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An Oxygen-Centered Tetranuclear Titanium Compound $Ti_4O(S_2)_4Cl_6$

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Abstract: Sealed tube reactions of titanium, sulfur, and sulfur monochloride give $Ti_4O(S_2)_4Cl_6$, **1**, and $Ti_4O(S_2)_4Cl_6{\cdot}2S_8$, **2**, depending on conditions. Each compound was characterized by single-crystal X-ray diffraction studies. Crystallographic parameters are as follows. Compound **1**: monoclinic space group $P2_1/c$; $a = 9.078$ (4) Å, $b = 11.007$ (4) Å, $c = 18.388$ (6) Å, $\beta = 91.95$ (3)°, $V = 1836$ (2) Å^3, and $d_{calcd} = 2.448$ g/cm^3 for $Z = 4$. The structure was refined to $R = 0.045$ and $R_w = 0.055$ for 1787 reflections having $I > 3\sigma(I)$. Compound **2**: orthorhombic space group *Pbcn*; $a = 27.820$ (11) Å, $b = 9.262$ (4) Å, $c = 13.602$ (5) Å, $V = 3505$ (4) Å^3, and $d_{calcd} = 2.255$ g/cm^3 for $Z = 4$. The structure was refined to $R = 0.040$ and $R_w = 0.048$ and 937 reflections with $I > 3\sigma(I)$. Compound **1** consists of $Ti_4O(S_2)_4Cl_6$ molecules having idealized D_{2d} symmetry. A flattened tetrahedron of Ti atoms with an oxygen atom in the center has four short disulfide bridged Ti–Ti contacts of 3.123 [4] Å and two longer Cl bridged Ti–Ti distances of 3.562 [5] Å. Compound **2** contains essentially identical molecules cocrystallized with S_8 molecules. Molecular orbital calculations on compound **1** by the Fenske–Hall method performed in an attempt to understand the metal–metal interactions suggest that there are no Ti–Ti bonds between any pair of metal atoms. The closer Ti···Ti distances can be attributed to strong bridging interactions by the S_2 groups.

Over the past several years an increasing research effort has focused on the field of early transition-metal cluster chemistry. This work has resulted in the discovery of many metal atom clusters, both discrete and extended. A large number of such compounds are known for molybdenum oxides (e.g., $InMo_4O_6$, $NaMo_2O_4$, $Ca_{5.45}Mo_{18}O_{32}$, $Zn_3Mo_3O_8$,[1] $K_2Mo_8O_{16}$,[2] and $In_{11}Mo_{40}O_{62}$[3]) as well as for niobium, zirconium, and lanthanide halides (e.g., Nb_3Cl_8,[4] $RbNb_4Cl_{11}$,[5] Nb_6I_8,[6] $KZr_6Cl_{15}C$, $CsKZr_6Cl_{15}B$,[7] $R_7I_{12}M$ (R = Sc, Y, Pr, Gd; M = Mn, Fe, Co, Ni)[8]). The metal atoms in the molybdenum oxides and niobium halides generally have enough electrons to support metal–metal bond formation, but in the case of zirconium and lanthanide clusters it is often (though not always) required that there be a heteroatom within the cluster to donate electrons and therefore stabilize metal–metal bonds and in turn cluster formation.

A recent review of chalcogenide-halide transition-metal clusters showed that although many compounds of this type exist the area was still fertile for research.[9] In our laboratory we are attempting to synthesize such discrete and extended clusters of group IVA and VA elements. In this paper we report the synthesis, structure, and a molecular orbital description of two crystalline modifications of $Ti_4O(S_2)_4Cl_6$, in which titanium atoms form an open tetrahedron with an oxygen atom in the center.

Experimental Section

Materials and Methods. Chemicals were obtained from the following sources. Ti (200 mesh powder), Alfa; sulfur, precipitated grade, Fischer; S_2Cl_2, STREM. The reactions were carried out in Pyrex tubes with the following dimensions: 15 cm (length) × 2$^1/_2$ cm (o.d.), wall thickness 4 mm.

