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A Novel Tetranuclear Compound: Crystal Structure and Mass Spectra of $[Re_4(C_6H_5NCOCH_3)_6(Cl)(\mu\text{-}O)(\mu\text{-}OH)(MeOH)_3][ReO_4]_2$

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The reaction between $Re_2(C_6H_5NCOCH_3)_4Cl_2$ and water in air yields a blue compound $[Re_4(C_6H_5NCOCH_3)_6(Cl)(\mu\text{-}O)(\mu\text{-}OH)(MeOH)_3][ReO_4]_2$. It crystallizes in a triclinic cell with $a = 12.356(3)$ Å, $b = 14.820(6)$ Å, $c = 20.064(6)$ Å, $\alpha = 103.38(3)°$, $\beta = 91.61(2)°$, $\gamma = 110.37(2)°$, $V = 3327(2)$ Å^3, and $Z = 2$. The X-ray crystallography revealed an unprecedented tetranuclear structure together with two perrhenate ions. The tetranuclear dication is formed by two quadruply bonded dirhenium units linked through an oxygen ligand and a hydroxy ligand. One unit uses two rhenium atoms and the other unit uses only one rhenium atom to form a Re−Re−O−Re−OH five-membered ring. The formula of this compound was further confirmed by mass spectral analysis.

Introduction

The synthesis and characterization of some amidato-bridged dirhenium compounds have presented some interesting ligand arrangements.[1] With sterically less bulky ligands, i.e., acetanilide, benzamide, and benzanilide, a cis arrangement of the $Re_2O_4N_4$ core (C_{2h} virtual symmetry) was observed. With the relatively bulky ligand 2,6-dimethylacetanilide, the trans arrangement of $Re_2O_4N_4$ (D_{2d} virtual symmetry) was observed. A similar variability with steric requirements has been seen in the dimolybdenum system.[2−6] In contrast, all amidato-bridged dichromium compounds with known structures have the trans (D_{2d}) ligand arrangement.[2−4,7] The structural differences seen in the four previously reported dirhenium compounds aroused our interest in checking their reactivities. We found that $Re_2(2,6\text{-xylyl-}NCOCH_3)_4Cl_2$, with a trans ligand arrangement, was very stable toward air and water, but all the cis compounds, i.e., $Re_2(C_6H_5NCOCH_3)_4Cl_2$, $Re_2(HNCOC_6H_5)_4Cl_2$, and $Re_2(C_6H_5NCOC_6H_5)_4Cl_2$, were reactive toward air and water. In the $Re_2(C_6H_5NCOCH_3)_4Cl_2$ case, the product of reaction with water and air was crystallized as a tetranuclear compound, in each half of which there was a trans ligand arrangement.

Experimental Section

$Re_2(C_6H_5NCOCH_3)_4Cl_2$, $Re_2(HNCOC_6H_5)_4Cl_2$, $Re_2(C_6H_5NCOC_6H_5)_4Cl_2$, and $Re_2(2,6\text{-xylyl-}NCOCH_3)_4Cl_2$ were synthesized as previously described.[1] UV−vis spectra were recorded on dichloromethane solutions with a Cary-17D spectrometer (800−200 nm). The ^{1}H NMR spectra were taken at room temperature in $CDCl_3$ on a Varian XL-200E spectrometer. The mass spectrometry data were collected on a ^{252}Cf-plasma desorption mass spectrometer.

