

A New Cubane-Type $\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-Se})_4$ Tetramer Tailored for Water Photooxidation Catalysis

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In an effort to tailor a transition metal complex for photoinduced water splitting, a new cubane-like ruthenium chalcogenide tetramer, $\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-Se})_4$, has been synthesized and structurally characterized by single-crystal X-ray diffraction. The orange-red compound crystallizes in the cubic space group $I\bar{4}3m$. The geometry of the Ru_4Se_4 units remains undistorted in the cubic symmetry $3m$. Such a high symmetry is exceptional among cubane-type cluster compounds. Ruthenium atoms are octahedrally coordinated by three selenium atoms and three CO groups. $\text{Ru}_4\text{Se}_4(\text{CO})_{12}$ clusters are linked via van der Waals forces by oxygen atoms which belong to CO ligands of two different cluster units. By stacking of the cluster units along the cubic axes two weakly coupled three-

dimensional frameworks are formed. First principles band structure calculations reveal the strong influence of both the C–O bonding, which leads to a large splitting into bonding and antibonding states, as well as of metal–ligand bonding. The latter gives rise to several very sharp Ru d bands of t_{2g} -like symmetry just below the valence band maximum E_v , which are expected to be useful for oxidation catalysis. While these states are bonding below -1.3 eV, they are antibonding near the edge of the valence band. For this reason, we expect a stabilization of the cubane core on depopulation of the highest occupied bands. Consequently, it is likely that a dynamic interrelation between electron transfer and crystal structure occurs.

Introduction

Photoinduced water splitting for fuel generation is a subject which over the years has received significant attention.^[1] The process has been demonstrated using UV-absorbing catalysts such as TiO_2 and SrTiO_3 , but it turned out to be very difficult to identify a catalyst which split water using visible light. The semiconducting compound RuS_2 , however, photo-oxidizes water with high quantum efficiency under assistance of an electrical potential involving Ru-centered interfacial coordination chemistry. RuS_2 has an energy gap of 1.3 eV, which is too low for water splitting, so a supporting potential is needed, for energetic reasons to provide the theoretical minimum energy (including losses) which ranges from 1.6 to 2.1 eV depending on the catalytic performance of the material concerned. Synthesizing suitable transition metal compounds with d-energy bands, separated by 2 eV, is therefore a significant challenge for solar fuel generation^[2,3] and the aim of this contribution.

In the past decades numerous efforts have been made to synthesize cubane-like cluster compounds in order to elucidate the relationship between geometry and electronic configuration.^[4] Our interest was stimulated by the fact that hydrogen-producing hydrogenase, e.g. from *Clostridium*

pasteurianum, contains redoxable thiocubane Fe_4S_4 cores.^[5] One of these cores is covalently bridged by a cysteinate thiol to an Fe_2S_2 subcluster (H-cluster).^[5,6] Besides sulfur, carbonyl and cyanide ligands coordinate the iron atoms. It is thought that multi-electron transfer, for example bi-electron transfer to reduce protons to yield dihydrogen, is corroborated with the presence of d-metal centers, which can vary their oxidation state over a wide range. In the past, Chevrel-type compounds were investigated, the characteristics of which are octahedral metal cores consisting of Re, Rh–Mo, Pt–Mo, Os–Mo and Ru–Mo, respectively, linked by chalcogen and halogen atoms.^[7] Light enhanced oxygen reduction was observed in $\text{Re}_6\text{S}_8\text{Cl}_2$ ^[8] while $\text{Re}_4\text{Mo}_2\text{Se}_8$ and $\text{Ru}_2\text{Mo}_4\text{Se}_8$ are of interest as catalysts for the reduction of molecular oxygen in acidic media.^[9,10] A facile chemical synthesis route using carbonyl compounds and elemental chalcogenides to tailor novel metal clustering compounds in the form of powder was recently reported.^[11] To prepare new ruthenium- and molybdenum-containing cluster compounds, which are known to be highly catalytic for many purposes, under increased pressures and temperatures, the $\text{Ru}_3(\text{CO})_{12}$ was treated in a selenium-saturated xylene solution. Using this preparation the new compound $\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-Se})_4$ could be obtained.

