lie on two-fold special positions), $F(000)$ = 992, $\bar{\lambda}$(Mo-K_α) = 0.710 69 Å, μ = 28.28 cm^{-1}.

Data collection and processing. AED2 diffractometer, ω–2θ scans, 3 106 unique data ($2\theta_{max.}$ = 45°, $\pm h, +k, +l$) measured using Mo-K_α *X*-radiation, initially corrected for absorption by means of ψ-scans (max. and min. transmission factors 0.1006, 0.0667 respectively), giving 2 350 reflections with $F \geqslant 6.0\sigma(F)$.

Structure analysis and refinement. From the inferred Re position, the program DIRDIF[12] followed by successive least-

Table 3. Fractional atomic co-ordinates with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Re(1)	0.5	0.5	0.5	C(25)	0.450 54(23)	0.877 29(17)	0.556 72(14)
Cl(1)	0.0	0.5	0.5	C(26)	0.385 68(23)	0.852 44(17)	0.487 54(14)
O(1)	0.386 0(3)	0.570 19(20)	0.440 80(17)	C(21)	0.256 30(23)	0.801 69(17)	0.485 11(14)
N(11)	0.480 7(4)	0.380 15(25)	0.422 31(20)	C(32)	−0.078 01(23)	0.777 73(16)	0.337 05(13)
C(12)	0.509 5(5)	0.411 8(4)	0.344 3(3)	C(33)	−0.215 46(23)	0.814 93(16)	0.325 03(13)
C(13)	0.655 4(5)	0.460 0(4)	0.338 5(3)	C(34)	−0.265 46(23)	0.889 69(16)	0.371 20(13)
C(14)	0.673 1(5)	0.566 5(3)	0.367 9(3)	C(35)	−0.178 01(23)	0.927 26(16)	0.429 40(13)
N(1)	0.678 6(3)	0.569 53(24)	0.451 76(21)	C(36)	−0.040 56(23)	0.890 06(16)	0.441 43(13)
C(2)	0.689 4(4)	0.671 7(3)	0.483 5(3)	C(31)	0.009 44(23)	0.815 29(16)	0.395 25(13)
C(3)	0.663 7(4)	0.663 0(3)	0.567 4(3)	C(42)	0.332 50(25)	0.737 91(23)	0.284 80(15)
B(1)	0.175 1(5)	0.775 0(4)	0.403 6(3)	C(43)	0.413 27(25)	0.770 03(23)	0.225 04(15)
O(1W)	0.161 6(3)	0.657 29(21)	0.399 11(17)	C(44)	0.427 8(25)	0.870 77(23)	0.211 04(15)
C(22)	0.191 79(23)	0.775 79(17)	0.551 88(14)	C(45)	0.361 57(25)	0.939 38(23)	0.256 79(15)
C(23)	0.256 65(23)	0.800 64(17)	0.621 06(14)	C(46)	0.280 80(25)	0.907 26(23)	0.316 55(15)
C(24)	0.386 02(23)	0.851 38(17)	0.623 49(14)	C(41)	0.266 27(25)	0.806 53(23)	0.330 55(15)

Table 4. Hydrogen-bonding parameters A–B $\cdots$ C–D

Atom A	Atom B	Atom C	Atom D	B $\cdots$ C/Å	ABC/°	BCD/°
Re(1)	O(1)	H(2W)	O(1W)	1.534(16)	159.9(6)	173.1(15)
O(1W)	H(1W)	Cl(1)		2.487(16)	153.8(15)	
N(1)	H(1)	Cl(1)		2.452(16)	162.0(15)	

squares cycles and difference Fourier syntheses[13] located all non-hydrogen atomic positions. At isotropic convergence, the final absorption correction was applied empirically using DIFABS.[14] Since the Re atom contributes to only half of all reflections, it was possible to refine all hydrogen atoms freely, but phenyl H atoms were refined in fixed, calculated positions.[13] Anisotropic thermal parameters were refined for all non-hydrogen atoms. A weighting scheme $w^{-1} = \sigma^2(F) + 0.000\ 147F^2$ gave satisfactory analyses. At final convergence R and R' = 0.0245 and 0.0331 respectively, S = 1.149 for 272 parameters with the difference map showing no feature above 0.55 e Å^{-3}. Illustrations were prepared using ORTEP[15] and PLUTO,[16] molecular geometry calculations utilised CALC,[17] and scattering factor data were taken from ref. 18. Bond lengths, angles, and fractional co-ordinates are given in Tables 1—4.

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

Acknowledgements

We thank the S.E.R.C. for support, and the S.E.R.C. and Amersham International plc for a C.A.S.E. award (to J. A. G.).

