Synthesis and *X*-Ray Crystal Structure of $[ReO(Cl)\{(2\text{-}OC_6H_4CH{=}NCH_2CH_2OCH_2)_2\}]$, an Example of Four-co-ordination by a Potentially Sexidentate Ligand†

Hilary J. Banbery, Ferida McQuillan, Thomas A. Hamor,* Christopher J. Jones,* and Jon A. McCleverty
Department of Chemistry, University of Birmingham, P.O. Box 393, Birmingham B15 2TT

The reaction between $[ReOCl_4]^-$ and the Schiff-base ligand $(2\text{-}HOC_6H_4CH{=}NCH_2CH_2OCH_2)_2$ in ethanol affords the monomeric complex $[ReO(Cl)\{(2\text{-}OC_6H_4CH{=}NCH_2CH_2OCH_2)_2\}]$. A single-crystal *X*-ray diffraction study shows that the rhenium atom has a distorted octahedral co-ordination geometry in which the ether oxygens of the potentially sexidentate ligand remain unco-ordinated so that an 11-membered chelate ring is formed.

Although several rhenium(v) complexes with quadridentate Schiff-base ligands have been described,[1-5] examples of corresponding complexes formed with polydentate facultative ligands containing more than four donor atoms are rare. In the case of complexes containing quadridentate ligands, species having a 1:1 ligand:rhenium stoicheiometry and binuclear species in which two $\{ReO\}^{3+}$ units are bound to a single quadridentate ligand have been reported.[1-5] In these complexes rhenium is co-ordinated to the oxo-oxygen and five other ligating atoms to give an overall co-ordination number of six. A single quadridentate ligand, containing oxygen and nitrogen donor atoms, cannot saturate an octahedral co-ordination sphere about rhenium present in the $\{ReO\}^{3+}$ moiety, thus either oligomerisation occurs or additional ligands are bound in order to achieve six-co-ordination. Recently quinquedentate ligands have been used[6,7] in an attempt to produce six-co-ordinate rhenium complexes which have a 1:1 ligand to rhenium stoicheiometry and in which six-co-ordination around rhenium(v), present as $\{ReO\}^{3+}$, is achieved without the presence of additional ligands. In the case of $(2\text{-}HOC_6H_4CH{=}NCH_2CH_2)_2NH$ a complex of the desired formula was obtained and the molecular structure of the analogous technetium complex $[TcO\{(2\text{-}OC_6H_4CH{=}NCH_2CH_2)_2N\}]$ was determined by *X*-ray diffraction methods.[6] However, in the case of $(2\text{-}HOC_6H_4CH{=}NCH_2CH_2)_2S$ the thioether sulphur remains unco-ordinated giving rise to a complex of formula $[ReO(Cl)\{(2\text{-}OC_6H_4CH{=}NCH_2CH_2)_2S\}]$, in which a chloride ligand completes a near octahedral co-ordination sphere around the rhenium ion.[7]

In a continuation of our investigations into the ability of facultative polydentate ligands to bind to and 'encapsulate' rhenium ions we have investigated the reaction between $[ReOCl_4]^-$ and the potentially sexidentate ligand $(2\text{-}HOC_6H_4CH{=}NCH_2CH_2OCH_2)_2$ (H_2L). The solid-state molecular structure of the resulting rhenium(v) complex [ReO(Cl)L] has been determined to establish which donor atoms of the ligand are bound to the rhenium, and at which co-ordination sites relative to the ReO group.

Discussion

Synthetic Studies.—The ligand H_2L may be prepared in high yield by the condensation reaction between 1,8-diamino-3,6-dioxaoctane and salicylaldehyde in ethanol. The i.r. spectrum of the white crystalline solid obtained contains bands attributable to the presence of phenyl and alkyl groups in addition to ν(C=N) at 1 640 cm^{-1}. The 270-MHz ^1H n.m.r. spectrum of the ligand contains two doublets and two triplets of total relative area 8 in the region δ 7.31—6.83 (relative to $SiMe_4$) attributable to the aryl protons. The two doublets appear at δ 7.23 (J_{HH} = 7.5) and 6.94 (J_{HH} = 8.5 Hz) and may be attributed to the protons adjacent to the aryl ring substituents. The two triplets arise from the remaining two aryl protons and may be regarded as doublets of doublets centred at δ 7.29 (J_{HH} = 7.5 and 8.5) and 6.85 (J_{HH} = 7.5 and 7.5 Hz). The azomethine =CH– protons appear as a singlet of relative area 2 at δ 8.31 and the OH protons as a singlet of relative area 2 at δ 13.43. The methylene protons appear as two singlets of relative areas 8:4 at δ 3.71 and 3.59 and the mass spectrum of H_2L exhibited a molecular ion at m/z = 358.

