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The Synthesis and X-ray Crystal Structure of the Trinuclear Complex $[\{ORe(OC_6H_4\text{-}2\text{-}CMe{=}NCH_2-)_2(\mu\text{-}O)\}_2Re(OC_6H_4\text{-}2\text{-}CMe{=}NCH_2-)_2]Cl\cdot H_2O\cdot 0.5CH_2Cl_2$

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Abstract

The reaction between $[ReOCl_4]^-$ and $(HOC_6H_4\text{-}2\text{-}CMe{=}NCH_2-)_2$ in the presence of air produces the trinuclear complex $[\{ORe(OC_6H_4\text{-}2\text{-}CMe{=}NCH_2-)_2(\mu\text{-}O)\}_2Re(OC_6H_4\text{-}2\text{-}CMe{=}NCH_2-)_2]Cl\cdot H_2O\cdot 0.5CH_2Cl_2$ which has been characterised by a single crystal X-ray diffraction study. The molecule contains a near linear axial $\{OReOReOReO\}^{7+}$ core with the 'equatorial' coordination sites on Re occupied by tetradentate $(OC_6H_4\text{-}2\text{-}CMe{=}NCH_2-)_2$ ligands. The mean terminal Re=O distance is 1.679 Å while the mean Re–O distance for the bonds *trans* to the terminal Re=O bonds is 2.074 Å. The mean Re–O distance for the bonds either side of the central Re atom in the chain is 1.792 Å.

Introduction

The reactions between $[ReO(PPh_3)_2Cl_3]$ and a variety of tetradentate Schiff base ligands LH_2 (including $LH_2 = (acac)_2enH_2$, $\{HOC(Me)CHC(Me){=}NCH_2-\}_2$ and sal_2enH_2, $\{OC_6H_4\text{-}2\text{-}CH{=}NCH_2-\}_2$) have been described by Wilkinson and co-workers [1, 2]. In the presence of air the reactions afforded complexes of the formula $[Re_2O_3L_2]$ but in the absence of air complexes of formula [ReOLCl] were obtained. These latter compounds were found to be air stable when the ligand L was derived from salicylaldehyde but when L = $acac_2en$ oxidation occurred to give $[Re_3O_4(acac_2en)_3]^+$ which was characterised by a single crystal X-ray diffraction study [2]. During our investigation of the reactions between $[ReOCl_4(H_2O)]^-$ and some tetradentate Schiff base ligands it has been found that the related complex $[Re_3O_4(Mesal_2en)_3]^+$ ($Mesal_2enH_2$ = $\{HOC_6H_4\text{-}2\text{-}CMe{=}NCH_2-\}_2$) can be synthesised. We have characterised this material by a single crystal X-ray diffraction study.

Discussion

Synthetic Studies

Previous reports of the synthesis of the ligand $Mesal_2enH_2$ have involved demetallation of its Cu(II) complex [3–5]. A simpler preparative procedure adopted here involves the direct reaction of 1,2-diaminoethane with 2-acetylphenol to give $Mesal_2enH_2$ in high yield. The reaction between $Mesal_2enH_2$ and $Bu^n{}_4N[ReOCl_4(H_2O)]$ in ethanol in the absence of air initially affords a green precipitate insoluble in most organic solvents. The infrared spectrum of this material contains bands attributable to the tetradentate ligand, including ν(C=N) at 1600 cm^{-1} compared to 1610 cm^{-1} for the free ligand, in addition to ν(Re=O) at 960 cm^{-1}. The elemental analysis of this compound is in accord with the formulation $[ReOCl(Mesal_2en)]\cdot H_2O$ but further characterisation has been precluded by the insoluble nature of the material.

Although $[ReOCl(Mesal_2en)]\cdot H_2O$ itself is insoluble in methanol it gradually dissolves in refluxing methanol exposed to the air to give a soluble brown complex. The infrared spectrum of this brown material exhibits bands attributable to the tetradentate ligand, with ν(C=N) at 1599 cm^{-1} in addition to a new band at 715 cm^{-1} attributable to the O–Re–O moiety [2]. A relatively weak band was observed at 968 cm^{-1} where ν(Re=O) would be expected to appear [2]. A conductivity measurement on a solution of the brown material in MeCN gave a value of 176 ohm^{-1} cm^2 mol^{-1} indicating that the compound was a salt, and the elemental analysis of a sample recrystallised from CH_2Cl_2 was in accord with the formulation $[Re_3O_4(Mesal_2en)_3]Cl\cdot 2H_2O\cdot CH_2Cl_2$. The 270 MHz ^1H NMR spectrum of the brown compound was in accord with the results of the X-ray diffraction study described below, indicating that the trimer retains its integrity in solution. The aromatic protons of the $Mesal_2en$ ligand appeared as partially overlapping sets of four doublets and four triplets with $^3J_{HH} = 8$ Hz. The doublets attributable to the protons adjacent to the O or

