onstrates the effect of both weakly bonding and nonbonding intermolecular forces on the charge density distribution in dimethyltellurium dichloride.

Summary and Conclusions

The first detailed experimental electron density study of a heavy-atom molecule, dimethyltellurium dichloride, has been carried out with sufficient resolution to reveal bonding and asymmetric lone-pair electron density by extension of the X-X deformation density technique. The following chemically significant features of the intramolecular and intermolecular bonding in the compound have been noted. (1) The bonding and lone-pair density in the molecule is consistent with the predictions of classical bonding models for AB_4E molecules. The asymmetric lone-pair density is predominantly localized and is found to occupy the third equatorial position of the distorted Ψ-trigonal-bipyramid. (2) The bonding density in the axial Te-Cl bonds of order 0.5 is polarized toward chlorine and has a distribution consistent with the interpretation that the covalent radius of the central atom in a tbp molecule is expanded in the axial direction. (3) The trans arrangement of electron density observed in the C-Te···Cl segments of the crystal suggests a donor-acceptor type interaction for the intermolecular bonding in $(CH_3)_2TeCl_2$. These observations provide direct experimental evidence in support of Alcock's thesis[28] on secondary bonding to nonmetallic elements. (4) The deviation of the C-Te···Cl angle from linearity and perturbations in the solid-state molecular geometry of $(CH_3)_2TeCl_2$ are a consequence of the intermolecular bonding in the compound in combination with the equilibrium packing configuration of the molecules. (5) The asymmetric lone-pair density distribution about Cl2 is consistent with an approximate sp^2 hybridization of the bonding orbitals and a nonbonding, presumably p orbital perpendicular to the trigonal hybrid. A pronounced polarization of asymmetric lone-pair density is observed about Cl1, which is in a nonbonded environment. (6) The influence of electrostatic forces of neighboring groups or atoms is evident in the distribution of nonbonding density about Cl1, Cl2, and Te. As in the case of bonding density, more charge is found directed toward the positive regions in the crystal than toward the negative regions in the crystal. (7) The difference between the chlorine atom electron distributions demonstrates the effect of both weakly bonding and nonbonding intermolecular forces on the charge density distribution in dimethyltellurium dichloride.

The observations made herein are consistent with the known structural data for tellurium(IV) compounds and with the results of recent electron density distribution studies on the distorted octahedral compounds, $(CH_3)_3TeCl$ and $(CH_3)_3TeBr$.[41] The full significance of the observations, however, must await further experimental studies with equal or higher resolution on other heavy-atom molecules, exploration of the sin θ/λ cutoff technique, a more accurate assessment of deformation density map errors, and the appearance of theoretical studies on molecules containing heavy-atom, main-group elements.

Acknowledgment. We gratefully acknowledge Drs. Michael W. Extine and B. Frenz for the development of several programs and Dr. Douglas Collins for helpful discussions concerning the treatment of errors.

Registry No. $(CH_3)_2TeCl_2$, 24383-90-2.

Supplementary Material Available: Listing of the root-mean-square amplitudes of thermal vibration, weighted least-squares planes, and the observed and calculated structure factors for both observed and unobserved data (19 pages). Ordering information is given on any current masthead page.

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Clusters in Catalysis. High Reactivity in an Electron-Rich Cluster with Weak Metal-Metal Bonds. Facile, Reversible Addition of Carbon Monoxide to $Os_4(CO)_{12}(\mu_3\text{-}S)_2$

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Abstract: The cluster complexes $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ (I) and $Os_4(CO)_{13}(\mu_3\text{-}S)_2$ (II) have been synthesized and characterized by IR and mass spectrometry and X-ray crystallographic analyses. For I: space group $P\bar{1}$; a = 8.491 (2) Å, b = 9.240 (2) Å, c = 14.389 (5) Å, α = 80.54 (2)°, β = 85.94 (2)°, γ = 68.31 (5)°, Z = 2, ρ_{calcd} = 3.728 g cm^{-3}. The structure was solved by the heavy-atom method. Least-squares refinement on 2930 reflections ($F^2 \geq 3.0_\sigma(F^2)$) produced the final residuals R_1 = 0.032 and R_2 = 0.034. I contains a butterfly cluster of four osmium atoms with sulfido ligands bridging the two open triangular faces and three carbonyl ligands on each metal atom. Electron counting shows that I is a 64-electron cluster, which implies that it should contain only four metal-metal bonds. However, the structural analysis shows the presence of five significant metal-metal interactions. Three of these, at 2.914 (1) Å, 2.935 (1) Å, and 2.940 (1) Å, are close to the normal single bond length of 2.877 (3) Å while the other two are significantly longer at 3.091 (1) Å and 3.002 (1) Å. The relationship of the bonding in this cluster to current theories of cluster bonding is discussed. These longer, weaker metal-metal bonds are very reactive. For example, I absorbs 1 mol of carbon monoxide at 1 atm /25 °C to produce II. For II: space group $P2_1/n$; at 26 °C, a = 10.195 (5) Å, b = 12.679 (4) Å, c = 17.236 (6) Å, β = 96.98 (4)°, Z = 4, ρ_{calcd} = 3.571 g cm^{-3}. The structure was solved by direct methods. Least-squares refinement on 2190 reflections ($F^2 \geq 3.0\sigma(F^2)$) produced the final residuals R_1 = 0.044 and R_2 = 0.043. II contains a planar cluster of four osmium atoms with only three metal-metal bonds. There are 2 triply bridging sulfido ligands and 13 carbonyl ligands (12 linear and 1 semibridge). II can be formed from I by addition of 1 mol of carbon monoxide to one of "hinge" metal atoms followed by complete cleavage of the two weak metal-metal bonds and a shift of a sulfur atom from one hinge metal atom to the other. Surprisingly, the CO addition is fully reversible, such that when heated to reflux in hexane solvent II reverts back to I quantitatively.