Cubane-Type Compounds

Cubane-like clusters $(\text{ML}_3)_4(\mu_3\text{-E})_4$, which contain tetrahedral structural units of four transition metal atoms, M_4 , and four main group non-metal atoms, E_4 , combined to give a cubic moiety, $\text{M}_4(\mu_3\text{-E})_4$, have been the subject of

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numerous papers.^[4,12–28] Most of the cubic clusters show a distortion from the idealized T_d symmetry to D_{2d} (with 4 short and 2 long distances or 2 short and 4 long distances) or D_2 symmetry. In a series of papers, Dahl and co-workers^[12–20] have analyzed the molecular and electronic structure of Fe- and Co-based cubane-like clusters such as $[\text{Cp}_4\text{Fe}_4(\mu_3\text{-S})_4]^n$ ($n = 0$ to $+2$),^[12,13] $[\text{Cp}_4\text{Fe}_4(\mu_3\text{-CO})_4]^n$ ($n = 0, +1$),^[14,15] $\text{Fe}_4(\text{CO})_{12}(\mu_3\text{-Se})_4$,^[4] $[(\text{NO})_4\text{Fe}_4(\mu_3\text{-S})_4]^n$ ($n = 0, -1$),^[16,17] $(\text{CO})_{12}\text{Fe}_4(\mu_3\text{-S})_4$,^[4] $[\text{Cp}_4\text{Co}_4(\mu_3\text{-S})_4]^n$ ($n = 0, +1$),^[18] $(\text{CO})_{12}\text{Co}_4(\mu_3\text{-Sb})_4$ ^[19] and $(\text{NO})_4\text{Co}_4(\mu_3\text{-NR})_4$.^[20]

Based on molecular orbital calculations using the Fenske–Hall model^[4] Dahl and co-workers have successfully explained many of the structural variations. Employing qualitative MO diagrams they suggested that for the clusters of cubane-like structures one set of four orbitals may be considered as the nonbonding lone pair localized on the four terminal ligands at low energy. There are groups of 24 orbitals corresponding to metal–Cp and metal–S bonds in $[\text{Cp}_4\text{Fe}_4(\mu_3\text{-S})_4]^n$ (Figure 1). At higher binding energies it follows a group of 12 orbitals mainly localized on the metal atoms. These metal-based orbitals have primarily d-orbital character and are responsible for the binding to the framework of the cluster, namely the bonds between the metal atoms along the edge of the tetrahedral metal core. The 24 antibonding combinations formed by M–L and M–E interactions are located at high energies. The interaction between the 12 metal-based orbitals forms two bonding sets, one of metal–metal bonding orbitals of symmetry $a_1 + e + t_2$ and a second set of metal–metal antibonding orbitals of symmetry $t_1 + t_2$.

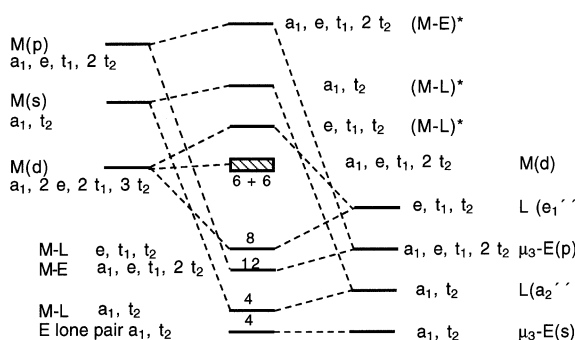


Figure 1. Qualitative energy orbital diagram of the cubane-type cluster unit $\text{Fe}_4(\text{CO})_{12}(\mu_3\text{-Se})_4$, inferred from molecular orbital calculations using the Fenske–Hall model (see ref.^[4]); the diagram can also be used to qualitatively explain the bonding conditions in the ruthenium counterpart, investigated in this work

Lauher estimated the bonding capabilities of various transition metal clusters, based upon extended Hückel calculations on bare Rh clusters.^[21] He proposed the molecular orbitals of a tetrahedral cluster to have six high-lying antibonding orbitals termed as $t_1 + t_2$ corresponding to the antibonding orbitals of metal–metal interaction of Dahl's model. Additionally, the 30 bonding cluster orbitals contain six orbitals of metal–metal interaction of symmetry $a_1 + e + t_2$ in agreement with Dahl's model. The remaining 24

