Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

The first 'hexaaqua-' complex of the $[Re_6Se_8]^{2+}$ cluster core, $[Re_6Se_8(OH)_2(H_2O)_4]\cdot 12H_2O$

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Received 20 July 2001
Accepted 7 August 2001
Online 10 August 2001

Key indicators

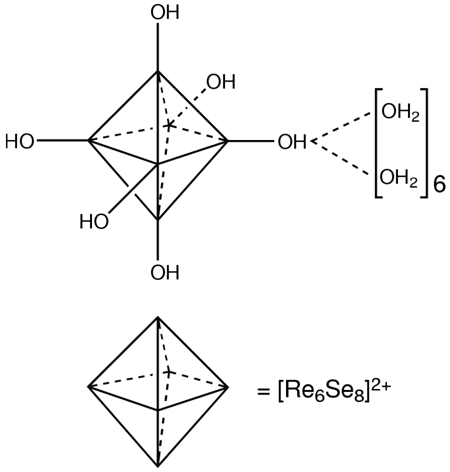
Single-crystal X-ray study
T = 100 K
Mean σ(Re–O) = 0.007 Å
R factor = 0.027
wR factor = 0.068
Data-to-parameter ratio = 29.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The first hexaaqua/hydroxo complex of the $[Re_6Se_8]^{2+}$ cluster species, tetraaquadihydroxohexarheniumoctaselenium dodecahydrate, is found to have unusual bonding that involves both inner and outer sphere aqua/hydroxo species. The Re, one of the Se atoms and one of the O atoms are located on a crystallographic mirror plane, and the second Se atom is located on a special position of site symmetry $3m$. Only the O atom in the outer coordination sphere occupies a general position. Crystallographically imposed symmetry prohibits unambiguous identification of the ligands as water or hydroxy O atoms. A lack of counter-ions in the interstices requires the molecular formula $[Re_6Se_8O_{18}]$ to be recast as $[Re_6Se_8(OH)_2(H_2O)_4]\cdot 12H_2O$

Comment

Since the advent of a facile preparation of the molecular cluster core $[Re_6Q_8]^{2+}$ (Q = S, Se) (Long *et al.*, 1996), extensive chemical and physical studies of these interesting species have become feasible. Recent work has demonstrated that the clusters are luminescent (Gray *et al.*, 1999; Yoshimura *et al.*, 1999). The lumniscence is strongly dependent upon the nature of the ligands coordinated at the Re apices and suggests the potential for creating a novel class of optical materials. The redox behavior of the cluster species is also ligand dependent, exhibiting reversible oxidations in the approximate ranges 200–300 and 800–1500 mV for the halide and phosphine ligated systems, respectively. In addition, the cluster core is remarkably robust and readily undergoes extensive substitution chemistry at the Re apices (Zheng *et al.*, 1997). The combined physical properties and favorable



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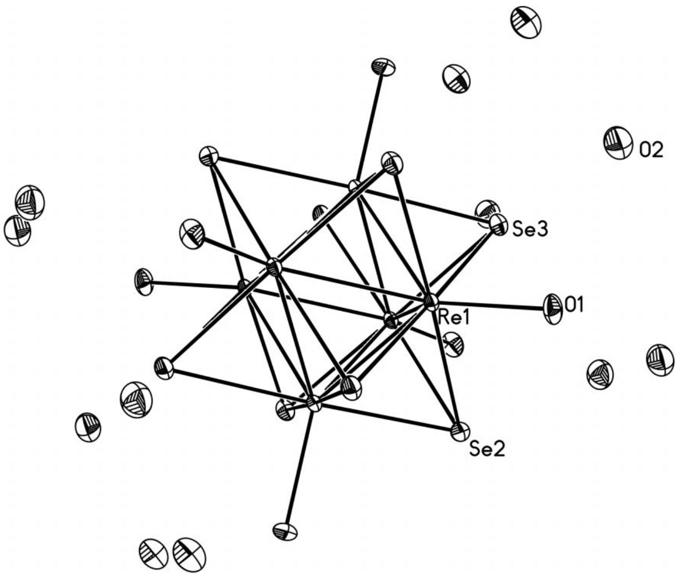

Figure 1
Displacement ellipsoid plot rendered with 50% probability ellipsoids.

chemistry make the $[Re_6Q_8]^{2+}$ cluster species an ideal precursor to molecular and supramolecular compounds with intriguing behaviors.

Our laboratory has pursued the preparation of discrete supramolecular species which feature geometries dictated by a $[Re_6Se_8]^{2+}$ cluster. Use of partial substitution of halides with inert phosphine ligands allows selection of isomers with fixed stereochemistry. The fixed stereochemistry directs self-assembly of multiple clusters into pre-determined arrangements in the presence of stoichiometric amounts of an appropriate ligand (typically a 4,4′-dipyridyl derivative). With an eye to the possibility of utilizing hydrogen bonding as the principal linking mode in these cluster assemblies, we have initiated the study of the hydroxide derivatives of the $[^n\text{Bu}_4\text{N}]_3[\text{Re}_5^{\text{III}}\text{Re}^{\text{IV}}\text{Se}_8\text{I}_6]$ cluster. Earlier work on the analogous $[Re_6S_8]^{2+}$ system has indicated that the cluster exists in solution as the aqua complex (Fedin *et al.*, 1998). Reported herein is the first persubstituted hexaaqua/hydroxide structure. The structure confirms the feasibility of the hydroxide substitution chemistry and provides the first structural data for the compound central to quantification of the cluster species' reactivities, $[Re_6Q_8(H_2O)_6]^{2+}$.

