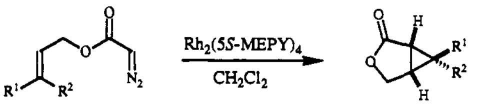
Table I. Enantioselectivity of $Rh_2(5S\text{-MEPY})_4$-Catalyzed Intramolecular Cyclopropanation Reactions

entry	**3**, synthetic method[a]	temp, °C	R^1	R^2	yield,[b] %	ee, %
a	A	25	H	H	74	88[c]
b	B	25	CH_3	CH_3	82	92[d]
c	A	40	H	C_6H_5	45	≥94[e,f]
d	B	25	C_6H_5	H	59	65[g]
e	A	40	H	CH_3CH_2	88	≥94[e,f]
f	B	25	$CH_3CH_2CH_2$	H	74	75[h]
g	A	40	H	$C_6H_5CH_2$	80	≥94[e,f]
h	A	40	H	c-$C_6H_{11}CH_2$	45	68[e]
i	A	40	H	$(CH_3)_2CHCH_2$	29	72[e]
j	A	40	H	$(n\text{-Bu})_3Sn$	78	≥94[e,f]

[a] Prepared from the corresponding allylic alcohols either by reaction with glyoxylic acid chloride (*p*-tolylsulfonyl)hydrazone (method A[21]) or by sequential diketene condensation, diazo transfer, and deacylation (method B[17]). [b] Isolated yield of purified (≥95% homogeneous) product. [c] $[\alpha]_D$ = +60.2° (c = 1.01, $CHCl_3$) relative to enantiomerically pure **4a**, $[\alpha]_D$ = +68.7° (c = 4.6, $CHCl_3$).[22] [d] $[\alpha]_D$ = +83.0° (c = 1.96 $CHCl_3$) relative to enantiomerically pure **4b**, $[\alpha]_D$ = +89.9° (c = 1.4, $CHCl_3$).[23] [e] Determined according to the method of Jones;[24] control experiments were executed with racemic mixtures of lactones. [f] The limit of accuracy of this NMR method based upon known mixtures of enantiomers was established to be ±1%. The limit of detection is generally accepted to be ±3%; therefore, % ee is denoted as ≥94% when only one enantiomer was detected.[24] [g] Determined by GLC separation of diastereomeric *l*-menthyl esters on a methylsilicone capillary column; a control experiment using racemic **4d** verified the absence of kinetic diastereoselection in ester formation. [h] Determined by GLC separation of diastereomeric (*S*)-(−)-1-phenylbut-1-yl esters on a Carbowax capillary column; a control experiment using racemic **4f** verified the absence of kinetic diastereoselection in ester formation.

The remarkable utility of these catalysts for effecting enantioselective intramolecular cyclopropanations was demonstrated in preliminary experiments with a series of allylic diazoacetates **3a–j** (Table I). Thus, slow addition (12–14 h) of **3a–j** to a solution of $Rh_2(5S\text{-MEPY})_4$ catalyst (1.0 mol %) in anhydrous CH_2Cl_2 delivered the corresponding 3-oxabicyclo[3.1.0]hexan-2-ones **4a–j** with very good to excellent enantioselectivities (65 to ≥94%). The absolute configuration of the lactones **4a–j** was assigned on the basis of comparison of the signs of rotation of the known cyclopropyl lactones **4a** and **4b**. Moreover, the structure of the (−)-menthyl ester of a derivative of lactone **4c** was established by single-crystal X-ray analysis.[25] The major competing reaction that accounted for the lower yields was the formation of carbene dimers. Examination of entries c–f reveals that intramolecular cyclopropanations of *Z* olefins proceeded with greater levels of enantioselectivity than the corresponding reactions of *E* isomers. The generality of this novel method for asymmetric synthesis of cyclopropanes was further enhanced by the fact that the readily available, enantiomeric $Rh_2(5R\text{-MEPY})_4$ catalyst **2** induced the intramolecular carbene additions of **3c,e,g–i** to give the enantiomers of **4c,e,g–i** with virtually identical efficiencies.



3a-j **4a-j**

In an attempt to increase the enantioselectivity of these processes, we replaced the methyl esters of **1** with isopropyl esters. However, no improvement for the cyclization of **3b** to give **4b** (89% ee, 83% yield) was observed when this catalyst was used. In preliminary experiments, we have also evaluated other chiral rhodium(II) catalysts having oxazolidinone ligands,[26] but these were found to be inferior to **1** and **2**.