The reaction between $[NBu^n{}_4][ReOCl_4]$ and H_2L proceeded smoothly in refluxing ethanol in the absence of air to produce a brown complex. The i.r. spectrum of this material contained bands consistent with the presence of the ligand L, including ν(C=N) at 1 610 cm^{-1}, and ν(Re=O) at 960 cm^{-1}. A satisfactory ^1H n.m.r. spectrum could not be obtained because of low solubility in suitable solvents. The fast-atom-bombardment mass spectrum of the complex contained a molecular ion at m/z = 592 attributable to $[M + H]^+$ along with a major fragment ion at m/z = 557 attributable to $[M - Cl + H]^+$. On the basis of these data and elemental analyses the complex was formulated as [ReO(Cl)L]. This formulation was confirmed by the single-crystal *X*-ray diffraction study described below.

Structural Studies.—Bond lengths and angles are listed in Tables 1 and 2, and atomic co-ordinates in Table 3. A view of the complex drawn with PLUTO[8] is shown in the Figure. The rhenium atom exhibits a pseudo-octahedral geometry with a maximum angular distortion of 14° [O(4)–Re–N(1) 166.0(3)°]. One phenolic oxygen of the ligand lies *trans* to the oxo group as has been observed in related complexes.[6,7] The other phenolic oxygen atom lies *cis* to the chloride ligand so that the chloride

---

† Chloro[*NN*′-3,6-dioxaoctane-1,8-diylbis(salicylideneiminato)(2−)]-oxorhenium(v).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Bond lengths (Å) for [ReO(Cl){(2-$OC_6H_4CH=NCH_2CH_2OCH_2)_2$}] with e.s.d.s in parentheses

Re-Cl	2.387(2)	C(1)-C(6)	1.393(12)
Re-O(1)	1.977(5)	C(2)-C(3)	1.375(13)
Re-O(4)	1.983(6)	C(3)-C(4)	1.399(15)
Re-O(5)	1.688(6)	C(4)-C(5)	1.364(14)
Re-N(1)	2.146(7)	C(5)-C(6)	1.411(12)
Re-N(2)	2.119(7)	C(6)-C(7)	1.449(12)
O(1)-C(1)	1.345(10)	C(8)-C(9)	1.520(13)
O(2)-C(9)	1.389(11)	C(10)-C(11)	1.504(15)
O(2)-C(10)	1.429(11)	C(12)-C(13)	1.501(14)
O(3)-C(11)	1.419(12)	C(14)-C(15)	1.470(11)
O(3)-C(12)	1.451(11)	C(15)-C(16)	1.411(13)
O(4)-C(20)	1.330(11)	C(15)-C(20)	1.388(12)
N(1)-C(7)	1.302(11)	C(16)-C(17)	1.377(13)
N(1)-C(8)	1.461(11)	C(17)-C(18)	1.382(14)
N(2)-C(13)	1.518(11)	C(18)-C(19)	1.378(13)
N(2)-C(14)	1.275(11)	C(19)-C(20)	1.401(11)
C(1)-C(2)	1.406(12)		