Preparation of $Ti_4O(S_2)_4Cl_6$, 1. Titanium powder (0.72 g, 15 mmol), sulfur (0.96 g, 30 mmol), and S_2Cl_2 (2.00 g, 15 mmol) were placed in a tube. The contents were frozen and sealed under vacuum. The tube was placed in an oven which was slowly warmed to 160 °C (over ca. 2 h) and kept there for 48 h. The oven was then turned off, and the tube was cooled to room temperature over a period of 12 h. The cooled tube was opened in a drybox, and the contents were placed in degassed mineral oil. A homogeneous mass of red, air-sensitive crystals was manually separated from unreacted sulfur. The product was washed with hexane and dried under vacuum. The isolated yield was 0.63 g, 25% based on Ti.

Preparation of $Ti_4O(S_2)_4Cl_6{\cdot}2S_8$, 2. Titanium powder (0.25 g, 5.2 mmol), sulfur (0.17 g, 5.3 mmol), and S_2Cl_2 (1.00 g, 7.4 mmol) were placed in a tube. The contents were frozen and sealed under vacuum. The tube was placed in an oven which was slowly warmed to 425 °C (over ca. 8 h) and kept there for 48 h. The oven was then turned off, and the tube was cooled to room temperature over a period of 12 h. The cooled tube was opened in a drybox, and the contents were placed in degassed mineral oil. A mass of red, air-sensitive needles was manually separated from unreacted sulfur. The product was washed with hexane and dried under vacuum. The yield was 0.21 g (14%).

Mass Spectrometry. The electron impact ionization mass spectrum for **2** was run on a VG Analytical 70S high resolution double focusing magnetic sector mass spectrometer, with attached VG Analytical 11/250 data system. The sample for the study was supplied in degassed mineral oil to protect the compound from oxygen and moisture. Directly prior to charging the mass spectrometer with the sample the mineral oil was washed away with hexane.

X-ray Crystallography. Both crystals in this study were mounted in thin-walled capillaries filled with degassed mineral oil to prevent decomposition in the air. Axial lengths and Laue class were confirmed with oscillation photographs. The general procedures were routine to this laboratory and have been already described. Lorentz, polarization, and empirical absorption corrections were applied to the data.[10]

Crystal Structure of $Ti_4O(S_2)_4Cl_6$, 1. A small red hexagonal crystal was selected from the product and was shown to be of good quality by polarized light microscopy. The crystal was mounted on the goniometer head of a Rigaku diffractometer. The data were collected as indicated in Table I. The solution and refinement of the structure proceeded straightforwardly in the monoclinic space group $P2_1/c$. The structure was solved with the direct methods part of the SHELXS-86 package, which revealed a large portion of the molecule. Additional least-squares cycles and difference Fourier maps revealed the positions of the remaining atoms. All atoms were refined anisotropically. No disorder or other nonroutine problems arose. The atomic positional parameters are given in Table II. Important bond distances and angles are listed in Table IV.

Crystal Structure of $Ti_4O(S_2)_4Cl_6{\cdot}2S_8$, 2. A thin red needle was mounted on the goniometer head of a Syntex P3 diffractometer. The data, collected as indicated in Table I, were collected at a slower than normal speed because of the generally low intensity of all reflections. The structure was solved in the orthorhombic space group *Pbcn*. The positions of the Ti atoms were found by using the direct methods part of the SHELXS-86 package. Alternating series of least-squares refinements and

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Table I. Crystal Data for $Ti_4O(S_2)_4Cl_6$, **1**, and $Ti_4O(S_2)_4Cl_6 \cdot 2S_8$, **2**

	1	**2**
formula	$Cl_6O_1S_8Ti_4$	$Cl_6O_1S_{24}Ti_4$
formula wt	676.83	1189.85
space group	$P2_1/c$	$Pbcn$
systematic absences	$h0l$: $l = 2n + 1$ $0k0$: $k = 2n + 1$	$0kl$: $k = 2n + 1$ $h0l$: $l = 2n + 1$ $kh0$: $h + k = 2n + 1$
a, Å	9.078 (4)	27.820 (11)
b, Å	11.007 (4)	9.262 (4)
c, Å	18.388 (6)	13.602 (5)
α, deg	90.0	90.0
β, deg	91.95 (3)	90.0
γ, deg	90.0	90.0
V, Å^3	1836 (2)	3505 (4)
Z	4	4
d_{calcd}, g/cm^3	2.448	2.255
crystal size, mm	0.25 × 0.15 × 0.05	0.40 × 0.10 × 0.05
μ (Mo Kα), cm^{-1}	34.065	27.206
data collection instrument	Rigaku AFC5R	Syntex P3
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)	
orientatn reflcns, no. range (2θ), deg	25, $20 < 2\theta < 30$	
temp, °C	21	
scan method	$\omega - 2\theta$	
data col. range, 2θ, deg	$4 \leq 2\theta \leq 45$	
no. unique data, total	2949	1388
with $F_o^2 > 3\sigma(F_o^2)$	1787	937
no. of params refined	172	159
trans. factors, max., min.	1.000, 0.808	0.996, 0.965
R^a	0.0448	0.0398
$R_w{}^b$	0.0552	0.0478
quality-of-fit indicator^c	1.041	0.930
largest shift/esd, final cycle	0.00	0.00
largest peak, e/Å^3	0.74	0.47