Several features of the structure of the title compound are of interest. Chief among these is the formulation as $[Re_6Se_8(OH)_2(H_2O)_4]\cdot 12H_2O$, (I). This formula is a strictly formal representation of the coordination environment based on the charge requirements of the 24 e$^-$ Re$^{\text{III}}$ cluster core. In the actual structure, the classification of apical ligands as OH$^-$ or H_2O is prohibited by crystallographically imposed symmetry. The structure may be generally described as the $[Re_6Se_8]^{2+}$ core with apical Re sites bound to an inner-sphere O atom (O1). In close hydrogen bonding contact is an outer coordination sphere of 12 water molecules generated from a single oxygen site (O2). Both O1 and O2 are the only unique O atoms in the structure. Hence, all Re—O bonds are equivalent, precluding distinction of the hydroxo and aqua ligands. An isomorphous structure of $[Mo_6Cl_8(OH)_4(H_2O)_{14}]$ shares this doubled hydration sphere feature and is also formulated according to charge balance considerations (Brosset, 1945). However, the title complex was prepared under highly basic conditions. This fact, combined with the observation of $[Re_6S_8(H_2O)_6]^{2+}$ under acidic conditions by Fedin and coworkers, suggests that the title compound should exist at least as the neutral title formula, if not as the hexahydroxo tetraanion.

In the neutral scenario, one might expect a lowering of symmetry allowing the proper identification of the ligands. Alternatively, one should observe a lengthening of the apparent Re—O bond due to a larger aqua occupancy in a disordered structure. In the case of the tetraanion, a completely different structure might be expected, and accompanying cations would be easily located. A search of the Cambridge Structural Database (Allen & Kennard, 1993) reveals that the observed bond length [2.146 (7) Å] lies near the mean Re—OH bond length [2.16 (6) Å] but is also within 3σ of the mean Re—OH$_2$ bond length [2.2 (1) Å]. Therefore, although the observed bond length is quite short, we cannot confidently state that the inner sphere consists entirely of hydroxo ligands. Furthermore, the expected four Na cations were not observed in the structure. A possible explanation is that the cluster core was oxidized during synthesis, but this is not supported by the structural parameters of the cluster core. The mean Re—Re and Re—Se bond lengths [2.6037 (6) Å and 2.56 (1) Å] do not differ significantly from those of the starting material. The Re—Re bond is only slightly shorter, and the Re—Se bond slightly longer.

In summary, we have prepared and reported the first structurally characterized 'hexaaqua/hydroxo' complex of the $[Re_6Se_8]^{2+}$ cluster core. While these data are of general interest and significance, the structure itself has proven to be quite fascinating. While formally $[Re_6Se_8(OH)_2(H_2O)_4]\cdot 12H_2O$, the true formula remains uncertain.

Experimental

The title compound was prepared by dissolving *ca* 50 mg (0.014 mmol) $[^n\text{Bu}_4\text{N}]_3[\text{Re}_5^{\text{III}}\text{Re}^{\text{IV}}\text{Se}_8\text{I}_6]$ in 100 ml acetone in a 250 ml round-bottomed flask. The resulting green–black solution was vigorously stirred and treated with a large excess of aqueous NaOH, added dropwise from concentrated solution. A straw yellow precipitate was rapidly formed. The mixture was stirred at room temperature for 24 h. The precipitate was collected and washed several times with acetone, dissolved in distilled water, filtered, and left to concentrate. Small golden rhombohedral crystals were obtained after two weeks.

Crystal data

$[Re_6Se_8(OH)_2(H_2O)_4]\cdot 12H_2O$	Mo $K\alpha$ radiation
$M_r = 2071.15$	Cell parameters from 5277 reflections
Trigonal, $R\bar{3}m$	$\theta = 2.4$–31.5°
$a = 15.1655$ (6) Å	$\mu = 34.58$ mm^{-1}
$c = 11.0678$ (7) Å	$T = 100$ (2) K
$V = 2204.48$ (19) Å^3	Rhombohedron, yellow
$Z = 3$	$0.02 \times 0.02 \times 0.01$ mm
$D_x = 4.680$ Mg m^{-3}	

Data collection

Bruker CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (Bruker, 2000)
$T_{\min} = 0.629$, $T_{\max} = 1.000$
13 294 measured reflections
905 independent reflections
665 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.065$
$\theta_{\max} = 31.5°$
$h = -22 \rightarrow 22$
$k = -22 \rightarrow 22$
$l = -16 \rightarrow 16$
63 standard reflections every 1818 reflections intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.068$
$S = 1.14$
905 reflections
31 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0145P)^2 + 149.2289P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 1.86$ e Å^{-3}
$\Delta\rho_{\min} = -2.54$ e Å^{-3}

Outer-sphere O atoms were initially modeled as water molecules, which refined satisfactorily. However, it was not possible to model a proper hydrogen-bonding scheme to the inner sphere O1 atoms. A single H-atom site was initially located between the two O atoms, but it invariably moved to form one of the two H atoms of the O2 water. When the O2 water molecules were included in the model, fixing an H atom to O1, regardless of occupancy, made refinement unstable. The final model neglected protons entirely for consistency and reflects the ambiguous relationship between inner- and outer-sphere molecules. The lack of H atoms accounts for the discrepancy between the title formula and the moiety formula.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SMART*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This structure was determined in the Molecular Structure Laboratory of the Department of Chemistry, University of Arisona, Tucson, AZ 85721, USA. The SMART1000 diffractometer was gratefully obtained with funds provided by NSF grant CHE9610374. The authors would like to thank Dr Michael D. Carducci for his assistance and helpful suggestions.

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