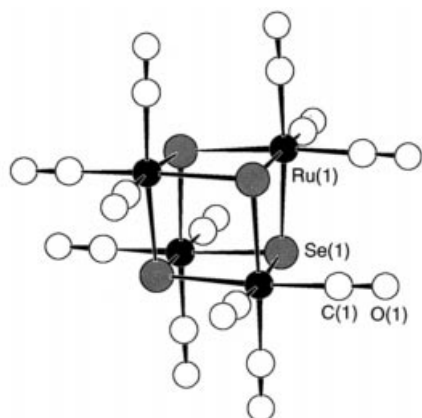
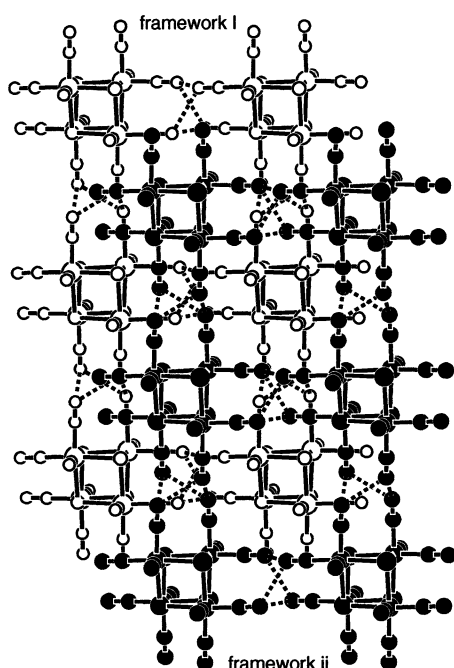
bonding cluster orbitals are used for M–L and M–E bonding. The occasionally observed distortion of the metal–metal tetrahedron can be explained by an incomplete occupation of the bonding or antibonding set of metal–metal orbitals.

The Model Catalyst

In $\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-Se})_4$, described in this paper, the 80 available valence electrons (i.e., 24 from the four $d^6\text{-Ru}^{2+}$ atoms, 24 from the 12 CO ligands and 32 from the four bridging Se^{2-} atoms) completely fill the four lone pairs of the Se atoms, the 24 ($4 + 12 + 8$) bonding metal–ligand orbitals and the six bonding ($a_1 + e + t_2$) as well as the six antibonding metal–metal MOs (Figure 1). From this one would expect the tetrahedral bonds to be metal–metal nonbonding and the cubane core to be stabilized by the metal–ligand bonds. This energy level scheme nicely explains the observed distances and symmetry of cubane-like clusters with 80 valence electrons such as $(\text{CO})_{12}\text{Ru}_4\text{Se}_4$, $\text{Cp}_4\text{Co}_4\text{S}_4$,^[21] $(\text{CO})_{12}\text{Fe}_4\text{S}_4$,^[4] $(\text{CO})_{12}\text{Fe}_4\text{Se}_4$ ^[4] and $(\text{CO})_{12}\text{Co}_4\text{Sb}_4$.^[19]

$\text{Ru}_4\text{Se}_4(\text{CO})_{12}$ crystallizes in the cubic space group $\bar{I}43m$. The coordination of the cubane-like Ru_4Se_4 core is illustrated in Figure 2 and the framework formed by the clusters in Figure 3. The ruthenium center is octahedrally coordinated by three selenium atoms and three CO groups (Figure 2). As is visible from Figure 3 the clusters are coupled by two pairs of oxygen atoms forming a common tetrahedron of 2.955 Å distance. The bonding angles Ru–Se–Ru and Se–Ru–Se are 95.05° and 84.71° . The six equivalent Ru–Ru distances amount to 3.778 Å corresponding to a nonbonding distance. The Ru–Se distance of 2.561 Å is comparable to the sum of covalent radii. The clusters are three-dimensionally interconnected via van der Waals bonds along the cubic axes and form an orthogonal framework. Due to the body-centered Bravais lattice, a second identical framework appears diagonally translated by $1/2, 1/2, 1/2$ with the origin in the center of the unit cell (Figure 2). Each oxygen atom of framework II (e.g. in cluster 3) is separated by the distance of 3.354 Å from four oxygen atoms belonging to framework I. These latter atoms show the distance to the cluster units 1 and 2, as well as the two oxygen atoms to cluster 2 and the two oxygen atoms to cluster 1 and a third cluster of framework I, not shown in Figure 4 for clarity reasons. Crystallographic data and atomic parameters are given in Tables 1 and 2. Bond lengths and angles are summarized in Table 3.