[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 $= [\sum w(|F_o| - |F_c|)^2 / (N_{obsd} - N_{parameters})]^{1/2}$.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Ti_4O(S_2)_4Cl_6$[a]

atom	x	y	z	B (Å^2)
Ti(1)	0.8851 (2)	0.1849 (2)	0.3755 (1)	1.07 (4)
Ti(2)	0.7921 (2)	0.4580 (2)	0.3873 (1)	0.98 (3)
Ti(3)	0.5264 (2)	0.2997 (2)	0.3323 (1)	0.94 (3)
Ti(4)	0.6366 (2)	0.2141 (2)	0.4869 (1)	0.94 (3)
Cl(10)	1.0597 (3)	0.0599 (3)	0.3394 (2)	3.74 (7)
Cl(13)	0.6992 (3)	0.1505 (3)	0.2725 (2)	2.78 (6)
Cl(20)	0.8749 (3)	0.6472 (3)	0.4019 (2)	3.60 (7)
Cl(24)	0.7225 (3)	0.4272 (2)	0.5196 (2)	2.42 (5)
Cl(30)	0.3401 (3)	0.2901 (3)	0.2524 (2)	3.18 (6)
Cl(40)	0.5639 (4)	0.1701 (3)	0.5981 (2)	3.59 (7)
O(1)	0.7117 (7)	0.2881 (6)	0.3957 (4)	1.9 (1)
S(1)	0.9725 (3)	0.3706 (3)	0.3099 (2)	2.79 (6)
S(2)	1.0308 (3)	0.3544 (3)	0.4172 (2)	2.63 (6)
S(3)	0.6596 (3)	0.4695 (3)	0.2731 (2)	2.33 (6)
S(4)	0.5311 (3)	0.5138 (2)	0.3570 (2)	2.15 (5)
S(5)	0.3964 (3)	0.3025 (3)	0.4440 (2)	2.32 (5)
S(6)	0.4412 (3)	0.1293 (3)	0.4122 (2)	2.36 (6)
S(7)	0.7539 (3)	0.0295 (3)	0.4503 (2)	2.55 (6)
S(8)	0.8969 (3)	0.1436 (3)	0.5043 (2)	2.49 (6)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(^4/_3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Ti_4O(S_2)_4Cl_6 \cdot 2S_8$[a]

atom	x	y	z	B (Å^2)
Ti(1)	0.05485 (8)	0.0142 (3)	0.2227 (2)	2.06 (5)
Ti(2)	0.02894 (9)	−0.2588 (3)	0.3481 (2)	2.19 (5)
O	0.000	−0.124 (1)	0.250	1.3 (2)
Cl(1)	0.0386 (1)	−0.1260 (4)	0.0656 (2)	2.59 (7)
Cl(2)	0.0500 (2)	−0.3825 (4)	0.4790 (3)	3.80 (9)
Cl(3)	0.1146 (1)	0.1453 (5)	0.1640 (3)	4.07 (9)
S(1)	0.0110 (1)	0.1866 (4)	0.3214 (3)	2.66 (8)
S(2)	−0.0330 (1)	−0.4326 (4)	0.2827 (3)	2.84 (8)
S(3)	0.0846 (1)	−0.0518 (4)	0.3830 (3)	2.48 (8)
S(4)	0.1055 (1)	−0.1952 (4)	0.2781 (3)	2.70 (8)
S(11)	0.3566 (2)	−0.0953 (5)	0.5630 (3)	4.1 (1)
S(12)	0.2989 (2)	−0.2099 (5)	0.6150 (3)	4.7 (1)
S(13)	0.2389 (2)	−0.0928 (6)	0.5876 (3)	5.4 (1)
S(14)	0.2069 (2)	−0.1771 (6)	0.4643 (4)	5.6 (1)
S(15)	0.2244 (2)	−0.0419 (6)	0.3510 (4)	5.9 (1)
S(16)	0.2809 (2)	−0.1361 (6)	0.2788 (3)	5.5 (1)
S(17)	0.3430 (2)	−0.0424 (5)	0.3265 (3)	4.7 (1)
S(18)	0.3727 (2)	−0.1793 (5)	0.4275 (3)	4.6 (1)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(^4/_3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table IV. Selected Averaged Bond Distances (Å) and Angles (deg) for $Ti_4O(S_2)_4Cl_6$, **1**, and $Ti_4O(S_2)_4Cl_6 \cdot 2S_8$, **2**

