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The Intermediacy of $Re_2(O_2CCH_3)_2Cl_4$ in the Conversion of $Re_2(O_2CCH_3)_4Cl_2$ to Re_3Cl_9

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The reactions of the dirhenium(III) acetate complex $Re_2(O_2CCH_3)_4Cl_2$ (Re≡Re) with the gaseous hydrogen halides HX (X = Cl, Br or I) at *c.* 340 °C provide an excellent high yield synthetic route to the trinuclear halide clusters Re_3X_9 (Re=Re) [1–3]. In the reaction involving HCl(g), we usually observe the formation of a trace amount of a bright blue solid that is transported to the cooler section of the reaction tube during the early stages of the reaction. With the expectation that this is a reaction intermediate, we have sought to isolate this product in sufficient quantities to fully characterize it.

The yield of this blue product can be optimized by the use of a slow flow of HCl(g) over the heated $Re_2(O_2CCH_3)_4Cl_2$ but with the other reaction conditions as reported previously [1–3]. The yield of Re_3Cl_9 was reduced (from *c.* 95% to *c.* 50%), and the blue product was obtained both as a blue powder and as dark blue crystals in different zones of the reaction tube. The blue product was easily separated by hand from the Re_3Cl_9.

The electronic absorption spectra of the blue powder and blue crystals were identical (Nujol mull, λ_{max} = 617 nm and shoulders at ≃420 and 345 nm); the 617 nm band is assigned to the $\delta \rightarrow \delta^*$ transition of the Re_2^{6+} core [4]. The infrared spectra (recorded as Nujol mulls from 4000–150 cm^{-1}) are also the same, and in the region 4000–400 cm^{-1} resemble closely the spectrum reported for $Re_2(O_2CCH_3)_2Cl_4$ [5]. Below 400 cm^{-1}, there is a cluster of well-defined absorptions between 390 and 330 cm^{-1} (390 m, 362 s, ≃355 sh, 341 s and 333 m–s) which include the ν(Re–Cl) modes. Bands at lower frequencies are as follows: 262 w, 253 vw, 180 m–w and 167 m–w.

The suspicion that this blue product is the complex $Re_2(O_2CCH_3)_2Cl_4$ has been confirmed by both EI and CI mass spectrometry. The pertinent experimental details have been described elsewhere [6]; a source temperature of 250 °C was used, and the probe temperature was 300 °C (+CI) or 350 °C (EI and –CI). The simplest spectrum was the negative ion CI spectrum (–CI). This gave the molecular ion $[M]^-$ at *m*/*z* 632; the cluster of peaks centered at *m*/*z* 632 showed the correct isotopic pattern for $[Re_2(O_2CCH_3)_2Cl_4]^-$. All other peaks in the negative ion CI spectrum were present in less than 1% relative abundance. The EI spectrum and positive ion CI spectrum (+CI) likewise showed the parent ion $[M]^+$ as the dominant peak (*m*/*z* 632, 100% relative abundance), but in these spectra there are also a few fragment ion peaks. In the EI spectrum, a cluster of peaks centered at *m*/*z* 597 (13% abundance) arises from the loss of chlorine from the molecular ion, i.e. $[M-Cl]^+$. In the +CI spectrum this same pattern is observed, but in much higher relative abundance (87%). Other *dirhenium*-containing ions are present in very low relative abundances (<10%).

To further characterize this product, we carried out an X-ray structure analysis on a single crystal that had been ground to an ovoid shape in order to alleviate absorption problems [7–10]. A dark blue ovoid crystal of approximate dimensions 0.20 × 0.10 × 0.08 mm was used. It was triclinic, space group $P\bar{1}$, with $a = 6.0619(8)$, $b = 8.4332(8)$, $c = 6.6229(8)$ Å; $\alpha = 99.24(1)^\circ$, $\beta = 108.59(1)^\circ$, $\gamma = 110.46(1)^\circ$, $V = 286.2(2)$ Å^3, $Z = 1$, and $D_{calc} = 3.668$ g/cm^3. X-ray diffraction data were collected at 20 °C for 1662 independent reflections having $4 < 2\theta < 60^\circ$ on an Enraf-Nonius CAD-4 diffractometer using graphite crystal monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection and reduction methods are the same as described elsewhere [7]. An empirical absorption correction was applied [8]; the linear absorption coefficient μ was 223.5 cm^{-1}. A secondary extinction correction was applied [9]; the final coefficient, refined in least squares, was 1.1×10^{-6} (in absolute units). The Re, Cl, C and O atoms were refined anisotropically, and corrections for anomalous scattering were applied to these atoms [10].** The acetate hydrogen atoms were not included. The final residuals were $R = 0.032$ and $R_w = 0.042$ for 1567 data with $I > 3\sigma(I)$. The highest peak in the final difference Fourier map had a height of 2.42 e/Å^3 and was close to the rhenium. Although the structure of this complex had first been reported almost ten years ago [11], the relatively low precision of that structure determination ($R = 0.089$, large standard deviations on the Re–O bond and acetate ligand parameters) convinced us of the need to redetermine the structure in view of the importance of this compound. An ORTEP representation of this structure is shown in Fig. 1; the pertinent structural parameters are listed in the caption to the Figure. The structure of this complex, which is based closely upon that of the $[Re_2Cl_8]^{2-}$ anion [4], accords with