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TABLE 1. Molecular geometry[a]

Selected bond lengths (Å)

Re(1)---N(1A)	2.032(15)	Re(2)---O(2B)	2.001(15)
Re(1)---N(2A)	2.083(15)	Re(2)---O(AB)	1.785(11)
Re(1)---O(1A)	1.988(12)	Re(2)---O(BC)	1.799(11)
Re(1)---O(2A)	1.997(13)	Re(3)---N(1C)	2.078(15)
Re(1)---O(A)	1.678(12)	Re(3)---N(2C)	2.056(20)
Re(1)---O(AB)	2.073(11)	Re(3)---O(1C)	1.966(16)
Re(2)---N(1B)	2.102(16)	Re(3)---O(2C)	1.964(12)
Re(2)---N(2B)	2.048(13)	Re(3)---O(BC)	2.076(12)
Re(2)---O(1B)	1.987(12)	Re(3)---O(C)	1.680(15)

Selected bond angles (°)

N(1A)–Re(1)–N(2A)	83.5(6)	O(2B)–Re(2)–O(AB)	93.1(6)
N(1A)–Re(1)–O(1A)	92.7(6)	N(1B)–Re(2)–O(BC)	85.8(6)
N(2A)–Re(1)–O(1A)	163.3(5)	N(2B)–Re(2)–O(BC)	88.8(5)
N(1A)–Re(1)–O(2A)	166.4(5)	O(1B)–Re(2)–O(BC)	93.4(5)
N(2A)–Re(1)–O(2A)	92.5(6)	O(2B)–Re(2)–O(BC)	93.9(6)
O(1A)–Re(1)–O(2A)	87.4(5)	O(AB)–Re(2)–O(BC)	172.1(5)
N(1A)–Re(1)–O(A)	91.9(6)	N(1C)–Re(3)–N(2C)	83.9(7)
N(2A)–Re(1)–O(A)	96.9(6)	N(1C)–Re(3)–O(1C)	91.1(7)
O(1A)–Re(1)–O(A)	99.5(5)	N(2C)–Re(3)–O(1C)	165.1(6)
O(2A)–Re(1)–O(A)	101.5(6)	N(1C)–Re(3)–O(2C)	160.5(6)
N(1A)–Re(1)–O(AB)	80.4(5)	N(2C)–Re(3)–O(2C)	93.6(6)
N(2A)–Re(1)–O(AB)	78.1(5)	O(1C)–Re(3)–O(2C)	86.5(6)
O(1A)–Re(1)–O(AB)	85.2(5)	N(1C)–Re(3)–O(BC)	77.5(6)
O(2A)–Re(1)–O(AB)	86.1(5)	N(2C)–Re(3)–O(BC)	79.1(6)
O(A)–Re(1)–O(AB)	171.2(5)	O(1C)–Re(3)–O(BC)	86.2(6)
N(1B)–Re(2)–N(2B)	84.4(6)	O(2C)–Re(3)–O(BC)	83.0(5)
N(1B)–Re(2)–O(1B)	92.0(5)	N(1C)–Re(3)–O(C)	98.5(7)
N(2B)–Re(2)–O(1B)	175.7(6)	N(2C)–Re(3)–O(C)	92.3(8)
N(1B)–Re(2)–O(2B)	176.7(5)	O(1C)–Re(3)–O(C)	102.3(7)
N(2B)–Re(2)–O(2B)	92.4(6)	O(2C)–Re(3)–O(C)	100.8(6)
O(1B)–Re(2)–O(2B)	91.2(5)	O(BC)–Re(3)–O(C)	170.8(7)
N(1B)–Re(2)–O(AB)	87.6(6)	Re(1)–O(AB)–Re(2)	171.9(8)
N(2B)–Re(2)–O(AB)	86.3(5)	Re(2)–O(BC)–Re(3)	170.5(8)
O(1B)–Re(2)–O(AB)	91.1(5)		

[a] e.s.d.s given in parentheses.