Preparation of $[Re_4(C_6H_5NCOCH_3)_6(Cl)(\mu\text{-}O)(\mu\text{-}OH)(MeOH)_3][ReO_4]_2$. A 0.01 g sample of $Re_2(C_6H_5NCOCH_3)_4Cl_2$ was dissolved in 10 mL of CH_2Cl_2 in a 100 mL beaker, and 10 mL of distilled water was added. After vigorous shaking for 2 min, a blue color developed from the originally yellow solution. Methanol (15 mL) was added to help mix the water with the dichloromethane, and the reaction was seen to be accelerated. After all $Re_2(C_6H_5NCOCH_3)_4Cl_2$ had reacted and the color had changed to deep blue, the solution was filtered and left in the open air to dry. This gave a blue solid with white plate crystals on the surface. The ^{1}H NMR spectrum of the latter proved them to be acetanilide. The blue solid was redissolved in methanol, and the solution was left in a refrigerator (5 °C) for slow evaporation. Dark blue, block crystals were formed during a period of 3 weeks. The yield of crude product was nearly 100%. It is soluble in many organic solvents. The visible absorption spectrum of this compound showed a very broad peak at 644 nm, a shoulder at 550 nm, and a sharp absorption peak at 387 nm. The ^{1}H NMR spectrum of a solution of the dried crystal powder had three peaks around 2.95 ppm that correspond to the CH_3 groups on the bridging $C_6H_5NCOCH_3$ ligands and a set of multiplets at 7.32 ppm representing the C_6H_5 group.

The reactions of the other three compounds with air and water were carried out in the same way. With $Re_2(HNCOC_6H_5)_4Cl_2$ and $Re_2(C_6H_5NCOC_6H_5)_4Cl_2$, the color changed from yellow to dark green and deep brown, respectively, but no crystals were obtained. There was no change observed for $Re_2(2,6\text{-xylyl-}NCOCH_3)_4Cl_2$, and the ^{1}H NMR spectra were the same before and after the reaction.

X-ray Crystallography. A dark blue, block-shaped crystal was mounted on the tip of a glass fiber with epoxy resin. Twenty-five reflections indexed in the range $20° \leq 2\theta \leq 27°$ gave a triclinic cell. The cell dimensions were confirmed by axial photographs. The data were collected on a Nicolet P3 diffractometer by employing the $2\theta-\omega$ scan method in the range $4° \leq 2\theta \leq 46°$. The total intensity decay during the data collection was 8.3%. The data were corrected for absorption and decay. Direct methods were used to locate the rhenium atoms, and the rest of the atoms were found on alternate difference Fourier maps. A large peak (3.25 e/Å^3) was found on the final Fourier map next to a rhenium atom. We attribute this to inadequacy of the ψ-scan absorption correction. The crystallographic data are listed in Table 1.

Results and Discussion

Structure of the Solid. The title compound consists of large tetranuclear cations, whose structure will be discussed in detail shortly, and perrhenate anions. There are two crystallographically distinct ReO_4^- ions, one of which refined reasonably well with Re−O distances in the range 1.63(3)−1.72(4) Å (average 1.69 Å) and O−Re−O distances in the range 105(2)−116(2)° (average 109.3°). Thermal parameters were moderately high for the four oxygen atoms in this ReO_4^- ion (6.9−12 Å^2, with an average of 8.5 Å^2). Thus, this ReO_4^- ion is evidently

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Table 1. Crystal Data for $[Re_4(C_6H_5NCOCH_3)_6(Cl)(\mu\text{-}O)(\mu\text{-}OH)(MeOH)_3][ReO_4]_2$

formula	$Re_6ClO_{19}N_6C_{51}H_{61}$
fw	2214.74
space group	$P\bar{1}$
a, Å	12.356(3)
b, Å	14.820(6)
c, Å	20.064(6)
α, deg	103.38(3)
β, deg	91.61(2)
γ, deg	110.37(2)
V, Å^3	3327(2)
Z	2
d_{calc}, g/cm^3	2.210
crystal size, mm	0.42 × 0.45 × 0.21
μ(Mo Kα), cm^{-1}	111.274
data collection instrument	Nicolet P3
wavelength of radiation monochromated in incident beam (Mo Kα), Å	0.710 73
orientation reflections: no.; range (θ), deg	25; $20 \leq 2\theta \leq 27$
temp, °C	20
scan method	$2\theta-\omega$
data collection range, deg	$4 \leq 2\theta \leq 46$
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	6094, 4885
no. of parameters refined	363
transmission factors: max, min	1.00, 0.59
R^a	0.073
$R_w{}^b$	0.086
quality-of-fit indicator^c	2.024
largest shift/esd, final cycle	0.02
largest peak, e/Å^3	3.247