Due to their potential as a new class of homogeneous reaction catalysts, transition-metal cluster compounds have attracted considerable attention.[1] Polynuclear coordination[2] and reactions at metal-metal bonds[3] are features that have no parallel at a single

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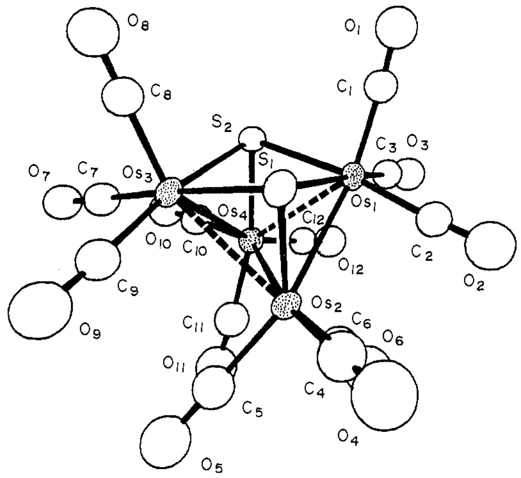

Figure 1. ORTEP drawing of $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ (I) showing 50% thermal motion probability ellipsoids. The dashed connections indicate the weakened metal–metal bonds.

Table I. Interatomic Distances with ESDs for $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ (I)

atoms	distance Å	atoms	distance Å
Os(1)–Os(2)	2.914 (1)	Os(3)–C(7)	1.910 (10)
Os(1)–Os(4)	3.091 (1)	Os(3)–C(8)	1.907 (11)
Os(2)–Os(4)	2.935 (1)	Os(3)–C(9)	1.890 (10)
Os(2)–Os(3)	3.002 (1)	Os(4)–C(10)	1.899 (12)
Os(3)–Os(4)	2.940 (1)	Os(4)–C(11)	1.877 (12)
Os(1)–S(1)	2.429 (2)	Os(4)–C(12)	1.874 (11)
Os(1)–S(2)	2.431 (2)	C(1)–O(1)	1.149 (11)
Os(2)–S(1)	2.376 (2)	C(2)–O(2)	1.163 (13)
Os(4)–S(2)	2.377 (2)	C(3)–O(3)	1.181 (11)
Os(3)–S(1)	2.425 (2)	C(4)–O(4)	1.171 (13)
Os(3)--S(2)	2.445 (2)	C(5)–O(5)	1.166 (12)
S(1)···S(2)	3.191 (3)	C(6)–O(6)	1.166 (14)
Os(1)–C(1)	1.884 (10)	C(7)–O(7)	1.154 (11)
Os(1)–C(2)	1.887 (11)	C(8)–O(8)	1.142 (12)
Os(1)–C(3)	1.892 (10)	C(9)–O(9)	1.165 (11)
Os(2)–C(4)	1.858 (12)	C(10)–O(10)	1.160 (13)
Os(2)–C(5)	1.878 (11)	C(11)–O(11)	1.165 (13)
Os(2)–C(6)	1.849 (13)	C(12)–O(12)	1.158 (12)
		Os(1)···Os(3)	3.551 (1)

Table II. Interatomic Angles with ESDs for $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ (I)

atoms	angle, deg	atoms	angle, deg
Os(1)–Os(2)–Os(4)	63.81 (1)	Os(3)–Os(2)–C(4)	127.5 (4)
Os(1)–Os(4)–Os(2)	57.76 (1)	Os(3)–Os(2)–C(5)	92.3 (3)
Os(2)–Os(1)–Os(4)	58.43 (1)	Os(3)–Os(2)–C(6)	138.9 (4)
Os(1)–Os(2)–Os(3)	73.75 (1)	S(1)–Os(2)–C(4)	85.0 (4)
Os(1)–Os(4)–Os(3)	72.09 (1)	S(1)–Os(2)–C(5)	124.9 (3)
Os(3)–Os(2)–Os(4)	59.34 (1)	S(1)–Os(2)–C(6)	142.3 (4)
Os(2)–Os(3)–Os(4)	59.19 (1)	C(4)–Os(2)–C(5)	89.9 (5)
Os(2)–Os(4)–Os(3)	61.47 (1)	C(4)–Os(2)–C(6)	93.3 (5)
Os(1)–S(1)–Os(2)	74.65 (7)	C(5)–Os(2)–C(6)	92.7 (5)
Os(1)–S(2)–Os(4)	80.04 (8)	Os(2)–Os(3)–C(7)	125.2 (3)
Os(1)–S(1)–Os(3)	94.04 (8)	Os(2)–Os(3)–C(8)	143.1 (3)
Os(1)–S(2)–Os(3)	93.49 (8)	Os(2)–Os(3)–C(9)	81.4 (3)
Os(3)–S(1)–Os(2)	77.41 (6)	Os(4)–Os(3)–C(7)	82.2 (3)
Os(3)–S(2)–Os(4)	75.12 (7)	Os(4)–Os(3)–C(8)	141.7 (3)
Os(2)–Os(1)–S(1)	51.85 (6)	Os(4)–Os(3)–C(9)	122.1 (3)
Os(4)–Os(1)–S(2)	49.21 (5)	S(1)–Os(3)–C(7)	175.1 (3)
Os(1)–Os(2)–S(1)	53.50 (6)	S(1)–Os(3)–C(8)	93.1 (3)
Os(1)–Os(4)–S(2)	50.75 (5)	S(1)–Os(3)–C(9)	91.7 (3)
Os(3)–Os(2)–S(1)	52.02 (5)	S(2)–Os(3)–C(7)	96.0 (3)
Os(3)–Os(4)–S(2)	53.50 (6)	S(2)–Os(3)–C(8)	92.4 (3)
Os(2)–Os(3)–S(1)	50.57 (6)	S(2)–Os(3)–C(9)	170.2 (3)
Os(4)–Os(3)–S(2)	51.38 (6)	C(7)–Os(3)–C(8)	91.4 (4)
Os(4)–Os(2)–S(1)	94.22 (6)	C(7)–Os(3)–C(9)	89.8 (4)
Os(2)–Os(4)–S(2)	91.74 (6)	C(8)–Os(3)–C(9)	95.4 (4)
Os(2)–Os(3)–S(2)	88.80 (6)	Os(1)–Os(4)–C(10)	139.3 (3)
Os(4)–Os(3)–S(1)	93.08 (6)	Os(1)–Os(4)–C(11)	130.6 (4)
Os(4)–Os(1)–S(1)	89.36 (5)	Os(1)–Os(4)–C(12)	91.1 (3)
Os(2)–Os(1)–S(2)	91.16 (5)	Os(2)–Os(4)–C(10)	148.4 (3)
S(1)–Os(1)–S(2)	82.08 (8)	Os(2)–Os(4)–C(11)	78.5 (3)
S(1)–Os(3)–S(2)	81.87 (8)	Os(2)–Os(4)–C(12)	119.4 (3)
Os(2)–Os(1)–C(1)	144.5 (3)	Os(3)–Os(4)–C(10)	95.5 (3)
Os(2)–Os(1)–C(2)	80.3 (3)	Os(3)–Os(4)–C(11)	108.1 (3)
Os(2)–Os(1)–C(3)	123.5 (3)	Os(3)–Os(4)–C(12)	159.6 (3)
Os(4)–Os(1)–C(1)	139.1 (3)	S(2)–Os(4)–C(10)	90.3 (3)
Os(4)–Os(1)–C(2)	124.9 (3)	S(2)–Os(4)–C(11)	161.5 (3)
Os(4)–Os(1)–C(3)	84.6 (3)	S(2)–Os(4)–C(12)	107.0 (3)
S(1)–Os(1)–C(1)	93.5 (3)	C(10)–Os(4)–C(11)	90.1 (5)
S(1)–Os(1)–C(2)	92.0 (3)	C(10)–Os(4)–C(12)	89.9 (5)
S(1)–Os(1)–C(3)	173.9 (3)	C(11)–Os(4)–C(12)	91.5 (5)
S(2)–Os(1)–C(1)	90.7 (3)	Os(1)–C(1)–O(1)	177.0 (9)
S(2)–Os(1)–C(2)	171.4 (3)	Os(1)–C(2)–O(2)	175.4 (10)
S(2)–Os(1)–C(3)	94.4 (3)	Os(1)–C(3)–O(3)	175.1 (9)
C(1)–Os(1)–C(2)	95.9 (4)	Os(2)–C(4)–O(4)	176.1 (11)
C(1)–Os(1)–C(3)	91.6 (4)	Os(2)–C(5)–O(5)	178.3 (9)
C(2)–Os(1)–C(3)	90.9 (4)	Os(2)–C(6)–O(6)	177.7 (12)
Os(1)–Os(2)–C(4)	106.4 (3)	Os(3)–C(7)–O(7)	175.6 (9)
Os(1)–Os(2)–C(5)	162.9 (3)	Os(3)–C(8)–O(8)	177.8 (9)
Os(1)–Os(2)–C(6)	91.6 (4)	Os(3)–C(9)–O(9)	176.9 (9)
Os(4)–Os(2)–C(4)	167.4 (4)	Os(4)–C(10)–O(10)	177.6 (11)
Os(4)–Os(2)–C(5)	100.7 (3)	Os(4)–C(11)–O(11)	175.8 (11)
Os(4)–Os(2)–C(6)	79.6 (4)	Os(4)–C(12)–O(12)	179.3 (10)