CMe=N substituents appeared at $\delta_{TMS} = 7.37$, 7.31, 7.01 and 6.92 ppm in the area ratio 1:2:1:2, in accord with the two terminal ligands being equivalent and the central ligand being unique. Similarly the triplets attributable to the protons not adjacent to the O or CMe=N substituents appeared at $\delta_{TMS} =$ 7.38, 6.66, 6.61 and 6.52 ppm in the area ratio 2:2:1:1. The methylene protons of the terminal ligands appeared as two complex multiplets at $\delta_{TMS} =$ 4.20 and 3.95 ppm while the methylene protons associated with the central ligand appeared as a singlet at $\delta_{TMS} = 3.83$ ppm, being in a more symmetric environment. The methyl protons of the central ligand appeared as a singlet at $\delta_{TMS} = 2.04$ ppm while those attributable to the terminal ligands appeared as two singlets at $\delta_{TMS} = 2.33$ and 2.36 ppm. Crystals of the brown complex suitable for X-ray analysis were obtained by slow crystallisation from CH_2Cl_2 solution.

Structural Studies

Fractional atomic coordinates from the single crystal X-ray diffraction study of $[\{ORe(OC_6H_4\text{-}2\text{-}CMe{=}NCH_2\text{–})_2(\mu\text{-}O)\}_2Re(OC_6H_4\text{-}2\text{-}CMe{=}NCH_2\text{–})_2]Cl{\cdot}H_2O{\cdot}0.5CH_2Cl_2$ have been deposited (see 'Supplementary Material'). Some selected bond lengths and angles are presented in Table 1 and the structure of the compound is illustrated in Fig. 1. The structure of the $[\{ReO(Mesal_2en)(\mu\text{-}O)\}_2Re(Mesal_2en)]^+$ cation is similar to that found [2] for $[\{ReO(acac_2en)(\mu\text{-}O)\}_2Re(acac_2en)]^+$ and contains a near linear $\{O{=}Re{-}O{-}Re{-}O{-}Re{=}O\}^{7+}$ core. As in $[Re_3O_4(acac_2en)_3]^+$, the sequence of Re–O bond lengths along the backbone of this cation suggests that three different bond orders are involved. Thus the terminal Re–O bonds are the shortest, with a mean length of 1.679 Å. *trans* to these are two long bonds with a mean length of 2.074 Å, while the two bonds on either side of the central rhenium atom have a mean

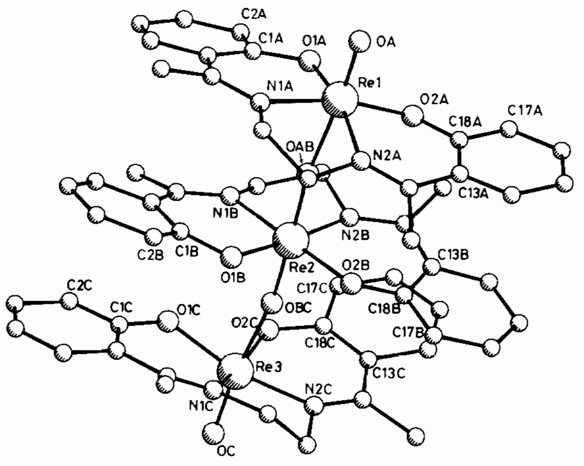

Fig. 1. The structure of the cation showing the numbering of atoms bound to rhenium. Hydrogen atoms have been omitted for clarity.

length of 1.792 Å. The two oxygen bridges in this system are therefore highly asymmetric.

The complex has an overall positive charge and is associated with a chloride anion. This charge can be explained by describing the central chain as involving Re(V) centres in $\{O{=}Re{-}{-}O{-}Re{-}O{-}{-}Re{=}O\}^{7+}$ consistent with the asymmetry of the oxygen bridges. The coordination around the central rhenium atom deviates only slightly from being perfectly octahedral with a maximum angular distortion of 7.9°. It is to be expected that there will be some angular distortion in such a trimeric complex, especially at the central rhenium atom, in order to accommodate three bulky Schiff base ligands around the O=Re–O–Re–O–Re=O backbone with the minimum of stereochemical strain. However, the terminal rhenium atoms exhibit considerably greater distortion from regular octahedral geometry with respect to the angles involving the Re=O double bonds. Our complex and the related $[Re_3O_4(acac_2en)_3]^+$ exhibit a similar degree of distortion; 11.2° for $[Re_3O_4(acac_2en)_3]^+$ and 12.3° for $[Re_3O_4(Mesal_2en)_3]^+$. This can be attributed to the electronic repulsion of the short, terminal Re=O bonds, which push both outer ligands towards the centre of the cation. However, the maximum angular distortion from octahedral for $[Re_3O_4(Mesal_2en)_3]^+$ occurs in the *trans*-O(Mesal$_2$en)–Re–N(Mesal$_2$en) bonds and is 16.7° for Re(1) and 19.5° for Re(3) (Table 1).