Thus, rhodium(II) catalysts **1** and **2** offer unique advantages for enantioselective intramolecular cyclopropanations, since both enantiomers of a cyclopropyl lactone may be efficiently prepared with high enantioselectivity from a single allylic diazo ester. Studies are in progress to determine the scope and limitations of these catalysts to effect enantioselective cyclizations of other unsaturated systems as well as catalysis in other carbenoid transformations.

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Synthesis and Structural Characterization of Eight-Coordinate Geometrical Isomers of $[ReH_2(mhp)_2(PPh_3)_2]PF_6$ That Retain Their Structural Identity in Solution

Malee Leeaphon, Phillip E. Fanwick, and
Richard A. Walton*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

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While the stabilization of geometric isomers of eight-coordinate complexes has been known to be possible in the solid state, the only examples of structurally characterized isomeric pairs are the lanthanide complexes *cis*- and *trans*-$SmI_2[O(CH_2CH_2OMe)_2]_2$,[1] and the two dodecahedral isomeric forms of $V(S_2CCH_3)_4$ that are present in single crystals of this complex.[2] In neither system is there evidence that the isomers retain a separate and distinct identity in solution.[3] Indeed, the preparation and characterization of such isomers *in solution* has generally been considered to be "difficult, if not impossible".[4] However, it has been recognized through the elegant studies of Archer and Donahue[5] on tungsten(IV) complexes with four bidentate or two tetradentate donors that, in some instances, eight-coordinate geometrical isomers can be separated and that such stereoisomers can be stereochemically rigid. Unfortunately, in none of these cases was it possible to assign a specific structure to any isomer although dodecahedral geom-

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(3) Isomers can also be obtained by varying a counterion as, for example, in the case of salts of the $[Nb(C_2O_4)_4]^{4-}$ anion, viz., $K_3(H_3NCH_2CH_2NH_3)[Nb(C_2O_4)_4]\cdot 4H_2O$ and $K_4[Nb(C_2O_4)_4]\cdot 3H_2O$. See: Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1987**, *26*, 2889.

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etries were believed to be present.[5] We now report the first instance where eight-coordinate geometrical isomers have been structurally characterized and where these stereoisomers retain their structural identity in solution. These complexes, which are of stoichiometry $[ReH_2(mhp)_2(PPh_3)_2]PF_6$ (mhp represents the monoanion of 2-methyl-6-hydroxypyridine), are of additional note because this case of geometrical isomerism is encountered in a polyhydride system of a type that is usually notorious for exhibiting stereochemical nonrigidity.[6]

Protonation of the seven-coordinate monohydride complex $ReH(mhp)_2(PPh_3)_2$[7] (0.100 g, 0.108 mmol) with aqueous HPF_6 (65%, 0.020 mL) in dichloromethane (5 mL) yields, after 5 min, orange crystals of *trans*-$[ReH_2(mhp)_2(PPh_3)_2]PF_6$ in high yield (82%). When this reaction is allowed to continue for longer periods, or when a dichloromethane solution of *trans*-$[ReH_2(mhp)_2(PPh_3)_2]PF_6$ is kept at room temperature, the trans isomer is found to convert very slowly to the yellow cis isomer.[8] The latter product can be isolated in a pure state after a period of several weeks. The ^1H NMR spectra of the complexes in CD_2Cl_2 (Figure S1, supplementary material) show hydride resonances that are shifted downfield of that for the parent complex $ReH(mhp)_2(PPh_3)_2$.[7] The hydride resonance of the cis isomer consists of a binomial triplet at δ +4.65 due to coupling to the phosphorus atoms of the two equivalent PPh_3 ligands (J_{P-H} = 46 Hz). The hydride resonances of the trans isomer consist of a doublet of doublets at δ +6.66 (J_{P-H} = 33 Hz, J'_{P-H} = 29 Hz) due to chemically equivalent but magnetically inequivalent hydride ligands, which are coupled to equivalent phosphorus atoms of the phosphine ligands. Consistent with this, the $^{31}P\{^1H\}$ spectra of the cis and trans isomers show singlets at δ +25.9 and +14.3, respectively, while the corresponding ^{31}P NMR spectra show a triplet for the cis isomer, with J_{P-H} = 49 Hz, and an apparent triplet[9] with J_{P-H} = 30 Hz for the trans isomer. The resonances due to the PF_6^- anions are present as septets centered at δ −144.2, in both cases.