The presented structure is a highly symmetrical example of a structure with cubane-like Ru_4Se_4 cores. Such a high symmetry is exceptional among cubane-type cluster compounds and to the best of our knowledge $\text{Ru}_4\text{Se}_4(\text{CO})_{12}$ is the first cubane-type compound of cubic symmetry described. All other known structures crystallize in lower symmetric space groups. For example in $\text{Ru}_4\text{Se}_4(\text{C–O})_{10}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$, whose cubane-like unit is closely related to our compound, the Ru–Se distances vary from

Figure 2. Cubane-type cluster unit $\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-Se})_4$ Figure 3. Arrays of cluster units of $\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-Se})_4$ interconnected via van der Waals bonds along the cubic axes forming an orthogonal framework; due to the body-centered Bravais lattice type, a second identical framework appears diagonally translated by $1/2, 1/2, 1/2$

2.552 to 2.577 Å, the inner bond angles Se–Ru–Se and Ru–Se–Ru range from 83.6 to 86.1° and from 93.4 to 96.4°. The average values (2.564 Å, 84.8° and 95°, respectively) are close to the angles and distances found in the present structure.^[27]

Density Functional Calculation

The partial, i.e. orbital-projected densities of states, as determined from self-consistent calculations, are displayed in Figures 5 and 6, where we have included Ru-4d, Se-4p as well as C- and O-2p states; all other states gave only negligible contributions to the total density of states in the en-

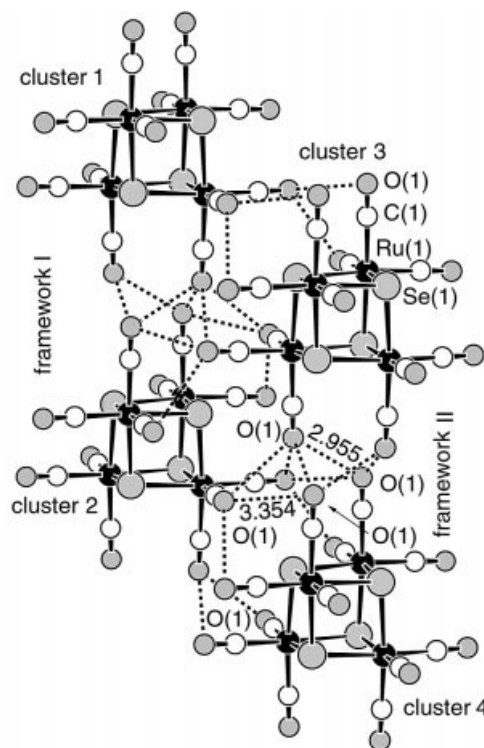


Figure 4. Section of Figure 3 showing the van der Waals bonds between cluster units of different frameworks

Table 1. Crystallographic data for $\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-Se})_4$ (estimated standard deviations are given in parentheses)

Empirical formula	$\text{Ru}_4\text{Se}_4(\text{CO})_{12}$
Formula mass [g mol ⁻¹]	1055.42
Crystal system	cubic
Space group	$I\bar{4}3m$ (no. 217)
μ [cm ⁻¹]	9.391
R values $R1$ and $wR2$	0.015, 0.046
a [Å]	10.308(1)
V [Å ³]	1095.4(2)
Temperature of data collection	25 °C
Z	2
$\rho_{\text{calcd.}}$ [g cm ⁻³]	3.200
$F(000)$	959

Table 2. Atomic coordinates and equivalent isotropic thermal parameters of $\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-Se})_4$

Atom	x/a	y/b	z/c	B_{eq}
Ru	0.12958(4)	0.12958(4)	0.87042(4)	0.0203(2)
Se	0.11836(7)	0.11836(7)	0.11836(7)	0.0219(3)
C	0.1260(5)	0.1260(5)	0.6833(6)	0.0279(11)
O	0.1229(5)	0.1229(5)	0.5741(5)	0.0476(14)

ergy interval shown. In particular, while at lower energies there exist C- and O-2s states we find Ru-4s bands above 7 eV. In order to study the octahedral-like crystal-field splitting at the Ru sites we have separated the 4d partial DOS into its xy , xz , yz and $3z^2 - r^2$, $x^2 - y^2$ components, which, in an ideal octahedron, correspond to the t_{2g} and e_g or-

Table 3. Distances and angles in $\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-Se})_4$

Distance [$\text{\AA}$]		Angle [$^\circ$]	
Ru–Ru	3.7780(7)	Se–Ru–Se	84.71(3)
Ru–Se	2.5611(9)	Ru–Se–Ru	95.05(3)
Ru–C	1.929(6)	Ru–C–O	179.2(8)
C–O	1.127(7)		
O–O	2.955(7)		
O–O	3.354(7)		

bitals. Finally, we give the calculated partial crystal orbital overlap populations (COOP) for selected bonds in Figure 7.