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

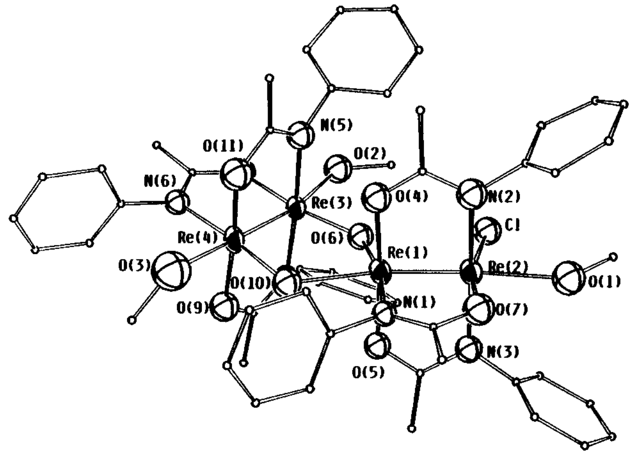

Figure 1. ORTEP drawing of $[Re_4(C_6H_5NCOCH_3)_6(Cl)(\mu\text{-}O)(\mu\text{-}OH)(MeOH)_3][ReO_4]_2$. Atoms are represented by 50% thermal ellipsoids except for carbon atoms, which are drawn as circles with arbitrary radii.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Re_4(C_6H_5NCOCH_3)_6(Cl)(\mu\text{-}O)(\mu\text{-}OH)(MeOH)_3][ReO_4]_2$

Bond Distances			
Re(1)−Re(2)	2.213(2)	Re(3)−Re(4)	2.200(2)
Re(1)−O(4)	1.99(2)	Re(3)−ReO(2)	2.28(2)
Re(1)−O(5)	2.02(2)	Re(3)−ReO(6)	1.94(2)
ReRe(1)−O(6)	1.88(2)	Re(3)−ReO(8)	2.06(2)
Re(1)−ReO(10)	2.29(2)	Re(3)−ReN(4)	2.12(2)
Re(1)−N(1)	2.07(3)	Re(3)−N(5)	2.10(2)
Re(2)−Cl(1)	2.34(1)	Re(4)−(3)	2.38(3)
Re(2)−O(1)	2.38(2)	Re(4)−O(9)	2.01(2)
Re(2)−O(7)	1.98(3)	Re(4)−ReO(10)	2.06(2)
Re(2)−N(2)	2.08(2)	Re(4)−ReO(11)	1.97(2)
Re(2)−N(3)	2.06(2)	Re(4)−ReN(6)	2.06(3)