	$Ti-Ti_{(short)}$	$Ti-Ti_{(long)}$	Ti–O	$Ti-Cl_b$
$Ti_4O(S_2)_4Cl_6$	3.123 [4]	3.562 [5]	2.006 [7]	2.541 [8]
$Ti_4O(S_2)_4Cl_6 \cdot 2S_8$	3.132 [5]	3.572 (3)	2.012 [9]	2.538 [2]

	$Ti-Cl_t$	$Ti-S_{(short)}$	$Ti-S_{(long)}$	S–S
$Ti_4O(S_2)_4Cl_6$	2.218 [5]	2.400 [2]	2.503 [4]	2.035 [3]
$Ti_4O(S_2)_4Cl_6 \cdot 2S_8$	2.202 [3]	2.409 [2]	2.512 [3]	2.039 [1]

	$Ti-Cl_b-Ti$	$Ti-O-Ti_{(short)}$	$Ti-O-Ti_{(long)}$	$O-Ti-Cl_t$	Ti–S–Ti
$Ti_4O(S_2)_4Cl_6$	89.0 [2]	102.2 [4]	125.2 [5]	169.8 [9]	79.1 [1]
$Ti_4O(S_2)_4Cl_6 \cdot 2S_8$	89.4 [1]	102.3 [2]	125.2 (1)	168.0 [4]	79.0 [1]

difference electron density maps revealed all the remaining atoms. All atoms were refined anisotropically. As in the previous structure no disorder or other nonroutine problems arose. The atomic positional parameters are given in Table III. Important average bond distances and angles are listed in Table IV.

Computational Procedures. The molecular orbital calculation on $Ti_4O(S_2)_4Cl_6$ was carried out by the approximate nonempirical Fenske–Hall molecular orbital method.[11] The method has been shown to be satisfactory for explaining the electronic structure and bonding in trinuclear complexes of several transition elements.[12] The atomic coordinates used in the calculation for the molecule were taken from the crystal structure data but idealized to give the molecule C_{2v} symmetry. In order to explore the nature of metal-metal interactions in the molecule, a "core" of $Ti_4O(S_2)_4Cl_6$, $[Ti_4O]^{14+}$, was also computed. The calculation for the core used the same atomic coordinates. The coordinate system for $Ti_4O(S_2)_4Cl_6$ was chosen so that the oxygen atom was located at the origin, and each pair of Ti atoms with a longer Ti–Ti distance was placed on the XY and YZ planes. A right-hand local coordinate system on each of the metal atoms was chosen as follows: the z-axis of the local system points toward the origin where the oxygen atom is located, the y-axis points toward the negative direction of the Z axis of the molecular coordinate system, and the x-axis is parallel to the XY plane of the molecular system.

Results

Compound 1. The structure consists of a normal packing of $Ti_4O(S_2)_4Cl_6$ molecules, each residing on a general position. The molecule consists of a distorted tetrahedron of titanium atoms with an oxygen atom in the center (Figure 1). There are four short disulfide bridged Ti–Ti edges of 3.123 [4] Å and two longer Cl bridged Ti–Ti edges of 3.562 [5] Å. The arrangement of ligand