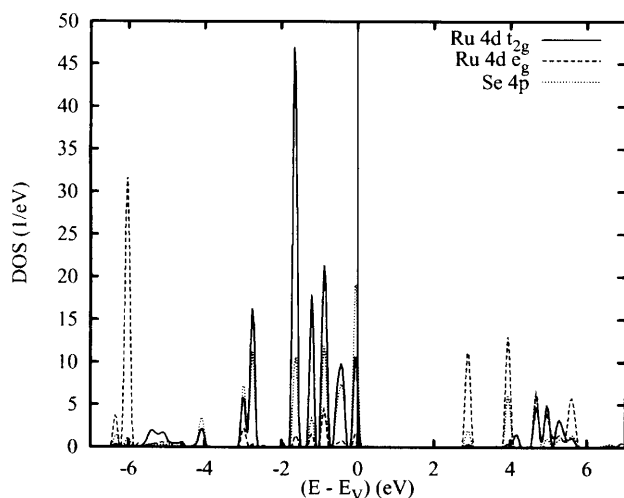


Figure 5. Partial Ru-4d- t_{2g} and - e_g as well as Se-4p densities of states; here and in the following figure energies refer to the valence band edge E_v

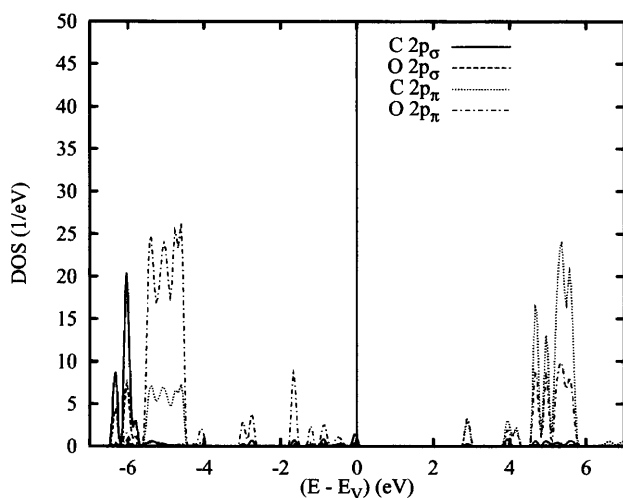


Figure 6. Partial C- and O-2p states of a single C–O pair separated into the p_π and p_σ states

In Figure 6 we display the C- and O-2p partial densities separated into their p_π and p_σ states. We observe two rather conspicuous groups of bands at ± 5 eV, each separated into four sub-bands due to the small overlap of the Ru-4d states

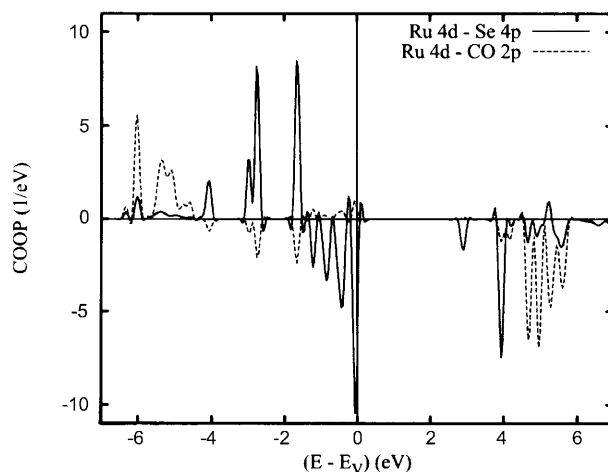


Figure 7. Partial crystal orbital overlap populations for selected bonds

with the bonding C–O orbitals as well as the low symmetry of the crystal field. According to additional analysis of the COOP, the two groups of bands at ± 5 eV result from strong splitting of the C- and O-2p states into bonding and antibonding bands due to π -type overlap across the short bond of only $1.12\text{\AA}$. As expected, the occupied and unoccupied states have larger contributions from O and C, respectively. Since the bonding and antibonding states resulting from this π -type overlap are completely filled and empty, respectively, the C–O bonding adds the largest contribution to the stability of the compound. Furthermore, since these states are located well below and above the Fermi energy the corresponding bonds cannot be broken by simple electron transfer. This striking feature of the C–O cubane core interaction is suspected to be also relevant for the C–O terminated ferredoxins in an iron-only hydrogenase.^[5]