Table 2. Bond angles (°) with e.s.d.s in parentheses

Cl-Re-O(1)	90.2(2)	C(2)-C(1)-C(6)	121.0(8)
Cl-Re-O(4)	85.9(2)	C(1)-C(2)-C(3)	118.6(9)
O(1)-Re-O(4)	85.1(2)	C(2)-C(3)-C(4)	121.5(9)
Cl-Re-O(5)	98.1(2)	C(3)-C(4)-C(5)	119.3(9)
O(1)-Re-O(5)	169.1(3)	C(4)-C(5)-C(6)	121.2(9)
O(4)-Re-O(5)	102.5(3)	C(1)-C(6)-C(5)	118.3(8)
Cl-Re-N(1)	85.7(2)	C(1)-C(6)-C(7)	123.0(7)
O(1)-Re-N(1)	83.8(3)	C(5)-C(6)-C(7)	118.7(8)
O(4)-Re-N(1)	166.0(3)	N(1)-C(7)-C(6)	127.3(8)
O(5)-Re-N(1)	89.7(3)	N(1)-C(8)-C(9)	112.9(8)
Cl-Re-N(2)	172.7(2)	O(2)-C(9)-C(8)	106.6(7)
O(1)-Re-N(2)	83.8(3)	O(2)-C(10)-C(11)	108.0(8)
O(4)-Re-N(2)	89.4(3)	O(3)-C(11)-C(10)	115.4(9)
O(5)-Re-N(2)	88.4(3)	O(3)-C(12)-C(13)	106.8(8)
N(1)-Re-N(2)	97.8(3)	N(2)-C(13)-C(12)	110.1(8)
Re-O(1)-C(1)	136.9(5)	N(2)-C(14)-C(15)	126.2(8)
C(9)-O(2)-C(10)	114.5(7)	C(14)-C(15)-C(16)	115.0(8)
C(11)-O(3)-C(12)	116.1(8)	C(14)-C(15)-C(20)	124.1(8)
Re-O(4)-C(20)	127.6(5)	C(16)-C(15)-C(20)	120.7(8)
Re-N(1)-C(7)	127.0(6)	C(15)-C(16)-C(17)	120.5(9)
Re-N(1)-C(8)	119.2(6)	C(16)-C(17)-C(18)	118.8(9)
C(7)-N(1)-C(8)	113.7(7)	C(17)-C(18)-C(19)	121.2(8)
Re-N(2)-C(13)	121.2(6)	C(18)-C(19)-C(20)	121.2(8)
Re-N(2)-C(14)	123.9(6)	O(4)-C(20)-C(15)	125.3(8)
C(13)-N(2)-C(14)	114.6(8)	O(4)-C(20)-C(19)	117.0(8)
O(1)-C(1)-C(2)	118.1(8)	C(15)-C(20)-C(19)	117.6(8)
O(1)-C(1)-C(6)	120.8(7)		

and two phenolic oxygen donor atoms occupy mutually *fac* co-ordination sites. The two imine nitrogen atoms are mutually *cis* and complete a mutually *fac* co-ordination arrangement with the ReO group. The two ether oxygen atoms of the ligand remain unco-ordinated leading to the formation of an unusually large 11-membered chelate ring. Such large chelate rings have been observed previously in polyethylene glycol complexes of molybdenum and confirmed by *X*-ray diffraction techniques in the case of [Mo(NO){HB(3,5-$Me_2C_3HN_2)_3$}{$OCH_2(CH_2OCH_2)_3CH_2O$}].[9] However, in these cases the metal co-ordination sphere is sterically saturated and no replaceable halide ligands are present. One other related rhenium complex, [ReOCl{(2-$OC_6H_4CH=NCH_2CH_2)_2S$}], had also been shown to contain a large nine-membered chelate ring through non-co-ordination of the thioether sulphur.[7]

The Re–O(ligand) bond lengths of 1.977(5) and 1.983(6) Å, for O(1) and O(4) respectively, compare favourably with similar bonds in other rhenium complexes containing Schiff-base ligands.[6,7] These have lengths in the range 1.972(8) to 2.018(7) Å. There is no significant difference between the two Re–O distances for this complex. The Re=O distance of 1.688(6) Å also compares favourably with those reported previously,[6,7] which had values of 1.684(6) and 1.724(8) Å. It is somewhat longer than a Tc=O bond[10] of 1.659(11) Å in [TcO($SC_6H_2Me_3$-2, 4, 6$)_4]^-$ but comparable to that of 1.685(6) Å in [TcO{(2-$OC_6H_4CH=NCH_2CH_2)_2N$}].[6] The Re–N bond lengths are 2.146(7) and 2.119(7) Å and Re–Cl is 2.387(2) Å. The two non-co-ordinated oxygen atoms, O(2) and O(3) in the Figure, are both more than 4.2 Å away from rhenium. The ability of the $\{ReO\}^{3+}$ moiety to accommodate a further four oxygen and two nitrogen atoms in the first co-ordination sphere, giving an overall co-ordination number of seven, may be inferred from a structural study[11] of Ba[TcO(edta)$]_2$ (edta = ethylenediaminetetra-acetate). This has shown that seven-co-ordination can be achieved in complexes containing the $\{TcO\}^{3+}$ moiety and, being of similar size to technetium, rhenium might also be expected to accommodate seven-co-ordination. However, the structural properties of the edta ligand are very different from those of the linear sexidentate ligand used here. The conformational requirements of the linear sexidentate ligand and the relatively weak ligating properties of the ether oxygens probably contribute to the failure of L to complete the co-ordination sphere of the $\{ReO\}^{3+}$ moiety. Attempts to induce co-ordination of at least one of the ether oxygen atoms by halide abstraction using Ag^+ were unsuccessful.