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**For the scattering factors used in the structure solution, see ref. 10b.

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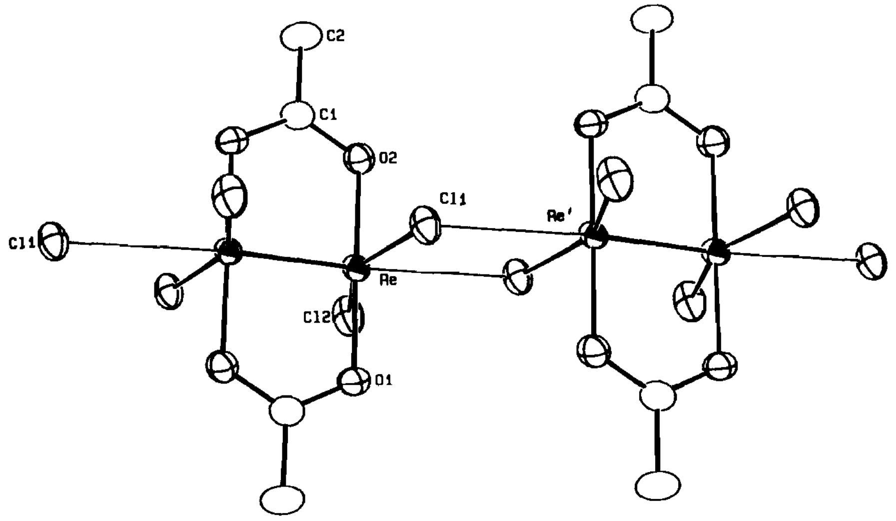

Fig. 1. ORTEP representation of the structure of $Re_2(O_2CCH_3)_2Cl_4$ showing the intermolecular interactions through Re–Cl··· Re' bridges. The thermal ellipsoids are drawn at the 50% probability level. Important bond lengths (Å) are as follows: Re–Re' = 2.2084(3), Re–Cl(1) = 2.338(1), Re'–Cl = 2.887(1), Re–Cl(2) = 2.289(1), Re–O(1) = 2.019(4), Re–O(2) = 2.006(4), O(1)–C(1) = 1.274(7), O(2)–C(1) = 1.281(7), C(1)–C(2) = 1.476(8); and angles (°) Re'–Re–Cl(1) = 101.99(3), Re'–Re–Cl(2) = 103.44(4), Re'–Re–O(1) = 90.4(1), Re'–Re–O(2) = 89.8(1), Re–Re'–Cl(1) = 175.81(3).

the results previously reported by Koz'min *et al.*, both for this complex [11] and its bromide analogue [12]. The *trans* disposition of acetate ligands is similar to that seen in the analogous structures of $Re_2(O_2CCMe_3)_2Cl_4$ [13] and $Re_2(O_2CPh)_2I_4$ [14].

The present study establishes the role of $Re_2(O_2CCH_3)_2Cl_4$ as an important intermediate in the conversion of $Re_2(O_2CCH_3)_4Cl_2$ to Re_3Cl_9. Clearly, the increase in cluster size ($Re_2 \rightarrow Re_3$) occurs at a point following the formation of $Re_2(O_2CCH_3)_2Cl_4$. Thus, we find that the treatment of $Re_2(O_2CCH_3)_2Cl_4$ with HCl(g) at 340 °C forms Re_3Cl_9, but we have not yet been able to isolate the putative species $\{Re_2(O_2CCH_3)Cl_5\}$ prior to the formation of the trinuclear cluster.

Supplementary Material

Further details concerning this structure solution, including tables of crystallographic data and data collection parameters, atomic positional parameters, anisotropic thermal parameters, and bond distances and bond angles are available from R.A.W.

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