An even larger splitting into bonding and antibonding states of about 16 eV is observed for the O- and C-2s and -2p $_\sigma$ states, where it gives rise to rather sharp peaks at about -24 and -8 eV, outside the energy range displayed in Figures 5–7. Yet, in contrast to the 2p $_\pi$ bands, both these bonding and antibonding orbitals are fully occupied and thus neither contribute to the overall stability nor determine the low energy excitations of the compound. Finally, we observe a fifth group of bands derived from C- and O-2p states at approximately -6 eV below the valence band maximum. It comprises predominantly C- and O-2p $_\sigma$ as well as Ru-4d orbitals.

Bonding of Ru to its neighboring ligands is strongly influenced by the presence of two different types of ligands, namely, three selenium atoms and three C–O pairs, as well as their pseudo-octahedral coordination of the ruthenium sites. Although the particular arrangement of the ligands reduces the local symmetry at the Ru sites to C_{3v} the pseudo-octahedral coordination still allows the interpretation of the Ru-4d partial DOS in terms of its t_{2g} and e_g components as they would grow out of an ideal cubic crystal field. Whereas the t_{2g} states appear mainly in the energy

range from -4.2 eV to E_v , the e_g orbitals contribute to the sharp peaks at -6 eV as well as in the energy range from 2.8 to 6 eV above the valence band maximum. Interestingly, a finite t_{2g} partial DOS is also observed between 4.5 and 6 eV.

Due to the peculiarities of the crystal structure with two different types of ligands, selenium atoms and carbon–oxygen pairs, the ligand contributions to both the $\text{Ru-4d-}t_{2g}$ and $-e_g$ states change across the energy spectrum. To be specific, the occupied $\text{Ru-4d-}t_{2g}$ states occurring in the upper part of the valence band are complemented with contributions from the Se-4p states resulting from π -type overlap. In contrast, contributions from the C-O-2p states to π -type metal–ligand bonding are rather small in this energy region. This is due to the bonding–antibonding splitting of the $2p_\pi$ states discussed above, which shifts these states to ± 5 eV. As a consequence, $\text{Ru-4d-}t_{2g}$ states, which form π bonds with the C-O-2p_π states, are also found near ± 5 eV.

A σ -type metal–ligand bonding is signalled by the ligand p contributions to the peak at approximately -6 eV as well as to the unoccupied $\text{Ru-4d-}e_g$ dominated bands. Again, due to the special octahedral-like coordination of the metal sites by two different types of ligands the d–p overlap changes across the spectrum. While the bonding $\text{Ru-4d-}e_g$ states overlap almost exclusively with the C-O-2p_σ orbitals, the $\text{Ru-4d-}e_g$ partial DOS above 2.8 eV is complemented by both Se-4p and small C-O-2p contributions. This finding is supported by the calculated COOP (Figure 7): Whereas the peak at approximately -6 eV results mainly from Ru-C-O bonding, the energy range from 2.8 to 4 eV is dominated by antibonding Ru-Se states. In conclusion, the cubane framework is predominantly stabilized by σ -type interaction between Ru and CO and π -type interactions between Ru and Se as depicted in Figure 8.

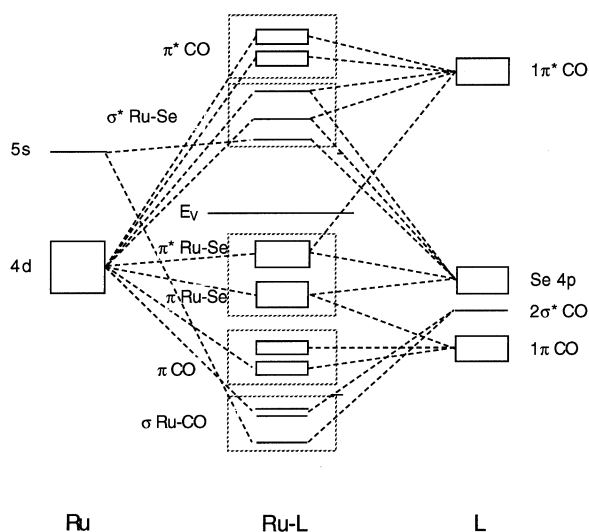


Figure 8. Qualitative energy orbital diagram of $\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-Se})_4$