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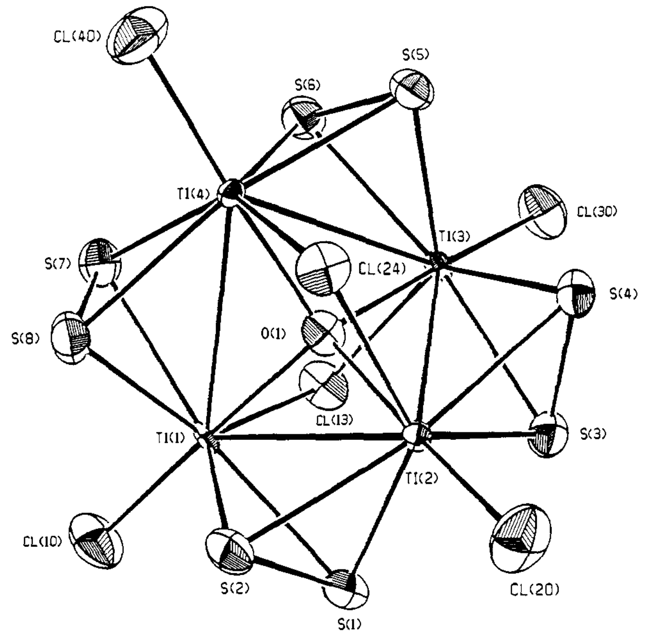

Figure 1. ORTEP drawing of $Ti_4O(S_2)_4Cl_6$, **1**. Atoms are represented by their ellipsoids at the 50% probability level.

atoms around each titanium atom can be described as a pentagonal bipyramid. The equatorial plane consists of two disulfide groups and one bridging chlorine atom, with the apical atoms being the oxygen atom and the terminal chlorine atom. The average distance of an equatorial atom from the least-squares mean plane is 0.060 [3] Å. All titanium atoms are found above the equatorial plane, shifted toward the terminal chlorine atom, by an average distance of 0.353 [5] Å. The average Cl–TiO angle is 169.8 [9]°. Of the six Ti–O–Ti angles, the four subtended by the shorter Ti···Ti edges have an average value of 102.2 [4]° and the other two average 125.2 [5]°. One sulfur atom of each disulfide bridge is consistently closer to one metal atom than to the other by about 0.1 Å (see Table IV). All other bond distances and angles are normal, and their average values appear in Table IV. A unit cell diagram is shown in Figure 2.

Compound 2. The structure of the titanium-containing molecule in this compound is similar to that in **1**. However, in this case the titanium tetramer resides on a 2-fold symmetry axis which passes through the central oxygen atom and two opposite short Ti···Ti edges. The only other significant difference is that the titanium tetramer cocrystallizes with two S_8 molecules. This results in a layered structure with alternating planes of the titanium tetramers and S_8 molecules as shown in Figure 3. The S_8 molecules assume the normal crown ring structure. All important averaged bond distances and angles are given in Table IV. The mass spectrum of **2** was observed at 485 °C and showed an isotopic pattern consistent with a $Ti_4O(S_2)_4Cl_6H^+$ ion.

Discussion

Recent experiments in this laboratory have shown the usefulness of S_2Cl_2 as a chlorinating/sulfurizing reagent in the synthesis of

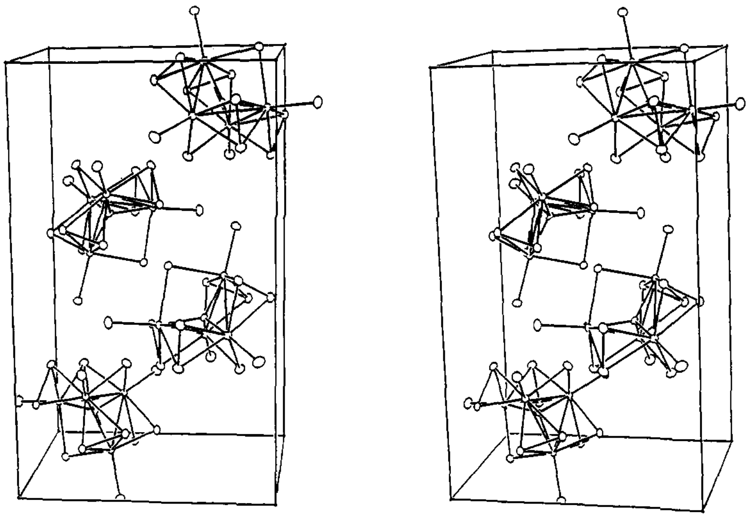

Figure 2. Unit cell diagram for $Ti_4O(S_2)_4Cl_6$, **1**. Axes orientation: c, down; b, across; a, toward viewer.