metal atom site. Another feature of cluster compounds which may have important implications upon reactivity in the existence of unusual electronic configurations. Stable, high-nuclearity clusters in which the metal atoms do not obey the 18-electron rule are abundant.[4] Recently, the electronic structures of these molecules have been rationalized by molecular orbital treatments which now form the basis for the skeletal electron pair theory.[4-5] Most importantly, it is conceivable that there may be types of cluster complexes where these irregular electronic configurations impart unusual reactivity upon the molecule and do so in ways that could be of use in some forms of catalysis. We have recently synthesized the cluster $Os_4(CO)_{12}(\mu_3\text{-}S)_2$,[6] I which has such as irregular electronic configuration and also shows structural evidence of distortions in the metal–metal bonding. We have now discovered that this molecule does have an unusually high reactivity toward carbon monoxide addition, and we will show how this reactivity can be traced to its unusual electronic structure.

Results and Discussion

The molecular formula of $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ was established by a combination of mass spectrometry (parent ion m/e = 1168 for ^{192}Os) and an X-ray crystallographic analysis. An ORTEP diagram of I is shown in Figure 1. The molecule consists of a butterfly cluster of four osmium atoms with two sulfido ligands bridging the open triangular faces. The internuclear separations in the core of cluster suggest the existence of five significant metal–metal interactions. However, two of these, Os(1)–Os(4) = 3.091 (1) Å and Os(2)–Os(3) = 3.002 (1) Å, are significantly longer than the other three, Os(1)–Os(2) = 2.914 (1) Å, Os(2)–Os(4) = 2.935 (1) Å, and Os(3)–Os(4) = 2.940 (1) Å. The latter three are only slightly longer than the osmium–osmium single bond distance of 2.877 (3) Å found in $Os_3(CO)_{12}$.[7] The Os(1)···Os(3) distance of 3.551 (1) Å is almost certainly non-

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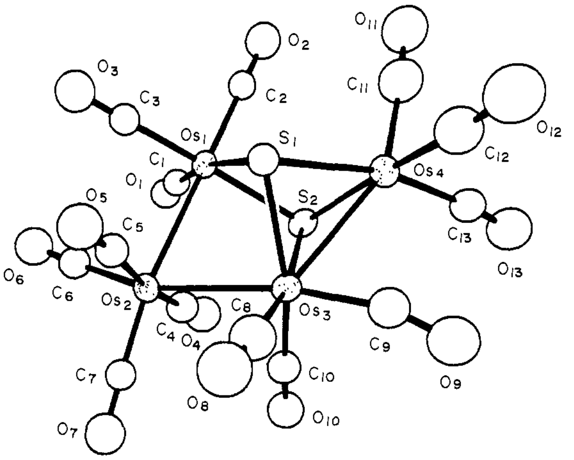

Figure 2. ORTEP drawing of $Os_4(CO)_{13}(\mu_3\text{-}S)_2$ (II) showing 50% thermal motion probability ellipsoids.

bonding. The metal–sulfur distances range from 2.377 (2)–2.445 (2) Å and are typical of the distances found for triply bridging sulfido ligands observed in triosmium clusters.[8] The S(1)···S(2) separation at 3.191 (3) Å indicates that there is little or no bonding interaction between the sulfur atoms. Each metal atom contains three linear carbonyl ligands although C(6)–O(6) on Os(2) and C(11)–O(11) on Os(4) are leaning toward neighboring metals, as indicated by the acute angles Os(4)–Os(2)–C(6) = 79.6 (4)° and Os(2)–Os(4)–C(11) = 78.5 (3)°, and could be described as semibridging. Complete listings of interatomic distances and angles are given in Tables I and II. Overall, the molecule has approximate C_2 symmetry.