Electron-Induced Structure Dynamics

The different weighting of the ligand contributions to the $\text{Ru-4d-}t_{2g}$ and $-e_g$ states in the whole energy spectrum has striking consequences for the bonding properties and lays ground for the possible catalytic activity of this material. To be specific, while the metal–carbonyl bonding occurs mainly far away from the valence band edge at ± 5 eV, bonding and antibonding Ru-Se states are found predominantly in the energy range from -3.2 eV to E_v . Strong bonding both within the carbonyl groups, as well as between these groups and the metal d states, shifts the corresponding states away from the gap. Furthermore, due to the rather weak π bonds both the $\text{Ru-4d-}t_{2g}$ bonding and antibonding states fall into the uppermost region of the occupied bands and give rise to the high density of states observed in this energy range. In particular, the antibonding sub-bands show up between -1.3 eV and E_v , hence, just below the Fermi energy. If these states are depopulated the Ru-Se bonds are strengthened and the cubane core that is built from penetrating coordination tetrahedra of both types of atoms will contract. In contrast, if these states are again populated, the bonding will decrease, thus causing a slight expansion of the cubane core. As a consequence, we expect substantial electron–lattice interaction, leading to a significant relationship between electron transfer and structural properties. To conclude, the presence of both strong C-O and rather weak Ru-Se bonds, which push the C-O bonding and antibonding states apart and leave room for antibonding Ru-Se states in the uppermost part of the valence band, thus provide the basis for a working mechanism for catalytic processes.

Conclusion

A new $\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-Se})_4$ tetramer has been synthesized and characterized experimentally and theoretically. The compound fits nicely into a series of other transition metal cluster compounds possessing cubane-like cores. However, in contrast to the companion compounds, the present material crystallizes with an unusual high symmetry (space group $I\bar{4}3m$). The cluster units are weakly coupled by van der Waals interactions. In order to investigate the electronic structure we combined molecular orbital considerations and state-of-the-art band structure calculations. The theoretical results confirm the wide band gap of the material of $E_g = 2.44$ eV. In the cubane core Ru is pseudo-octahedrally coordinated by 3 Se and 3 CO ligands. The electronic structure of $\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-Se})_4$ is dominated by three different types of bonds each having a characteristic strength: (i) strong π -type C-O overlap shifts the corresponding bonding and antibonding states far below and above the valence band maximum and is responsible for the overall stability of the compound; (ii) σ -type overlap of $\text{Ru-4d-}e_g$ states with O/C-2p as well as Se-4p states as resulting from the pseudo-octahedral coordination of Ru likewise places these states at energies well below and above the edge of the valence

band; (iii) finally, rather weakly p-bonded Ru-4d- t_{2g} and Se-4p states dominate in the upper part of the valence band. The respective antibonding states are found at binding energies below 1.3 eV. As a consequence, on depopulation of these states the bonding within the cubane core will increase and the core itself will contract while repopulation will lead to a corresponding expansion. The thus expected coupling between electron and structural dynamics might support electron transfer processes and, hence, might be relevant for catalytic processes.

The prepared $\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-Se})_4$ compound fulfils the most important theoretical criteria to act as photocatalyst for water oxidation: (i) a sufficiently large energy gap (2.44 eV) with valence states, which – as a consequence of photooxidation – are able to transfer electrons via Ru-d states; (ii) the oxidation states of ruthenium atoms in the compound can be increased to allow formation of peroxo complexes, which are able to release oxygen; (iii) the coupling between electronic and structural dynamics may favour multi-electron transfer.

However, preliminary photoelectrochemical experiments using small crystals of the synthesized complex have indicated a material property which at the moment seriously limits an application: A very high electrical resistivity was found, which has to be overcome by suitable doping techniques, by substituting ligands or by preparation of ultrathin layers.