The X-ray structures of *cis*- and *trans*-$[ReH_2(mhp)_2(PPh_3)_2]PF_6$ were determined on crystals grown from acetone/heptane and 1,2-dichloroethane/heptane, respectively.[10] The P-Re-P angles in these two structures are ca. 129° and 169°, respectively, a difference that is the origin of our designation of these two species as the "cis" and "trans" isomers. The key features of the two structures are shown in Figure 1. Both structures are based upon a dodecahedral geometry.[11] Each contains a pair of chelating mhp ligands, which in the trans isomer are approximately in the same plane.[12] A key difference in the structures of the two isomers is the disposition of the hydride ligands. The two hydride ligands in the cis isomer form a plane with the rhenium center that is approximately perpendicular to that of the P-Re-P plane. In contrast, the hydride ligands in the trans isomer are approximately coplanar with the P-Re-P unit.[13] On the basis

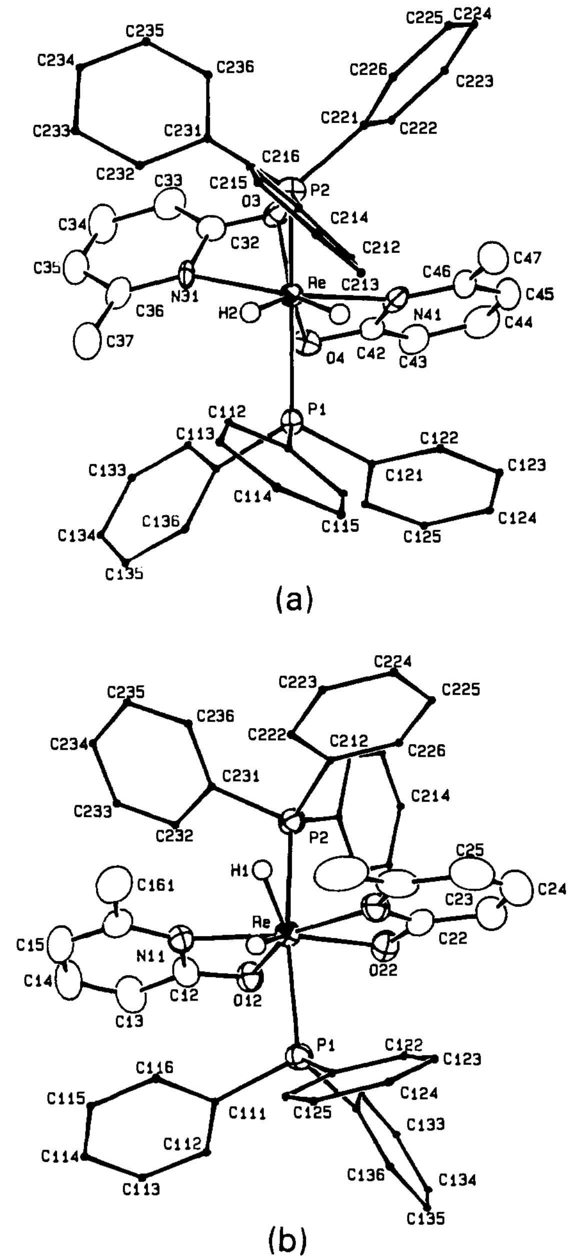

Figure 1. ORTEP view of the structure of (a) the *cis*-$[ReH_2(mhp)_2(PPh_3)_2]^+$ cation and (b) the *trans*-$[ReH_2(mhp)_2(PPh_3)_2]^+$ cation. The thermal ellipsoids are drawn at the 50% probability level, except for the phenyl carbon atoms and the hydride ligands, which are drawn with arbitrary radii. Hydrogen atoms of the mhp and phosphine ligands have been omitted for clarity. Some important representative bond distances (Å) and angles (deg) are as follows. Cis isomer: Re–P(1) = 2.406 (2), Re–O(3) = 2.106 (4), Re–N(31) = 2.133 (5), Re–H(1) = 1.61 (6), Re–H(2) = 1.58 (7), P(1)–Re–P(2) = 128.97 (6), H(1)–Re–H(2) = 61 (3), N(31)–Re–N(41) = 140.9 (2), O(3)–Re–O(4) = 76.9 (2), P(1)–Re–H(1) = 66 (2), P(1)–Re–H(2) = 67 (2), N(31)–Re–H(2) = 82 (2), O(3)–Re–N(31) = 62.6 (2), P(1)–Re–O(4) = 77.7 (1), P(2)–Re–O(3) = 77.9 (1). Trans isomer: Re–P(1) = 2.461 (1), Re–O(12) = 2.111 (3), Re–N(11) = 2.098 (3), Re–H(1) = 1.64 (4), Re–H(2) = 1.61 (4); P(1)–Re–P(2) = 168.76 (3), H(1)–Re–H(2) = 56 (2), N(11)–Re–N(21) = 149.1 (1), O(12)–Re–O(22) = 87.4 (1), P(1)–Re–H(1) = 126 (1), P(1)–Re–H(2) = 70 (2), N(11)–Re–H(1) = 79 (1), O(12)–Re–N(11) = 61.8 (1), P(1)–Re–O(22) = 85.76 (8), P(2)–Re–O(12) = 91.78 (7).

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(6) See, for example: Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1, and references contained therein.

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(8) All reactions were carried out under a nitrogen atmosphere.