Electron counting procedures show that the cluster core of I contains 64 electrons, assuming each sulfur atom serves as a 4 electron donor. Thus, if each metal atom is to obey the 18-electron rule, the cluster should contain only 4 metal–metal bonds. Such a cluster would be referred to as "electron precise". Likewise an electron precise cluster with 5 metal–metal bonds would have only 62 core electrons. Since I has evidence of 5 significant metal–metal interactions but also has 64 electrons, we have chosen to refer to it as electron rich.

An alternative method of rationalizing electronic configurations in polyhedral cluster complexes is through the skeletal electron pair theory.[4–5] The polyhedral configuration of the cluster core of I which consists of the four metal atoms and the two sulfur atoms could be regarded as a nido-pentagonal bipyramid. For this arrangement the skeletal electron pair theory predicts the existence of a stable structure in the presence of eight skeletal electron pairs. This is precisely the number of skeletal electron pairs in I. According to this theory one would expect that the five metal–metal bonds would be essentially equal in strength although formally they might all be weaker than a conventional two-center, two-electron bond.

The fact that I has sets of two long and three shorter metal–metal bonds shows that its metal–metal bonding is not explained uniformly by either theory. It appears that I would very much like to break one metal–metal bond and be electron precise, but instead it opts for two weakened bonds. The presence of the triply bridging sulfido ligands may play an important role in this matter. Other examples of electron-rich clusters with heteronuclear bridging ligands have appeared in the recent literature. These are $Ru_4(CO)_{13}(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}Bu\text{-}t)$ $(\mu\text{-}PPh_2)$,[9] $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$,[10] and $Ru_4(CO)_8$[glyoxal bis(isopropylimine)].[11] All are butterfly clusters with 64-electron configurations. The first has two adjacent elongated metal–metal bonds. The second has three elongated bonds while the third has only one elongated bond.

Table III. Interatomic Distances with ESDs in $Os_4(CO)_{13}(\mu_3\text{-}S)_2$ (II)

atoms	distance Å	atoms	distance Å
Os(1)–Os(2)	2.910 (1)	Os(4)···C(9)	2.61 (2)
Os(2)–Os(3)	2.897 (1)	Os(4)–C(11)	1.88 (2)
Os(3)–Os(4)	2.800 (1)	Os(4)–C(12)	1.91 (2)
Os(1)–S(1)	2.473 (4)	Os(4)–C(13)	1.97 (2)
Os(1)–S(2)	2.472 (4)	C(1)–O(1)	1.13 (2)
Os(1)–C(1)	1.90 (2)	C(2)–O(2)	1.12 (2)
Os(1)–C(2)	1.91 (1)	C(3)–O(3)	1.14 (2)
Os(1)–C(3)	1.93 (2)	C(4)–O(4)	1.12 (2)
Os(2)–C(4)	1.99 (2)	C(5)–O(5)	1.16 (2)
Os(2)–C(5)	1.93 (2)	C(6)–O(6)	1.18 (2)
Os(2)–C(6)	1.90 (2)	C(7)–O(7)	1.19 (2)
Os(2)–C(7)	1.86 (2)	C(8)–O(8)	1.15 (2)
Os(3)–S(1)	2.451 (4)	C(9)–O(9)	1.17 (2)
Os(3)–S(2)	2.457 (4)	C(10)–O(10)	1.21 (2)
Os(3)–C(8)	1.95 (2)	C(11)–O(11)	1.15 (2)
Os(3)–C(9)	1.87 (2)	C(12)–O(12)	1.13 (2)
Os(3)–C(10)	1.87 (2)	C(13)–O(13)	1.14 (2)
Os(4)–S(1)	2.402 (4)	S(1)···S(2)	3.032 (6)
Os(4)–S(2)	2.426 (4)	Os(1)···Os(4)	3.659 (1)

Table IV. Interatomic Bond Angles with ESDs for $Os_4(CO)_{13}(\mu_3\text{-}S)$ (II)