Experimental Section

$\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-Se})_4$: 18 mg of selenium ($2.8 \cdot 10^{-2}$ mmol Se_8 ; ALFA, powder, –325 mesh, 5N) was dissolved in 100 mL of xylene (Merck, mixture of isomers, scintillation grade) under reflux at 140 °C. Then 72.87 mg of $\text{Ru}_3(\text{CO})_{12}$ ($1.14 \cdot 10^{-1}$ mmol; STREM crystalline, 99%) was added to the solution and dissolved. The solution was then brought to ambient temperature. This solution (ca. 35–40 mL) was used to fill an ampoule of Duran glass and sealed under vacuum using a water-jet pump. Further treatment was performed in a high-pressure Morey-type autoclave with a Teflon inset and a Teflon seal. The ampoule was placed in the autoclave and heated. A counterpressure was applied filling the autoclave vessel to 80 vol% with water. The autoclave was heated to 250 °C for 30 d. After cooling, the ampoule was broken and the product separated using a PTFE filter. The residue was washed with small portions of diethyl ether. Optical analysis using a light microscope revealed that besides a black powder, which was identified as elemental ruthenium by X-ray powder diffractometry, orange red crystals had been formed with a yield of 5% (4.5 mg). – Depending on the reaction time orange-red crystals up to 100 μm length grew in a black powder of Ru particles of nanometer size. This growth behaviour is very similar to the preparation of the carbidocarbonyl $\text{Ru}_6\text{C}(\text{CO})_{17}$ described by Johnson et al.^[29] and by Braga et al.^[30] which could also only be obtained in a moderate yield. – The purity of the crystals and the Ru/Se ratio of unity was confirmed within an error bar of 3% by using Energy Dispersive X-ray fluorescence. The carbon monoxide content was measured thermogravimetrically and the gases released were analysed by mass spectrometry. – FTIR measurements were performed using a Bruker IFS 113v spectrometer. By means of attenuated total reflection, two strong peaks at 2079 and 2008 cm^{-1} in the CO region were detected

employing a micro KRS5 crystal at 45°. – To determine the energy gap of the compound an absorption measurement was performed in the range from 400 to 800 nm using a Leitz microscope. – X-ray data collection was carried out with an Enraf–Nonius CAD-4 diffractometer at 293 K using Mo- K_α ($\lambda = 71.073\text{pm}$) radiation monochromatized by a graphite crystal. Data were collected employing the 2Θ - ω scan technique in the range $3^\circ < 2\Theta < 60^\circ$. The total number of reflections was 936 from which 191 were independent [$R_i = 0.035$, 169 observed ($I > 2\sigma(I)$)]. The dimensions of the prismatic crystal were $0.12 \times 0.10 \times 0.09\text{ mm}$. The structure was solved by direct methods using SHELXS-90^[31] in the space group $I23$. But an inspection of the resulting atomic coordinates showed that the higher symmetry $I\bar{4}3m$ was also fulfilled. The refinement of 23 parameters in $I\bar{4}3m$ with SHELX-97^[31] converged with $R_1(\text{on } F) = 0.015$ and $wR_2(\text{on } F^2) = 0.046$. The crystallographic data (excluding structure factors) for the structure reported in this publication have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-155020. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. – In order to obtain more insight into the electronic properties of solid $\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-Se})_4$, band structure calculations were performed as based on density functional theory and the local density approximation (LDA). In doing so, we account in an optimal balance for both the electron–lattice and the electron–electron interaction, both of which are known to strongly influence the properties of transition metal compounds. For the LDA the parametrizations by both Moruzzi, Janak and Williams as well as by Vosko, Wilk and Nusair were used without essentially any difference in the results.^[32,33] As a calculational scheme we employed the augmented spherical wave (ASW) method^[34] (see ref.^[35] for a more recent treatment), which is one of the most efficient band structure methods in use today and offers the advantage of a minimal basis set similar to atomic orbitals. The latter fact allows, in particular, for an intuitive interpretation of the results. The basis set included Ru-5s, -5p, -4d, Se-4s, -4p as well as C- and O-2s, -2p states. Care was taken to ensure convergence of the results with respect to the completeness of the basis set as well as the fineness of the k space grid; the Brillouin zone sampling used up to 158 points within the irreducible wedge. The interpretation of the electronic properties from the calculated band structure and partial densities of states was complemented by an analysis of the crystal orbital overlap population (COOP), which allows access to the chemical bonding in more detail.^[36] – In the present work we performed two different sets of calculations. In the first set we used the experimentally determined lattice constants and atomic positions. In contrast, in the second set of calculations we used a hypothetical crystal structure where the Se atoms were adjusted to positions corresponding to an ideal cubic Ru–Se core and where, hence, some degeneracies were restored. This way we were able to make closer connection to symmetry considerations employed in previous work, which were based on an ideal cubic arrangement, and thus to cross-check our results obtained for the measured crystal structure.

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