The three ligands and their coordinated rhenium atoms are each coplanar to within ± 1 Å and all of the phenyl rings are planar to within 0.04 Å. The phenyl rings C(1A)–C(6A) and C(1B)–C(6B) lie nearly parallel to one another at an angle of 12.8° (Fig. 1). Similarly, the phenyl rings C(13B)–C(18B) and C(13C)–C(18C) make an angle of 13.6°. In each case they overlie one another with interplanar distances of *c*. 3.7 Å. Energetically, it is favourable for the rings to overlap in this way with the possibility of inter-ring π-bonding interactions, and these interactions may contribute towards the distortion of coordination around the terminal rhenium atoms. The chloride ion is disordered between two sites with occupancy factors of 0.6(2) and 0.4(2). Each molecule of the complex is also associated with a molecule of water and half a molecule of dichloromethane in the sample selected for X-ray studies.

Experimental

Synthetic Studies

Reagents were used as received and solvents were dried by standard techniques before use. $Bu_4N[ReOCl_4(H_2O)]$ was prepared according to a previously described method [6]. Infrared spectra were recorded from KBr discs using a PE 297 instrument. ^1H NMR spectra were obtained at 270 MHz using a Jeol JNM GX270 instrument.

$\{HOC_6H_4\text{-}2\text{-}CMe{=}NCH_2\text{-}\}_2(Mesal_2enH_2)$

1,2-Diaminoethane (0.25 g, 4.1 mmol) was added dropwise to 2-acetylphenol (1.13 g, 8.3 mmol) and the resulting mixture heated on a steam bath for 30 min. After cooling the yellow solid which had formed was washed with diethyl ether and dried *in vacuo* to give a quantitative yield of the product. *Anal.* Found: C, 72.8; H, 6.7; N, 9.4. Calc. for $C_{18}H_{20}N_2O_2$: C, 73.0; H, 6.8; N, 9.5%.

$[\{ORe(OC_6H_4\text{-}2\text{-}CMe{=}NCH_2\text{-})_2(\mu\text{-}O)\}_2Re(OC_6H_4\text{-}2\text{-}CMe{=}NCH_2\text{-})_2]Cl$

$[Bu_4N][ReOCl_4(H_2O)]$ (297 mg, 0.49 mmol) and $Mesal_2H_2$ (150 mg, 0.5 mmol) were added to dry ethanol (30 cm^3) and the mixture heated under reflux under a nitrogen atmosphere for 2 h. After this time the resulting green powder (134 mg, 50%) was collected by filtration, washed with ethanol and dried in air. *Anal.* Found: C, 39.0; H, 3.3; N, 5.6. Calc. for $C_{18}H_{18}N_2O_3ReCl\cdot H_2O$: C, 39.3; H, 3.7; N, 5.1%. This material was then suspended in methanol and the mixture heated under reflux in air for 30 min. After this time a brown solution had formed. The solvent was then removed *in vacuo* and the solid obtained recrystallised from dichloromethane. *Anal.* Found: C, 39.3; H, 3.5; N, 4.9. Calc. for $C_{54}H_{54}N_6O_{10}Re_3Cl\cdot 2H_2O\cdot CH_2Cl_2$: C, 39.70; H, 3.6; N, 5.1%.

Structural Studies

Crystals of $C_{54}H_{54}N_6O_{10}Re_3Cl\cdot H_2O\cdot 0.5CH_2Cl_2$, are monoclinic, space group $P2_1/n$, $a = 19.353(2)$, $b = 11.371(11)$, $c = 27.426(5)$ Å, $\beta = 108.93(1)°$, $U = 5709.0$ Å^3, $Z = 4$, $M = 1601.6$, $D_{calc} = 1.863$ g cm^{-3}, λ(Mo Kα) = 0.71069 Å, $\mu = 68.5$ cm^{-1}, $F(000) = 3092$, $T = 293$ K.

The diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. A total of 10 427 reflections were scanned in the range $\theta = 2-25°$ of which 7403 were unique and 5405 were considered observed $[F > 5\sigma(F)]$ and were used in the analysis. The structure was determined by Patterson and Fourier methods and refined by blocked full-matrix least-squares [7]. An empirical absorption correction [8] was applied. Isotropic thermal parameters were assigned to all except the three rhenium atoms and the chloride ion; these were refined with anisotropic thermal parameters. Unit weights produced a satisfactory weighting analysis. The refinement was terminated when all shifts were less than one fifth of their e.s.d.s, and $R = 0.0537$ for the 5405 observed reflections. The residual electron density in a final difference map was +2.03 to −1.26 e Å^{-3}.

Computations were carried out on the University of Birmingham Honeywell computer and on the Amdahl 5890-300E at the University of Manchester Regional Computer Centre with the SHELX [7], DIFABS [8] and PLUTO [9] programs.

Supplementary Material

Fractional atomic coordinates and temperature factors have been deposited with the Cambridge Crystallographic Data Centre.

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