atoms	angle, deg	atoms	angle, deg
Os(1)–Os(2)–Os(3)	70.70 (2)	S(1)–Os(3)–C(9)	104.0 (5)
Os(2)–Os(3)–Os(4)	127.01 (3)	S(1)–Os(3)–C(10)	164.0 (5)
Os(2)–Os(1)–S(1)	84.63 (9)	S(2)–Os(3)–C(8)	168.0 (6)
Os(2)–Os(1)–S(2)	86.44 (9)	S(2)–Os(3)–C(9)	101.5 (6)
Os(2)–Os(1)–C(1)	87.7 (5)	S(2)–Os(3)–C(10)	94.0 (5)
Os(2)–Os(1)–C(2)	179.2 (5)	C(8)–Os(3)–C(9)	87.0 (8)
Os(2)–Os(1)–C(3)	88.9 (5)	C(8)–Os(3)–C(10)	94.4 (7)
S(1)–Os(1)–S(2)	75.5 (1)	C(9)–Os(3)–C(10)	90.2 (7)
S(1)–Os(1)–C(1)	168.2 (5)	Os(3)–Os(4)–S(1)	55.6 (1)
S(1)–Os(1)–C(2)	94.6 (5)	Os(3)–Os(4)–S(2)	55.5 (1)
S(1)–Os(1)–C(3)	95.9 (5)	Os(3)–Os(4)–C(11)	150.1 (6)
S(2)–Os(1)–C(1)	95.0 (5)	Os(3)–Os(4)–C(12)	112.5 (6)
S(2)–Os(1)–C(2)	93.5 (5)	Os(3)–Os(4)–C(13)	110.1 (5)
S(2)–Os(1)–C(3)	170.7 (5)	S(1)–Os(4)–S(2)	77.8 (1)
C(1)–Os(1)–C(2)	93.1 (6)	S(1)–Os(4)–C(11)	103.0 (6)
C(1)–Os(1)–C(3)	92.9 (7)	S(1)–Os(4)–C(12)	93.7 (6)
C(2)–Os(1)–C(3)	91.1 (7)	S(1)–Os(4)–C(13)	165.7 (5)
Os(1)–Os(2)–C(4)	84.9 (5)	S(2)–Os(4)–C(11)	102.8 (6)
Os(1)–Os(2)–C(5)	86.2 (5)	S(2)–Os(4)–C(12)	167.9 (6)
Os(1)–Os(2)–C(6)	91.9 (5)	S(2)–Os(4)–C(13)	93.8 (5)
Os(1)–Os(2)–C(7)	170.8 (5)	C(11)–Os(4)–C(12)	87.4 (8)
Os(3)–Os(2)–C(4)	89.5 (5)	C(11)–Os(4)–C(13)	90.1 (8)
Os(3)–Os(2)–C(5)	85.6 (5)	C(12)–Os(4)–C(13)	92.6 (8)
Os(3)–Os(2)–C(6)	162.6 (5)	Os(1)–S(1)–Os(3)	86.0 (1)
Os(3)–Os(2)–C(7)	100.1 (5)	Os(1)–S(1)–Os(4)	97.3 (1)
C(4)–Os(2)–C(5)	170.8 (7)	Os(3)–S(1)–Os(4)	70.5 (1)
C(4)–Os(2)–C(6)	89.6 (8)	Os(1)–S(2)–Os(3)	86.0 (1)
C(4)–Os(2)–C(7)	94.3 (7)	Os(1)–S(2)–Os(4)	96.7 (1)
C(5)–Os(2)–C(6)	92.7 (7)	Os(3)–S(2)–Os(4)	70.0 (1)
C(5)–Os(2)–C(7)	94.2 (7)	Os(1)–C(1)–O(1)	175 (2)
C(6)–Os(2)–C(7)	97.3 (7)	Os(1)–C(2)–O(2)	178 (1)
Os(2)–Os(3)–S(1)	85.3 (1)	Os(1)–C(3)–O(3)	175 (2)
Os(2)–Os(3)–S(2)	87.0 (1)	Os(2)–C(4)–O(4)	175 (2)
Os(2)–Os(3)–C(8)	85.8 (6)	Os(2)–C(5)–O(5)	174 (1)
Os(2)–Os(3)–C(9)	168.6 (5)	Os(2)–C(6)–O(6)	177 (1)
Os(2)–Os(3)–C(10)	81.5 (5)	Os(2)–C(7)–O(7)	177 (1)
Os(4)–Os(3)–S(1)	53.9 (1)	Os(3)–C(8)–O(8)	176 (1)
Os(4)–Os(3)–S(2)	54.5 (1)	Os(3)–C(9)–O(9)	164 (1)
Os(4)–Os(3)–C(8)	124.2 (6)	Os(3)–C(10)–O(10)	175 (1)
Os(4)–Os(3)–C(9)	64.4 (5)	Os(4)–C(11)–O(11)	174 (2)
Os(4)–Os(3)–C(10)	129.8 (5)	Os(4)–C(12)–O(12)	177 (2)
S(1)–Os(3)–S(2)	76.3 (1)	Os(4)–C(13)–O(13)	174 (1)
S(1)–Os(3)–C(8)	93.5 (6)		

It is conceivable that these weakened metal–metal bonds could be sites of anomalous and high reactivity. We have found that

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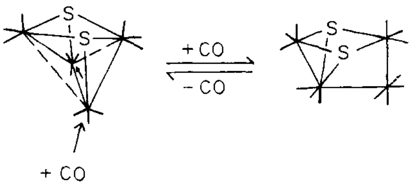
Table V. Crystallographic Data for X-ray Diffraction Studies

formula	$Os_4S_2O_{12}C_{12}$	$Os_4S_2O_{13}C_{13}$
temp, (±5 °C)	23	26
space group	$P\bar{1}$, no. 2	$P2_1/n$, no. 14
a, Å	8.491 (2)	10.195 (5)
b, Å	9.240 (2)	12.679 (4)
c, Å	14.389 (5)	17.236 (6)
α, deg	80.55 (2)	90.0
β, deg	85.94 (3)	96.98 (4)
γ, deg	68.31 (2)	90.0
V, Å^3	1034.6 (6)	2211 (3)
M_r	1161.05	1189.07
Z	2	4
ρ_{calcd}, g cm^{-3}	3.73	3.57
measurement of intensity data		
radiatn	Mo K$\bar{\alpha}$ (0.71073 Å)	Mo K$\bar{\alpha}$ (0.71073 Å)
monochromator	graphite	graphite
detector aperture, mm		
horizontal ($A + B \tan \theta$)		
A	3.0	3.0
B	1.0	1.0
vertical	4.0	4.0
cryst faces	$001, 00\bar{1}, \bar{1}\bar{1}0, 110$ $0\bar{1}0, 101, \bar{1}0\bar{1}$	$01\bar{1}, 0\bar{1}1, 011$ $0\bar{1}\bar{1}, 10\bar{1}, \bar{1}00$
cryst size, mm	0.03 × 0.14 × 0.37	0.10 × 0.12 × 0.19
cryst orientatn		
directn; deg from ϕ axis	normal to $2\bar{2}\bar{1}$; 3.15	a^*; 5.3
reflctns measd	$h, \pm k, \pm l$	$h, k, \pm l$
max 2θ, deg	46	49
scan type	moving crystal, stationary counter	
ω scan width		
$A + 0.347 \tan \theta$	0.95	0.90
background	0.25 additional scan at each end of scan	
ω scan rate (variable)		
max deg min^{-1}	10.0	10.0
min deg min^{-1}	1.5	1.4
no. of reflctns measd	4033	4014
data used ($F^2 \geqslant 3.0\sigma(F)^2$)	2930	2190
treatment of data		
absorption correction		
coeff, cm^{-1}	262.9	231.9
grid	14 × 14 × 4	14 × 6 × 10
transmission coeff		
max	0.46	0.19
min	0.05	0.04
P factor	0.01	0.01
final residuals R_1	0.032	0.044
R_2	0.034	0.043
esd of unit weight	2.12	2.39
largest shift/error value of final cycle	0.08	0.11
largest peaks in final diff fourier, e/Å^3	0.88	2.49

this is the case in I, but the reactivity assumes a rather unusual and surprising form.