Bond Angles			
Re(2)−Re(1)−O(4)	93.0(6)	Re(4)−Re(3)−O(6)	101.4(7)
Re(2)−Re(1)−O(5)	91.8(5)	Re(4)−Re(3)−O(8)	91.2(6)
Re(2)−Re(1)−O(6)	105.7(6)	Re(4)−Re(3)−N(4)	88.2(7)
Re(2)−Re(1)−O(10)	171.1(6)	Re(4)−Re(3)−N(5)	89.4(8)
Re(2)−Re(1)−N(1)	87.1(6)	O(2)−Re(3)−O(6)	94.3(8)
O(4)−Re(1)−O(5)	174.7(8)	O(2)−Re(3)−O(8)	73.1(8)
O(4)−Re(1)−O(6)	90.7(9)	O(2)−Re(3)−N(4)	90.1(9)
O(4)−Re(1)−O(10)	90.2(7)	O(2)−Re(3)−N(5)	91.4(9)
O(4)−Re(1)−N(1)	87.9(9)	O(6)−Re(3)−O(3)	176.4(9)
O(5)−Re(1)−O(6)	90.3(8)	O(6)−Re(3)−N(4)	91.4(8)
O(5)−Re(1)−O(10)	84.7(7)	O(6)−Re(3)−N(5)	92.0(9)
O(5)−Re(1)−N(1)	90.0(9)	O(8)−Re(3)−N(4)	88.3(8)
O(6)−Re(1)−O(10)	82.5(9)	O(8)−Re(3)−N(5)	88.7(9)
O(6)−Re(1)−N(1)	167.2(8)	N(4)−Re(3)−N(5)	176.2(9)
O(1)−Re(1)−N(1)	84.8(9)	Re(3)−Re(4)−O(3)	170.8(7)
Re(1)−Re(2)−Cl(1)	102.2(2)	Re(3)−Re(4)−O(9)	93.2(7)
Re(1)−Re(2)−O(1)	168.7(7)	Re(3)−Re(4)−O(10)	95.1(6)
Re(1)−Re(2)−O(7)	93.1(6)	Re(3)−Re(4)−O(11)	93.8(7)
Re(1)−Re(2)−N(2)	89.0(7)	Re(3)−Re(4)−N(6)	90.4(7)
Re(1)−Re(2)−N(3)	89.9(7)	O(3)−Re(4)−O(9)	93.8(9)
Cl(1)−Re(2)−O(1)	88.9(7)	O(3)−Re(4)−O(10)	78.9(9)
Cl(1)−Re(2)−O(7)	164.7(6)	O(3)−Re(4)−O(11)	79.3(9)
Cl(1)−Re(2)−N(2)	93.4(9)	O(3)−Re(4)−N(6)	96(1)
Cl(1)−Re(2)−N(3)	91.0(8)	O(9)−Re(4)−O(10)	89.7(8)
O(1)−Re(2)−O(7)	75.8(9)	O(9)−Re(4)−O(11)	173(1)
O(1)−Re(2)−N(2)	88.7(9)	O(9)−Re(4)−N(6)	88.9(9)
O(1)−Re(2)−N(3)	91.6(8)	O(10)−Re(4)−O(11)	90.0(9)
O(7)−Re(2)−N(2)	86.(1)	O(10)−Re(4)−N(6)	174(1)
O(7)−Re(2)−N(3)	90(1)	O(11)−Re(4)−N(6)	90.7(9)
N(2)−Re(2)−N(3)	176.(1)	Re(1)−O(6)−Re(3)	136.(1)
Re(4)−Re(3)−O(2)	164.2(5)	Re(1)−O(10)−Re(4)	123.(1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

librating moderately, but not excessively. The other one, however, refined to a badly distorted result, although it was still recognizable. No doubt the poor behavior of this ReO_4^- ion under refinement contributes to the somewhat high residuals.

The cationic part of this compound, $[Re_4(C_6H_5NCOCH_3)_6(Cl)(\mu\text{-}O)(\mu\text{-}OH)(MeOH)_3]^{2+}$, is a tetranuclear species with a very novel structural type. It is represented in the ORTEP drawing in Figure 1, and important bond distances and bond angles are listed in Table 2. It contains two quadruply bonded dirhenium units, and these two units are connected by an oxygen ligand and a hydroxy ligand to form a five-membered ring containing three rhenium atoms. The three remaining axial positions of these dirhenium units are occupied by methanol molecules. The possibility that there are methoxy groups on the axial positions can be excluded by checking the Re−O bond distances and Re−Re−O bond angles. The Re−O bond distances in this case are in the range of 2.28(2)−2.38(3) Å, which is much longer than the rhenium to methoxy bond distance of 2.033(3) Å in $Re_2(DTolF)_4(OMe)_2$.[8] The nonlinearity of the Re−Re−O units also implies the neutral nature of the axial ligands since the methoxy group (MeO^-) would cause the Re−Re−O angle to approach 180°.[8] The distinction between the μ-oxo ligand and the μ-hydroxo ligand can be clarified by looking at the bond distances. The oxo ligand, O(6), is tightly bonded to both rhenium atoms with an Re(1)−O(6) distance of 1.88(2) Å and an Re(3)−O(6) distance of 1.94(2) Å. On the other hand, the hydroxo ligand, O(10)H, is strongly bonded to only one rhenium atom (2.06(3) Å for the Re(4)−O(10) bond distance) and rather weakly bonded to another rhenium atom (2.29(2) Å for the Re(1)−O(10) distance). The bidentate coordination mode of the remaining amidato ligands persists, but the ligand arrangement around the dimetal units has been changed from cis to trans.