References

1 K. M. Kadish, L. A. Bottomley, and D. Schaeper, *Inorg. Chim. Acta*, 1979, **36**, 219; K. Wieghardt, C. Pomp, B. Nuber, and J. Weiss, *Inorg. Chem.*, 1986, **25**, 1659; C. Pomp, H. Duddeck, K. Wieghardt, B. Nuber, and J. Weiss, *Angew. Chem.*, 1987, **99**, 927; *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 924.

2 M. Schröder, *Pure Appl. Chem.*, 1988, **60**, 517.

3 C-M. Che, T-W. Tang, and C-K. Poon, *J. Chem. Soc., Chem. Commun.*, 1984, 641; C-M. Che, K-Y. Wong, and T. C. W. Mak, *ibid.*, 1985, 546; C-M. Che, S-S. Kwong, and C-K. Poon, *ibid.*, p. 986; C-M. Che, K-Y. Wong, and T. C. M. Mak, *ibid.*, p. 988; C. M. Che, S. S. Kwong, and C. K. Poon, *Inorg. Chem.*, 1985, **24**, 1601; C-M. Che and K. Y. Wong, *J. Chem. Soc., Chem. Commun.*, 1986, 229; C-M. Che and W-K. Cheng, *ibid.*, p. 1519; *J. Am. Chem. Soc.*, 1986, **108**, 4644; K. Y. Wong, C. M. Che, and F. C. Anson, *Inorg. Chem.*, 1987, **26**, 737.

4 M. Schröder and W. P. Griffith, *J. Chem. Soc., Chem. Commun.*, 1979, 58; C. D. Ellis, J. A. Gilbert, W. R. Murphy, jun., and T. J. Meyer, *J. Am. Chem. Soc.*, 1983, **105**, 4842; G. Green, W. P. Griffith, D. Hollinshead, S. V. Ley, and M. Schröder, *J. Chem. Soc., Perkin Trans. 1*, 1984, 681; J. T. Groves and R. Quinn, *J. Am. Chem. Soc.*, 1985, **107**, 5790; C-M. Che, K-Y. Wong, W-H. Leung, and C-K. Poon, *Inorg. Chem.*, 1986, **25**, 345; C-M. Che, W-K. Cheng, W-H. Leung, and T. C. W. Mak, *J. Chem. Soc., Chem. Commun.*, 1987, 418; T. C. Lau and J. K. Kochi, *ibid.*, p. 798; C-M. Che and W-H. Leung, *ibid.*, p. 1376.

5 A. Fremi and J. Valenti, *J. Inorg. Nucl. Chem.*, 1961, **16**, 240; N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *J. Chem. Soc.*, 1964, 1061.

6 F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 867; M. A. Freeman, F. A. Schulz, and C. N. Reilley, *ibid.*, 1982, **21**, 567.

7 B. Bosnich, C-K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102.

8 C. M. Che, K. Y. Wang, and C. K. Poon, *Inorg. Chem.*, 1985, **24**, 1797.

9 J. T. Groves and R. Quinn, *Inorg. Chem.*, 1984, **23**, 3844.

10 S. A. Zuckman, G. M. Freeman, D. E. Troutner, W. A. Volkert, R. A. Holmes, D. E. Van der Veer, and E. K. Barefield, *Inorg. Chem.*, 1981, **20**, 2386; S. Jurisson, E. O. Schlemper, D. E. Troutner, L. R. Canning, D. P. Nowotnik, and R. D. Neirinckx, *ibid.*, 1986, **25**, 543; M. A. A. F. De C. T. Carrondo, *Inorg. Chim. Acta*, 1980, **44**, L7.

11 A. Davison and A. G. Jones, *Int. J. Appl. Radiat. Isot.*, 1982, **33**, 875; D. Brenner, A. Davison, J. Lister-Jones, and A. G. Jones, *Inorg. Chem.*, 1984, **23**, 3793.

12 DIRDIF, P. T. Beurskens, W. P. Bosman, H. M. Doesbury, Th. E. M. van den Hark, P. A. J. Prick, J. H. Noordik, G. Beurskens, R. O. Gould, and V. Parthasarathia, Applications of Direct Methods to Difference Structure Factors, University of Nijmegen, Netherlands, 1983.

13 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.

14 N. Walker and D. Stuart, DIFABS, Program for Empirical Absorption Corrections, *Acta Crystallogr., Sect. A*, 1983, **39**, 159.

15 P. D. Mallinson and K. W. Muir, ORTEP II (interactive version), *J. Appl. Crystallogr.*, 1985, **18**, 51.

16 W. D. S. Motherwell, PLUTO, University of Cambridge, 1976.

17 R. O. Gould and P. Taylor, CALC (FORTRAN 77 version), University of Edinburgh, 1985.

18 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.

Received 14*th December* 1987; *Paper* 7/2183