For instance, even though I is formally electron rich,[12] it readily engages in a nucleophilic addition reaction with carbon monoxide. At room temperature, under 1 atm of CO, I absorbs 1 mol of CO per mole of cluster to form the complex $Os_4(CO)_{13}(\mu_3\text{-}S)_2$, II. The molecular formula of II was established by mass spectrometry and its structure was determined by an X-ray crystallographic analysis. An ORTEP drawing of II is shown in Figure 2. Interatomic distances and angles are listed in Tables III and IV, respectively. Compound II contains a planar cluster of four osmium atoms with only three metal–metal bonds. The Os(1)–Os(2) and Os(2)–Os(3) distances at 2.910 (1) Å and 2.897 (1) Å are similar to the distance of 2.877 (3) Å found in $Os_3(CO)_{12}$.[7] The Os(3)–Os(4) distance at 2.800 (1) Å is significantly shorter. This shortening could be due to the fact that this bond contains two single-atom bridging ligands, S(1) and S(2). The Os(1)···Os(4) separation at 3.659 (1) Å indicates the absence of any significant bonding interaction. Two triply bridging sulfido ligands bridge the metal atoms Os(1), Os(3), and Os(4) on opposite sides of the Os_4 plane. The osmium–sulfur distances range from 2.406 (4) to 2.473 (4) Å and are similar to those found in I and other sulfido–osmium clusters.[11] The S(1)···S(2) separation at 3.032 (6) Å is nonbonding. Each metal atom contains three carbonyl ligands except Os(2) which contains four. All the carbonyl ligands are of the linear terminal type, except for C(9)–O(9) for which the carbon atom makes a close approach to the neighboring metal atom Os(4), Os(4)···C(9) = 2.61 (2) Å, and the Os(3)–C(9)–O(9) angle is 164 (1)°. This ligand is thus best regarded as a semibridge. Electron counting procedures show that II is electron precise and thus all the metal atoms obey the 18-electron rule.

Scheme I



The formation of II from I is probably accomplished through the addition of CO to one of the "hinge" osmium atoms, Os(2) or Os(4), of the Os_4 butterfly. Cleavage of the two weak met-

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[12] We note that within the framework of the skeletal electron pair theory I would be regarded as electron deficient.[4]

Table VI. Final Fractional Atomic Coordinates with ESDs for $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ (I)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Os(1)	0.35893 (6)	−0.03378 (5)	0.23714 (4)	O(10)	0.739 (1)	0.231 (1)	0.4298 (9)
Os(2)	0.20962 (6)	0.30515 (5)	0.17683 (4)	O(11)	0.537 (1)	0.501 (1)	0.1700 (10)
Os(3)	0.21546 (5)	0.25828 (5)	0.38822 (4)	O(12)	0.855 (1)	0.004 (1)	0.1800 (9)
Os(4)	0.53199 (6)	0.19067 (5)	0.27723 (4)	C(1)	0.315 (2)	−0.212 (2)	0.299 (1)
S(1)	0.0887 (4)	0.1502 (3)	0.2848 (2)	C(2)	0.273 (2)	−0.032 (1)	0.119 (1)
S(2)	0.4493 (4)	0.0061 (3)	0.3844 (2)	C(3)	0.579 (2)	−0.161 (1)	0.201 (1)
O(1)	0.284 (1)	−0.316 (1)	0.3389 (1)	C(4)	0.028 (2)	0.339 (2)	0.101 (1)
O(2)	0.211 (1)	−0.032 (1)	0.0499 (10)	C(5)	0.150 (2)	0.524 (2)	0.169 (1)
O(3)	0.711 (1)	−0.242 (1)	0.1736 (8)	C(6)	0.360 (2)	0.293 (2)	0.076 (1)
O(4)	−0.092 (1)	0.359 (1)	0.0573 (10)	C(7)	0.330 (2)	0.343 (1)	0.461 (1)
O(5)	0.117 (1)	0.659 (1)	0.1636 (9)	C(8)	0.119 (2)	0.177 (1)	0.499 (1)
O(6)	0.450 (2)	0.289 (1)	0.0107 (11)	C(9)	0.036 (2)	0.456 (1)	0.369 (1)
O(7)	0.389 (1)	0.398 (1)	0.5091 (8)	C(10)	0.662 (2)	0.212 (2)	0.373 (1)
O(8)	0.058 (1)	0.128 (1)	0.5631 (8)	C(11)	0.533 (2)	0.381 (2)	0.208 (1)
O(9)	−0.079 (1)	0.575 (1)	0.3598 (9)	C(12)	0.732 (2)	0.076 (1)	0.217 (1)