The only other examples of tetranuclear rhenium compounds containing metal−metal bonds are the quite different rectangular anions $[Re_4Cl_8(\mu\text{-}O)_2(\mu\text{-}OMe)(\mu\text{-}Cl)]^{2-}$ and $[Re_4Cl_8(\mu\text{-}O)_2(\mu\text{-}OMe)_2]^{2-}$.[9]

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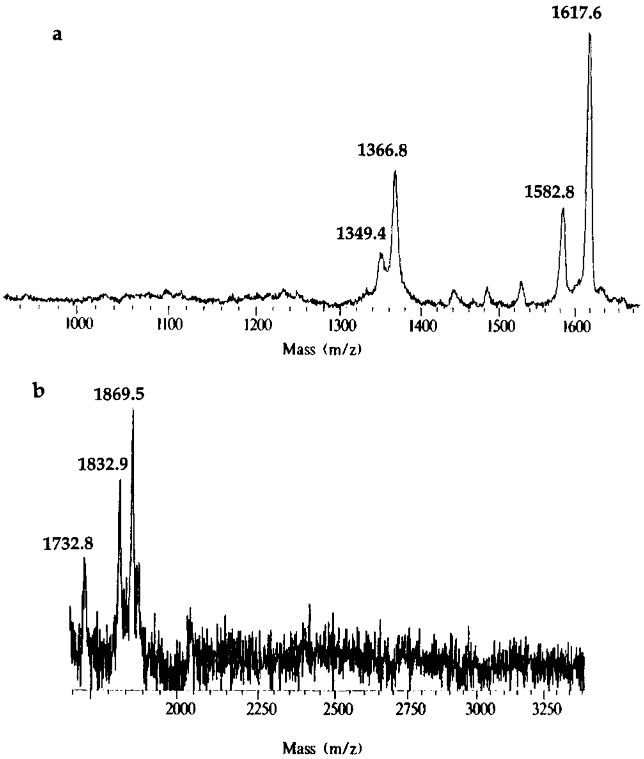

Figure 2. Positive ion mass spectrum for $[Re_4(C_6H_5NCOCH_3)_6(Cl)(\mu\text{-}O)(\mu\text{-}OH)(MeOH)_3][ReO_4]_2$: (a) low-mass region; (b) high-mass region.

Mass Spectrometry. Both the cation and the anion part of $[Re_4(C_6H_5NCOCH_3)_6(Cl)(\mu\text{-}O)(\mu\text{-}OH)(MeOH)_3][ReO_4]_2$ were detected by ^{252}Cf-plasma desorption mass spectrometry, a technique well-known to cause relatively little fragmentation. The mass spectrum of the positive ions is illustrated in Figure 2. The peak at *m/z* 1617.6 is assigned to $[Re_4(C_6H_5NCOCH_3)_6Cl(O)(OH)]^+$ (isotopically averaged mass 1618.23), i.e., $[M - (MeOH)_3]^+$, where M is the entire original cation. The peak at *m/z* 1582.8 can be assigned to $[M - (MeOH)_3 - Cl]^+$ (mass 1582.78). The peaks at *m/z* 1366.8 and 1349.4 seem to be due to $[Re_4(C_6H_5NCOCH_3)_4Cl(O)(OH)_2]^+$ (mass 1366.92) and $[Re_4(C_6H_5NCOCH_3)_4Cl(O)(OH)]^+$ (mass1349.92), respectively. The peak at *m/z* 1732.8 is assigned to $[M + H_2O]^+$ (mass 1732.38), where the water may have come from moisture in the matrix used for sample preparation. The peaks at *m/z* 1869.5 and 1832.9 are assigned $[M - (MeOH)_3 + H](ReO_4)^+$ (mass 1869.45) and $[M - (MeOH)_3 - Cl](ReO_4)^+$ (mass 1832.98), respectively. The negative ion spectrum (Figure 3) shows $^{187}ReO_4^-$ (mass 250.95; average mass of O (16.00) used because ^{16}O has 99.76% abundance) at *m/z* 251.1, $^{185}ReO_4^-$ (mass 248.95) at *m/z* 249.1, $^{187}ReO_3^-$ (mass 234.95) at *m/z* 235.1, and $^{185}ReO_3^-$ (mass 232.95) at *m/z* 233.1. ^{185}Re has 37.07% natural abundance while ^{187}Re has 62.93%. The presence of ReO_3^- where apparently Re is in the V oxidation state can be attributed to the unique nature of gas phase chemistry, which can be revealed in mass spectrometry but is not easily observed in condensed phases.

