Inorganica Chimica Acta, 44 (1980) L7–L8
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

A Novel Linear O–Re–O–Re–O–Re–O System: the synthesis and X-ray Structure of Di-μ-oxo-bis{[NN'-ethylenebis(acetylacetiminato)]oxorhenium(V)}[NN'-ethylenebis(acetylacetiminato)] rhenium(V) Perrhenate

MARIA A. A. F. de C. T. CARRONDO, A. ROBERT MIDDLETON, ANDRZEJ C. SKAPSKI, ANTHONY P. WEST and GEOFFREY WILKINSON

Chemical Crystallography and Inorganic Chemistry Laboratories, Imperial College, London SW7 2AY, U.K.

Received August 14, 1979

We have recently shown [1] that interaction of oxotrichlorobis(triphenylphosphine)rhenium(V), $ReOCl_3(PPh_3)_2$, with Schiff bases H_2L, without precautions to exclude air gives complexes of stoichiometry $Re_2O_3L_2$ that have a single μ-oxo bridge, whilst reaction under an inert atmosphere gives the complexes ReOClL. The latter complexes were air stable when the Schiff base ligand contained phenyl groups (H_2L = sal_2en, sal_2prop, sal_2phen). However, the complex containing $acac_2en$ reacts with oxygen to give brown crystals of stoichiometry $Re_4C_{36}H_{54}N_6O_{14}$·solvent(dichloromethane, benzene or methanol), X-ray crystallographic study of which has shown that the complex is $[Re_3O_4(acac_2en)_3]^+[ReO_4]^-$.

The compound is obtained by refluxing $ReOCl_3(PPh_3)_2$ (1 g, 1.2 mmol), H_2acac_2en (0.27 g, 1.2 mmol) and triethylamine (0.33 ml, 2.4 mmol) in dry degassed toluene (100 ml). The resulting solution was filtered and evaporated to dryness. The residue was washed with water and diethylether, and redissolved in dichloromethane–benzene. Dry oxygen was passed through this solution (0.5 hr) and the solution allowed to evaporate.

Initial precipitation gave dark brown composite needles of the dichloromethane solvate, whilst on further standing red brown plates were formed which are triclinic. The latter proved suitable for structural study, and have unit-cell dimensions a = 14.897(1), b = 32.259(2), c = 12.344(1) Å, α = 90.57(1), β = 103.84(1), γ = 100.59(1)° (at 12 °C), V = 5652.8 Å^3, space group $P\bar{1}$. X-ray intensity data were collected on a Siemens four-circle automatic diffractometer. With Cu-Kα radiation a total of 6151 independent reflections were measured (to θ = 38°), of which 874 were judged to be 'unobserved'.

Direct methods with the program MULTAN were used to locate the eight independent rhenium atoms, while Fourier syntheses yielded the rest of the structure. Least-squares refinement has now reached R = 0.048. The unique portion of the structure consists of two independent $[Re_3O_4(acac_2en)_3]^+$ cations, two tetrahedral perrhenate anions, three benzene molecules, plus some further solvent, probably dichloromethane, which is disordered and has not yet been fully characterised. It is the cations which are of interest. There are no chemically significant differences between the two crystallographically independent cations, and mean values of bond lengths and angles will therefore be used.

Since the first complex containing a linear O–Re–O–Re–O system, $Re_2O_3(dtc)_2$, was reported [2–4], the number of similar species has grown. The title cation is the first example of a linear O–Re–O–Re–O–Re–O system. Around this backbone the quadridentate $acac_2en$ ligands complete an octahedral coordination about each of the rhenium(V) atoms as shown in Fig. 1. The only related systems are the 'ruthenium red' cation $[Ru_3O_2(NH_3)_{14}]^{6+}$ [5–7] and its ethylenediamine analogue $[Ru_3O_2(en)_2(NH_3)_{10}]^{6+}$ [8, 9], which also contain two linear oxygen bridges.

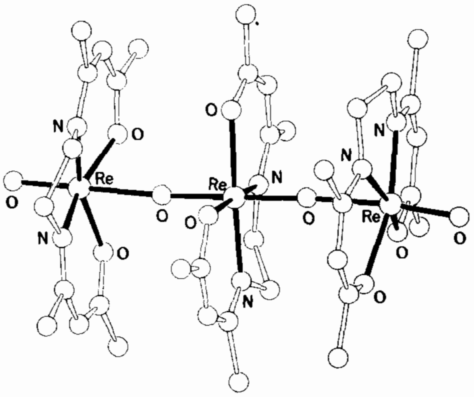

Fig. 1. Structure of the $[Re_3O_4(acac_2en)_3]^+$ cation.