Table VII. Final Fractional Atomic Coordinates with ESDs for $Os_4(CO)_{13}(\mu_3\text{-}S)_2$ (II)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Os(1)	0.66776 (9)	0.27970 (9)	0.46353 (5)	O(11)	0.410 (2)	0.141 (2)	0.6421 (10)
Os(2)	0.65375 (10)	0.35285 (8)	0.30274 (5)	O(12)	0.090 (2)	0.314 (2)	0.5262 (10)
Os(3)	0.39643 (9)	0.27621 (9)	0.33173 (5)	O(13)	0.175 (2)	−0.012 (2)	0.4394 (11)
Os(4)	0.32529 (10)	0.19981 (8)	0.47318 (5)	C(1)	0.823 (2)	0.204 (2)	0.447 (1)
S(1)	0.4461 (6)	0.3601 (5)	0.4601 (3)	C(2)	0.675 (2)	0.233 (2)	0.570 (1)
S(2)	0.5140 (6)	0.1383 (5)	0.4127 (3)	C(3)	0.765 (2)	0.406 (2)	0.496 (1)
O(1)	0.910 (2)	0.155 (1)	0.4342 (9)	C(4)	0.706 (2)	0.206 (2)	0.280 (1)
O(2)	0.682 (2)	0.203 (1)	0.6313 (10)	C(5)	0.598 (2)	0.486 (2)	0.341 (1)
O(3)	0.831 (2)	0.475 (2)	0.5172 (10)	C(6)	0.835 (3)	0.393 (2)	0.316 (1)
O(4)	0.729 (2)	0.121 (2)	0.2696 (11)	C(7)	0.617 (2)	0.391 (2)	0.198 (1)
O(5)	0.571 (2)	0.571 (2)	0.3597 (9)	C(8)	0.327 (3)	0.406 (2)	0.281 (2)
O(6)	0.946 (2)	0.419 (2)	0.3281 (10)	C(9)	0.221 (2)	0.232 (2)	0.329 (1)
O(7)	0.595 (2)	0.410 (2)	0.1304 (10)	C(10)	0.409 (2)	0.205 (2)	0.238 (1)
O(8)	0.292 (2)	0.485 (2)	0.2550 (11)	C(11)	0.371 (3)	0.164 (3)	0.579 (2)
O(9)	0.112 (2)	0.208 (2)	0.3085 (10)	C(12)	0.175 (3)	0.271 (2)	0.504 (1)
O(10)	0.418 (2)	0.152 (2)	0.1805 (10)	C(13)	0.228 (2)	0.066 (2)	0.456 (1)

al–metal bonds accompanied by a shift of the sulfur atom from the hinge metal atom where the CO was added to the other would complete the process (Scheme I). The cleavage of two metal–metal bonds would require the utilization of four electrons. Two electrons are supplied by the added carbonyl group while the other two would come from the residual electron pair contained in I. Surprisingly, when heated to reflux in hexane solvent, II reverts back to I quantitatively. Thus, the CO addition is fully reversible.

Recently, a facile opening and closing of a metal–metal bond in the heteronuclear triosmium cluster $Os_3(CO)_9$ $(\mu_3\text{-}S)(\mu_3\text{-}NSiMe_3)$ was proposed to explain an unusual occurrence of isomers.[13] Reversible addition of donors to the clusters $(C_5H_5)MnFe_2(CO)_8(\mu_3\text{-}PPh)$;[14] $Ru_3(CO)_8(C{\equiv}CR)(\mu\text{-}PPh_2)$;[15] $Fe_3(CO)_9(\mu_3\text{-}Te)_2$;[16] $FeCo_2MSAsMe_2(C_5H_5)(CO)_8$, M = Mo, W;[17] and $Ru_5(CO)_{15}C$,[18] was accomplished through the facile opening and closing of metal–metal bonds.

We believe the opening and closing of metal–metal bonds in cluster complexes may be faciliated by heteronuclear bridging ligands which will also help to preserve the identity of the cluster in the course of the bond cleavages.[19] Most importantly, we believe that the cleavages in I are promoted by the two "extra" electrons which cause the weakening in two of the metal–metal bonds.

It is hoped that the reversible opening and closing we have observed in the I–II system may permit the selective incorporation of other ligands into the cluster and ultimately form the basis for catalytic cycles.

Experimental Section

The compounds $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ (I) and $Os_4(CO)_{13}(\mu_3\text{-}S)_2$ (II) are air stable in the solid state and in soln. They were isolated from their preparations by TLC on silica gel, using methylene chloride/hexane, 1/20 v/v solvent. $HOs_3(CO)_{10}(\mu\text{-}SC_6F_5)$ was made by a procedure analogous to that used for the preparation of $HOs_3(CO)_{10}(\mu\text{-}SC_6H_5)$.[20]

Infrared spectra were recorded on a Perkin-Elmer 237 IR spectrophotometer calibrated with polystyrene (1601.4 cm^{-1}). Mass spectra were run on an AEI MS-902 mass spectrometer at Cambridge University.

Preparation of $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ (I). We have found that the yield of I can be improved by using $HOs_3(CO)_{10}(\mu\text{-}SC_6F_5)$ as a precursor instead of $HOs_3(CO)_{13}(\mu\text{-}SC_6H_5)$ as reported previously.[6] $HOs_3(CO)_{10}(\mu\text{-}SC_6F_5)$(0.80) G was refluxed in nonane solvent for 1.5 h. The solvent was removed and the red-brown residue was chromatographed by TLC. I is a minor product which is the third product band (the second red band) to elute. It is preceded by residual starting material, $Os_3(CO)_9(\mu_3\text{-}S)_2$ (yellow), and $Os_4(CO)_{12}(\mu_3\text{-}S)$ (red), and is followed by several other bands some of which have been characterized.[6] Details of the preparation and characterization of the other compounds will be reported. I can be crystallized from hexane solvent by cooling to −20 °C. Total yield is more than 2–3%, but the yield seems to be increased when pyrolysis is performed in the presence of small amounts of the thiol. IR (ν_{CO}) in hexane; 2069 vs, 2062 vs, 2055 vs, 2015 m, 2010 m, 1992 s cm^{-1}. The mass spectrum of I shows a parent ion m/e = 1168 for ^{192}Os and ions corresponding to the loss of each of 12 carbonyl ligands.

Preparation of $Os_4(CO)_{13}(\mu_3\text{-}S)_2$, (II). I (10 mg) was placed in a 50-mL flask in 15 mL of methylene chloride solvent under an atomsphere of carbon monoxide. After 24 h at room temperature the solution changed from red to red-orange. The only product observed by infrared spectroscopy was II, and I disappeared completely. II can be purified by TLC and crystallized from hexane solutions at −20 °C. IR (ν_{CO}) in hexane; 2087 s, 2069 w, 2061 s, 2044 w, 2026 vs, 2022 s, 1990 m, 1981 w, 1974 m, 1931 m. The mass spectrum shows a parent ion m/e = 1196 for ^{192}Os and ions corresponding to the loss of each of 13 carbonyl ligands.