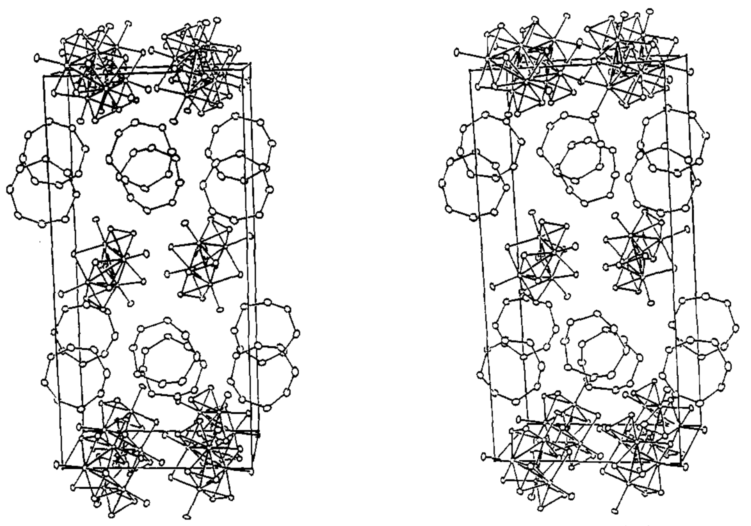

Figure 3. Unit cell diagram for $Ti_4O(S_2)_4Cl_6{\cdot}2S_8$, **2**. Axes orientation: a, down; c, across; b, toward viewer.

Table V. Total Gross Population in Atomic Orbitals of a Titanium Atom

	$3d_{z^2}$	$3d_{x^2-y^2}$	$3d_{xy}$	$3d_{xz}$	$3d_{yz}$	4s	4p	total
$[Ti_4O]^{14+}$	0.22	0.0	0.0	0.06	0.07	0.01	0.0	0.36
$Ti_4O(S_2)_4Cl_6$	0.52	0.67	0.79	0.28	0.35	0.14	0.08	2.83

transition and lanthanide metal clusters.[13] Our initial experiments with titanium have led to the formation of $Ti_4O(S_2)_4Cl_6$, **1**, and $Ti_4O(S_2)_4Cl_6{\cdot}2S_8$, **2**. Although, the reagents and apparatus were degassed in a normal way before reactions took place, oxygen atoms were incorporated in the structures. Their source is presumed to be air trapped inside the reagents. This conclusion is supported by the fact that the yields of the products were significantly increased when the degassing step was omitted from the experiments. This suggests the possibility of incorporating other atoms into the cluster. Work toward this end is currently in progress. The influence of the reaction conditions on determining the nature of the products is not yet well understood, although it is evident that temperature and stoichiometry play a major role. Reactions at higher temperatures give **2** while those at lower temperatures with excess sulfur and S_2Cl_2 produce **1**. We have not yet optimized the yields of these reactions, but the trends stated above suggest reaction conditions for future experiments.

The mass spectrum of **2** showed an isotopic pattern similar to that calculated for $Ti_4O(S_2)_4Cl_6$ but shifted by +1 amu; this result is consistent with the formulation of the parent ion as $Ti_4O(S_2)_4Cl_6H^+$. The hydrogen atom may have been incorporated into the structure either during the preparation of the sample for mass spectrometry or, more likely, while the sample was being heated on the mass spectrometer probe.

With the highly unusual and complex structure of the $Ti_4O(S_2)_4Cl_6$ molecule having been established, our attention was directed to the questions of bonding and electronic structure. As a first approach, each of the anionic components is assigned its ordinary formal charge, viz., S_2^{2-}, Cl^-, and O^{2-}; the titanium atoms must then be regarded as Ti^{4+} ions, and the entire structure must be rationalized in terms of metal–ligand bonds only. Direct Ti–Ti bonding, even across the four shorter edges of the Ti_4 tetrahedron, could not be invoked because there would be no available electrons. However, these four distances, with an average value of 3.12 Å, might be construed as being within the range of weak bonding.[14,15] If such weak bonding were to be postulated, the necessary fractional electron density would have to be "borrowed" from the various metal–ligand bonds. In an effort to see if this sort of picture could be given serious consideration, the electronic structure of the $Ti_4O(S_2)_4Cl_6$ molecule was investigated by a molecular orbital calculation at the level of the Fenske–Hall approximation.