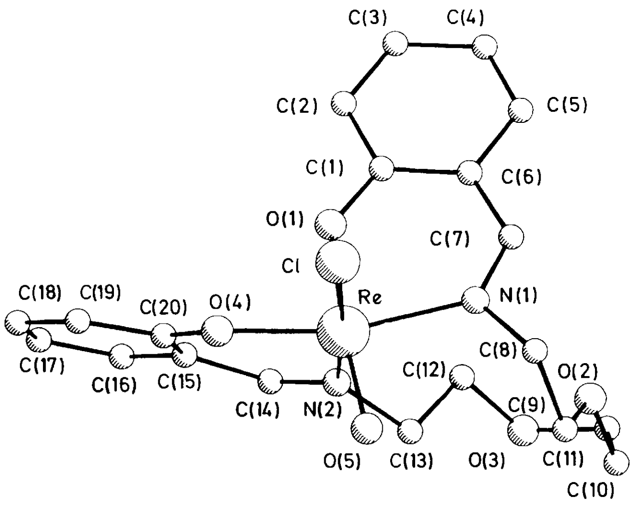

Figure. A view of [ReO(Cl){(2-$OC_6H_4CH=NCH_2CH_2CH_2OCH_2)_2$}] showing the atom labelling. Hydrogen atoms have been omitted for clarity

Experimental

Synthetic Studies.—Materials. Commercial reagents were used as supplied; 1,8-diamino-3,6-dioxaoctane was obtained from Merck and [NBu^n_4][$ReOCl_4$] was prepared according to a previously described procedure.[12] Methanol and ethanol were dried over magnesium and redistilled before use; other solvents were used as received without further purification.

Apparatus.—Infrared spectra were recorded using a PE 297 instrument, ^1H n.m.r. spectra using a JEOL GX 270 (270 MHz) instrument, and mass spectra on a Kratos MS80 machine using positive argon-ion fast-atom bombardment.

Preparations.—(2-$HOC_6H_4CH=NCH_2CH_2OCH_2)_2$. 1,8-Diamino-3,6-dioxaoctane (2.00 g, 0.0135 mol) in ethanol (10 cm^3) was added to a solution of salicylaldehyde (3.295 g, 0.27

Table 3. Fractional atomic co-ordinates (× 10^5 for Re, × 10^4 for all other atoms) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	12 041(3)	10 615(2)	19 271(4)	C(7)	−286(8)	2 051(4)	3 145(10)
Cl	2 650(2)	1 932(1)	1 878(3)	C(8)	−1 053(9)	2 124(5)	515(11)
O(1)	1 920(5)	1 134(3)	4 177(6)	C(9)	−2 359(9)	1 747(5)	−348(10)
O(2)	−2 897(6)	1 605(3)	701(7)	C(10)	−4 094(9)	1 210(5)	110(12)
O(3)	−3 395(7)	316(4)	2 005(10)	C(11)	−4 221(10)	877(6)	1 438(14)
O(4)	2 791(6)	486(3)	2 339(6)	C(12)	−1 939(10)	427(5)	2 702(12)
O(5)	305(6)	979(3)	21(7)	C(13)	−1 418(9)	242(5)	1 531(13)
N(1)	−166(7)	1 813(3)	1 952(8)	C(14)	684(8)	−277(4)	2 888(10)
N(2)	124(7)	254(4)	2 240(9)	C(15)	2 118(8)	−456(4)	3 363(10)
C(1)	1 533(8)	1 415(4)	5 197(9)	C(16)	2 491(9)	−1 066(5)	4 100(11)
C(2)	2 275(6)	1 268(5)	6 755(10)	C(17)	3 778(10)	−1 310(5)	4 499(12)
C(3)	1 941(11)	1 582(5)	7 815(11)	C(18)	4 691(9)	−952(5)	4 145(11)
C(4)	875(11)	2 032(5)	7 375(11)	C(19)	4 330(8)	−361(4)	3 403(9)
C(5)	155(10)	2 167(5)	5 859(11)	C(20)	3 040(8)	−93(4)	3 024(9)
C(6)	476(9)	1 866(4)	4 730(10)				

mol) in ethanol (10 cm^3). The yellow solution was stirred overnight (18 h) at room temperature then filtered. The ethanol was removed from the filtrate by evaporation to give a yellow oil which was triturated with diethyl ether (2 × 40 cm^3) to afford a yellow solid which was isolated by filtration (4.75 g, 99%) (Found: C, 67.7; H, 6.9; N, 8.0. Calc. for $C_{20}H_{24}N_2O_4$: C, 67.4; H, 6.8; N, 7.9%).