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When hexane solutions of II are refluxed for 5 h under a slow purge with N_2, II is converted quantitatively back into I.

Crystallographic Analyses. Crystals of I and II suitable for diffraction measurements were obtained as described above. The crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite monochromatized Mo K$\bar{\alpha}$ radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines.

For I the space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. For II the space group $P2_1/n$ was established from the systematic absences observed in the data. Crystal data and data collections parameters are listed in Table V. All data processing was performed on a Digital Equipment Corp. PDP 11/45 computer with the Enraf-Nonius SDP program library (Version 16), or a VAX 11/750 with the VAXSDP purchased from B. A. Frenz and Assoc., College Station, TX. Absorption corrections of a Gaussian integration type were done for both structures. Neutral atom scattering factors were calculated by the standard procedures.[21a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[21b] Full-matrix least-squares refinements minimized the function $\sum_{hkl}w(|F_{obsd}| - |F_{calcd}|)^2$, where $w = 1/(\sigma(F)^2)$, $\sigma(F) = \sigma(F_{obsd}^2)/2F_{obsd}$ and $\sigma(F_{obsd}^2) = [\sigma(I_{raw})^2 + (PF_{obsd}^2)^2]^{1/2}/Lp$.

The structure of I was solved by a combination of Patterson and difference Fourier techniques. Only the osmium and sulfur atoms were refined anisotropically. Interatomic distances and angles with errors obtained from the inverse matrix obtained from the final cycle of least-squares refinement are listed in Tables I and II. Fractional atomic coordinates are listed in Table VI. Structure factor amplitudes are available.[22]

The structure of II was solved by a combination of direct methods and difference Fourier techniques. The four metal atoms were located in an electron-density map based on the phasing (MULTAN) of 160 reflections ($E_{min} \geq 2.10$). Only the osmium and sulfur atoms were refined anisotropically. Table III and IV list interatomic distances and angles with estimated standard deviations. Fractional atomic coordinates are listed in Table VII. Thermal parameters and structure factor amplitudes are available.[22]

Acknowledgment. We thank the National Science Foundation for support of this research through Grant CHE 80-19041, the Alfred P. Sloan Foundation for a fellowship to R.D.A., and Dr. Brian Johnson, University Chemistry Labs, Cambridge, for obtaining the mass spectra.

Registry No. I, 83928-36-3; II, 83928-37-4; $HOs_3(CO)_{10}(\mu\text{-}SC_6F_5)$, 83928-38-5; CO, 630-08-0.

Supplementary Material Available: Tables of structure factor amplitudes and thermal parameters are available for both structures (29 pages). Ordering information is given on any current masthead page.

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(21) "International Tables for x-ray Crystallography"; Kynoch Press: Birmingham, England, **1975**; Vol. IV. (a) Table 2.2B, p 99-101; (b) Table 2.3.1, p 149-150.

(22) See supplementary material.

Total Synthesis of a Mycobactin: Mycobactin S2

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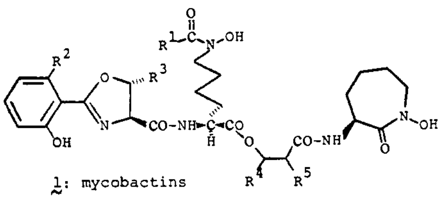
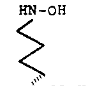
Received June 11, 1982

Abstract: The synthesis of mycobactin S2, **1** (R^2, R^3, R^5 = H; R^1, R^4 = CH_3), is described. Mycobactin S2 is identical with natural mycobactin S except that the long hydrocarbon chain, R^1, is replaced by a methyl group. The synthesis was performed in a convergent manner by forming the ester linkage between the synthetic derivatives **13** and **28** of cobactin and mycobactic acid, respectively, followed by removal of the hydroxamate and phenol protecting groups. Compound **28** was obtained by saponification of the methyl ester, **27**, which was in turn prepared by dehydrative cyclization of the serine-containing dipeptide, **26**, with $SOCl_2$. Compound **26** was prepared by standard peptide coupling techniques from 2-(benzyloxy)benzoic acid, L-serine, and the previously reported **25**. Compound **13** was prepared by the dehydrative cyclization of α-*N*-Boc-L-ϵ-hydroxynorleucine *O*-benzylhydroxamate, **7**, to give **8**, followed by α-N deprotection and coupling with D-β-hydroxybutyric acid. Chirality was preserved throughout the synthesis giving a product with all S chiral centers, as in natural mycobactin S.

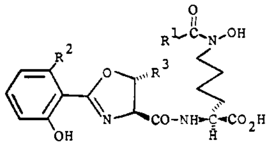
Microbial iron chelators or *siderophores* are important in the study of iron metabolism[1-3] and in the development of drugs for the treatment of iron-overloaded patients.[4-6] These compounds have evolved over millions of years for the purpose of sequestering iron(III) and enabling its transport through the outer membrane of the producing species.[7] The siderophores' high affinity and specificity for Fe(III) is due to the chemical nature of the chelating functional groups, which consist of either catecholate or hydroxamic acid residues.



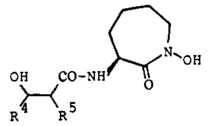
1: mycobactins



2



3: mycobactic acids



4: cobactins

R^2, R^3, R^5 = H or CH_3

R^1, R^4 = CH_3, C_2H_5 or long chain

The mycobactins, **1**, are perhaps the most structurally complex of the known siderophores. This family of compounds was characterized mainly by Snow and co-workers.[8] They demonstrated that all the mycobactins possess a nearly identical molecular nucleus with variations only in stereochemistry of the chiral centers and in the peripheral groups (R^1–R^5 in structure **1**). All the mycobactins form extremely stable hexadentate iron(III) complexes, by binding the iron with two hydroxamic acids and an 2-hydroxyphenyloxazoline residue. It is evident that these chelating moieties constitute the main challenge to a mycobactin synthesis. A mycobactin analogue lacking the three hydroxyl groups necessary for iron chelation was synthesized over a decade ago.[9] However, the first synthesis of a mycobactin containing

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