Calculations

The calculation on the $Ti_4O(S_2)_4Cl_6$ molecule results in a molecular orbital diagram with 56 doubly occupied valence molecular orbitals. Among the occupied MO's, there are 20 a_1-type, 14 b_1- and b_2-type, and eight a_2-type orbitals. Because of the length of the table which lists these molecular orbitals together with their energies and percent characters, it is included in the Supplementary Material rather than in this report. However, important features of the orbitals will be presented here and discussed. The diagram of the occupied MO's shows that a great number of them have at least 10% metal character. This is expected because of the number of ligand atoms which are bonded to titanium atoms in different ways. Simple interpretation of the bonding scheme is difficult to achieve because of the mixed characters of many molecular orbitals. A notable feature of the MO diagram is that no occupied molecular orbital has more than 33% metal character. Therefore, when considering metal–metal bonding in the compound, a question naturally arises: is there any direct metal–metal bonding interaction that leads to a recognizable non-zero bond order between any pair of metal atoms?

To consider this problem, we may look at a hypothetical system which consists of just the metal frame and the oxygen at the center, namely, $[Ti_4O]^{14+}$. The technique is similar to that used for the study of the trinuclear cluster compounds,[12] known as "clusters in molecules". The Fenske–Hall MO calculation on $[Ti_4O]^{14+}$ led to four doubly occupied valence MO's. The metal character in the orbitals ranges from 11% to 22% indicating that the four molecular orbitals represent highly ionic Ti–O bonds. This may also be seen through the total gross Mulliken population in the atomic orbitals of the metal. As shown in Table V, for each titanium atom, only the $3d_{z^2}$ orbital is populated with a non-negligible amount of charge. Since the z-axis of the local coordinate system on each titanium atom points directly to the central oxygen atom, the charge densities in the $3d_{z^2}$ orbitals should be due to the Ti–O bonding. Therefore, the results do not reveal any electronic charge distribution in $[Ti_4O]^{14+}$ which can described as metal–metal bonding. Also listed in Table V are the same populations for the $Ti_4O(S_2)_4Cl_6$ molecule which show that all 3d AO's are now populated with certain amounts of charge. In comparison to $[Ti_4O]^{14+}$, the largely increased population on Ti is obviously due to electron donation from the terminal and bridging chlorine and sulfur ligands forming bonds to the metal atoms.

Another approach to the metal–metal bonding question is to consider the overlap population between each pair of metal atoms. Such populations have been obtained for both $[Ti_4O]^{14+}$ and $Ti_4O(S_2)_4Cl_6$ by the present calculations. It turns out that in either case the overlap population between any pair of Ti atoms is nearly zero. The present Fenske–Hall MO calculations do not, therefore, provide any evidence supporting the existence of metal–metal bonds in the $Ti_4O(S_2)_4Cl_6$ molecule.

The population analysis does, however, provide a basis for explaining the existence of both shorter and longer Ti⋯Ti distances. The overlap population between a pair of bridging S atoms and a Ti atom (0.36) is nearly twice as large as the population between a bridging Cl atom and a Ti atom (0.19). These results suggest a stronger S_2–Ti bonding interaction than that between bridging Cl and Ti, and this may be why a pair of Ti atoms bridged by a disulfide ligand approach each other more closely than two Ti atoms bridged by a Cl atom.

Let us now turn to some unoccupied molecular orbitals in $Ti_4O(S_2)_4Cl_6$. It is interesting to note that the LUMO and the next two higher MO's all have a dominant contribution from the Ti atoms. The metal character in each case is more than 80%. An important feature of these MO's is that each of them is a bonding linear combination of the metal valence AO's. If one could have more valence electrons in the Ti_4O core, these MO's would be occupied. Thus if similar compounds with metal atoms having more electrons can be made, the metal–metal distances would be expected to be shorter than in the present case, as a result of metal–metal bonding.

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Supplementary Material Available: Full listing of bond distances, bond angles, isotropic equivalent displacement parameters for $Ti_4O(S_2)_4Cl_6$, **1**, and $Ti_4O(S_2)_4Cl_6{\cdot}2S_8$, **2**, and valence molecular orbitals, their energies, and percent characters for $Ti_4OS_8Cl_6$ (14 pages); tables of observed and calculated structure factors for $Ti_4O(S_2)_4Cl_6$, **1**, and $Ti_4O(S_2)_4Cl_6{\cdot}2S_8$, **2** (14 pages). Ordering information is given on any current masthead page.

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