[ReO(Cl){(2-$OC_6H_4CH{=}NCH_2CH_2OCH_2)_2$}]. The ligand, (2-$HOC_6H_4CH{=}NCH_2CH_2OCH_2)_2$ (0.15 g, 0.42 mmol), was dissolved in dry ethanol (160 cm^3) and dry dinitrogen passed through the solution to remove dioxygen. The salt [$NBu^n{}_4$][$ReOCl_4$] (0.267 g, 0.46 mmol) was added, and the colour of the solution rapidly changed to red-brown. Dinitrogen was again passed through the solution for *ca.* 1 min to remove free HCl and the solution was then heated under reflux for 90 min during which time it became bright green. A green powder was deposited on cooling the solution to room temperature and this was isolated by filtration, washed with ethanol (10 cm^3), and dried *in vacuo* (0.132 g, 53%) (Found: C, 40.7; H, 3.9; N, 4.9. Calc. for $C_{20}H_{22}ClN_2O_5Re$: C, 40.4; H, 3.7; N, 4.7%).

Structural Studies.—Crystal data. $C_{20}H_{22}ClN_2O_5Re$, M = 592.06, monoclinic, space group $P2_1/n$, a = 10.820(2), b = 20.508(3), c = 9.612(2) Å, β = 114.58(2)°, U = 1 939.6 $Å^3$, Z = 4, D_c = 2.028 g cm^{-3}, λ(Mo-K_α) = 0.710 69 Å, μ = 67.8 cm^{-1}, $F(000)$ = 1 152, T = 293 K.

Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer, using graphite-monochromated Mo-K_α radiation. 4 340 Reflections were measured in the range $2 < \theta < 25°$, 2 795 of which having $I > 2.5\sigma(I)$ were used in the analysis. The structure was solved by Patterson and Fourier methods[13] and refined by full-matrix least squares using anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were placed in calculated positions (C–H 1.08 Å) riding on their respective carbon atoms. Two isotropic thermal parameters were refined for the hydrogen atoms, one for those linked to the phenyl rings and the other for the remainder.

The calculations were terminated when all shift/estimated standard deviation (e.s.d.) ratios were less than 0.020 and R = 0.033; unit weights resulted in a satisfactory weighting analysis; residual electron density +0.9 to −1.3 e $Å^{-3}$. An empirical absorption correction was applied using DIFABS.[14]

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

Acknowledgements

We are grateful to the S.E.R.C. and Amersham International plc for their support (to H. J. B. and F. McQ.).

References

1. A. R. Middleton, A. F. Masters, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1979, 542.
2. M. A. A. F. de C. T. Carrondo, A. R. Middleton, A. C. Skapski, A. P. West, and G. Wilkinson, *Inorg. Chim. Acta*, 1980, **44**, L7.
3. U. Mazzi, E. Roncari, R. Rossi, V. Bertolasi, O. Traverso, and L. Magon, *Transition Met. Chem. (Weinheim, Ger.)*, 1980, **5**, 169.
4. A. Marchi, A. Duatti, R. Rossi, L. Magon, U. Mazzi, and A. Pasquetto, *Inorg. Chim. Acta*, 1984, **81**, 15.
5. E. Roncari, U. Mazzi, R. Rossi, A. Duatti, and L. Magon, *Transition Met. Chem. (Weinheim, Ger.)*, 1981, **6**, 169.
6. F. Refosco, F. Tisato, U. Mazzi, G. Bandoli, and M. Nicolini, *J. Chem. Soc., Dalton Trans.*, 1988, 611.
7. H. J. Banbery, F. McQuillan, T. A. Hamor, C. J. Jones, and J. A. McCleverty, *Polyhedron*, 1989, **8**, 559.
8. W. D. S. Motherwell, PLUTO, Program for plotting molecular and crystal structures, Report 'Cambridge Crystallographic Files,' University of Manchester Regional Computer Centre, Manchester, 1981.
9. N. Al Obaidi, P. D. Beer, J. P. Bright, C. J. Jones, J. A. McCleverty, and S. S. Salam, *J. Chem. Soc., Chem. Commun.*, 1986, 239.
10. T. A. Harmor, W. Hussain, C. J. Jones, and J. A. McCleverty, *Inorg. Chim. Acta*, 1988, **146**, 181.
11. E. Deutsch, K. Libson, S. Jurisson, and L. F. Lindoy, *Prog. Inorg. Chem.*, 1984, **30**, 75.
12. T. Lis and B. Jezowska-Trzebiatowska, *Acta Crystallogr., Sect. B*, 1976, **33**, 1248.
13. G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1978; SHELXS 86, Program for the solution of crystal structures, University of Göttingen, 1987.
14. N. Walker and D. Stuart, *Acta Crystallogr., Sect A*, 1983, **39**, 158.

Received 29th November 1988; *Paper* 8/04723E