The sequence of Re–O bond lengths along the backbone of the cation suggests that three different bond orders are involved. Thus the terminal Re–O bonds are the shortest with a mean length of 1.683(5) Å, *trans* to these are two long bonds with a mean length of 2.076(12) Å, while the two bonds on either side of the central rhenium atom are 1.785(7) Å in length. The two oxygen bridges in this system are therefore highly asymmetric.

Average bond lengths to the Schiff bases are unexceptional, with Re–O of 2.069 Å (range 2.03–2.12 Å) and Re–N of 2.034 Å (range 1.99–2.07 Å). There is, however, a difference between these ligands in that the central one is relatively undistorted, while the outer ones are both pushed towards the centre of the cation, with a mean O(terminal)–Re–O(Schiff) angle of 96.2° (range 94.2–98.6°) and a mean O(terminal)–Re–N(Schiff) angle of 99.5° (range 97.2–101.2°). These angles are a consequence of the short terminal

Re–O multiple bonds with their resultant electronic/steric repulsion.

Other data are in accord with the above, thus the complex is diamagnetic in the solid state and gives a conducting solution in nitromethane (λ_M = 69) indicative of a 1:1 electrolyte. The i.r. spectrum is dominated by ligand bands including a strong band at 1572 cm^{-1} $\nu(C=N)$, a shift to lower wavenumber being consistent with the quadridentate ligand. A band at 968 cm^{-1} due to the terminal $\nu(Re=O)$ is more intense than that in $Re_2O_3(acac_2en)_2$ but weaker than in $ReOCl(acac_2en)$ [1], whilst the strong band at 715 cm^{-1} similar to that in $Re_2O_3(acac_2en)_2$ can be assigned to the μ-oxo bridges. A further strong band at 905 cm^{-1} is due to the perrhenate anion.

The Raman spectrum has a broad band at *ca.* 1580 cm^{-1} $\nu(C=N)$ and a band of medium intensity at 968 cm^{-1} due to the terminal $\nu(Re=O)$. Weak bands appear at 895 cm^{-1}, 926 cm^{-1}, 960 cm^{-1} and 980 cm^{-1} corresponding to the bands in a spectrum of $KReO_4$. The strongest band in this region occurs at 854 cm^{-1} and is due to the Re_3O_4 backbone.

The n.m.r. spectrum has a complex doublet at 1.4–1.5 ppm (6) due to the methyl protons, and sharp singlets at 2.78 ppm (2) and 4.91 ppm (1) due to the methylene and methyne protons respectively.

Acknowledgements

We thank the British Council for a Scholarship (to M.A.A.F. de C.T.C.), the Science Research Council for a Research Studentship (to A.R.M.), and the Wiltshire County Council Education Authority for a maintenance grant (to A.P.W.).

References

1 A. R. Middleton, A. F. Masters and G. Wilkinson, *J. Chem. Soc. Dalton,* 542 (1979).
2 S. R. Fletcher, J. F. Rowbottom, A. C. Skapski and G. Wilkinson, *Chem. Comm.,* 1572 (1970).
3 J. F. Rowbottom and G. Wilkinson, *J. Chem. Soc. Dalton,* 826 (1972).
4 S. R. Fletcher and A. C. Skapski, *J. Chem. Soc. Dalton,* 1073 (1972).
5 J. M. Fletcher, B. F. Greenfield, C. J. Hardy, D. Scargill and J. L. Woodhead, *J. Chem. Soc.,* 2000 (1961).
6 C. K. Jφrgenson and L. E. Orgel, *Mol. Phys., 4,* 215 (1961).
7 M. A. A. F. de C. T. Carrondo, W. P. Griffith, J. P. Hall and A. C. Skapski, *Biochim. Biophys. Acta,* submitted for publication.
8 P. M. Smith, T. Fealey, J. E. Earley and J. V. Silverton, *Inorg. Chem., 10,* 1943 (1971).
9 J. E. Earley and T. Fealey, *Inorg. Chem., 12,* 323 (1973).