Reaction Chemistry. Among the four amidato-bridged dirhenium compounds, only the three with a cis arrangement of the $Re_2O_4N_4$ core (C_{2h} virtual symmetry) are prone to react with oxygen in an aqueous medium. The fourth compound, $Re_2(2,6\text{-xylyl-}NCOCH_3)_4Cl_2$, is unreactive toward water and air. Whether this reactivity difference is due to its trans structure type or to the bulkiness of the N-substituent is not clear.

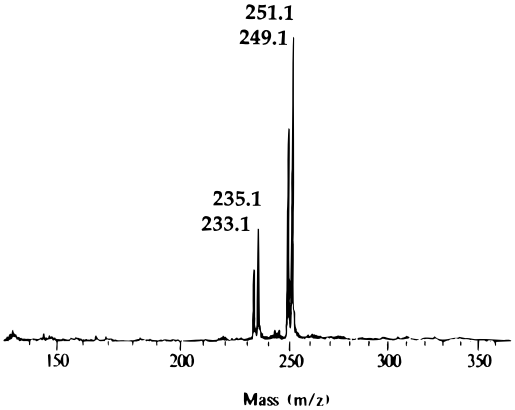

Figure 3. Negative ion mass spectrum for $[Re_4(C_6H_5NCOCH_3)_6(Cl)(\mu\text{-}O)(\mu\text{-}OH)(MeOH)_3][ReO_4]_2$.

The product of the reaction of $Re_2(C_6H_5NCOCH_3)_4Cl_2$ with water has been structurally characterized, and the amidato ligand arrangement was found to have changed from cis to trans. The reaction can be summarized by the following equation:

$$3Re_2(C_6H_5NCOCH_3)_4Cl_2 + 3MeOH + 2O_2 + 6H_2O \xrightarrow{CH_2Cl_2} 6C_6H_5NHCOCH_3 + [Re_4(C_6H_5NCOCH_3)_6(Cl)(\mu\text{-}O)(\mu\text{-}OH)(MeOH)_3][ReO_4]_2 + 5HCl$$

The acetanilide appeared as colorless plates whose identity was confirmed by ^{1}H NMR. Needless to say, there is little chance of accounting mechanistically for this complicated reaction. The occurrence of a reorganization in the arrangement of the three remaining amido ligands on each of the metal atoms is an interesting detail, as is the fact that while one-third of the rhenium is oxidized all the way to Re^{VII}, the remaining two-thirds is not oxidized at all. The persistence of the tetranuclear cation in the mass spectrum, with only the loss of the methanol molecules, is also notable.

It may be pointed out that the partial oxidation of Re^{III} to ReO_4^-, which then forms a compound with cationic Re_2^{6+} species, is a phenomenon that was observed very early in the study of quadruply-bonded dirhenium compounds. In 1963, Taha and Wilkinson[10] reported a number of binuclear rhenium compounds, several of which were formulated on the basis of analytical data with $Re(\mu\text{-}O)_2Re$ units. These were later shown[11,12] to contain instead $Re_2(O_2CR)_4^{2+}$ or $Re_2(O_2CR)_3Cl_2^+$ cations together with ReO_4^- anions. Just a few years ago,[13] it was found that, on exposure to air, $Re_2Cl_4(PMe_3)_4$ gives rise to $[Re_2Cl_4(PMe_3)_4]ReO_4$. Thus, the present observations are, in this respect at least, not unprecedented.

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Supporting Information Available: Complete tables of bond distances and angles, positional and isotropic equivalent thermal parameters, and anisotropic thermal parameters (10 pages). Ordering information is given on any current masthead page.

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