(9) This resonance appears as a triplet with $J_{P-H} \simeq$ 30 Hz rather than a doublet of doublets since J_{P-H} is very similar to J'_{P-H} (33 vs 29 Hz from the ^1H NMR spectrum) and this difference is not resolvable.

(10) Crystal data for *cis*-$[ReH_2(mhp)_2(PPh_3)_2]PF_6\cdot(CH_3)_2CO$ (T = −96 °C): space group *Pbca*, a = 19.292 (2) Å, b = 22.399 (2) Å, c = 22.314 (2) Å, V = 9642 (3) Å^3, Z = 8, d_{calcd} = 1.56 g/cm^3; Enraf-Nonius diffractometer, Mo Kα radiation; 6884 unique reflections with 4° < 2θ < 45° collected, 4536 reflections with $I > 3\sigma(I)$ used in refinement; all non-hydrogen atoms except those of the disordered acetone solvent molecule refined anisotropically; empirical absorption correction applied (μ = 27.17 cm^{-1}); R = 0.036, R_w = 0.049, GOF = 1.525. Crystal data for *trans*-$[ReH_2(mhp)_2(PPh_3)_2]PF_6\cdot C_2H_4Cl_2$ (T = −62 °C): space group $P\bar{1}$, a = 13.382 (2) Å, b = 13.723 (2) Å, c = 15.593 (2) Å, α = 107.06 (1)°, β = 96.54 (1)°, γ = 114.05 (1)°, V = 2408 (2) Å^3, Z = 2, d_{calcd} = 1.62 g/cm^3; Enraf-Nonius diffractometer, Mo Kα radiation; 6280 unique reflections with 4° < 2θ < 45° collected, 5706 reflections with $I > 3\sigma(I)$ used in refinement; all non-hydrogen atoms refined anisotropically; disordered $C_2H_4Cl_2$ solvent molecule; empirical absorption correction applied (μ = 28.29 cm^{-1}); R = 0.023, R_w = 0.030, GOF = 1.015.

(11) Significant distortions from an idealized dodecahedral geometry arise because of the disparate sets of ligands that are present. The hydrido and oxygen donor atoms can be viewed as sitting at the A sites and the nitrogen and phosphorus atoms at the B sites of an MA_4B_4 dodecahedron. See, for example: Kepert, D. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1987; Chapter 2, p 84.

(12) Least-squares planes calculations on the O(12)–N(11)–Re–O(22)–N(21) plane show that the largest displacements of any of the five atoms that form the plane is 0.068 (3) Å for O(22).

(13) Least-squares planes calculations on the Re–P(1)–P(2)–H(1)–H(2) plane show that H(1) is 0.069 (42) Å and H(2) is 0.061 (47) Å from the plane.

of the crystallographic data and ^1H NMR spectral data, both isomers appear to be classical dihydrides. The H–H distances and H–Re–H angles[14] are normal for classical hydrides.[15] In addition, T_1 measurements for both isomers are consistent with this conclusion.[16] The ^1H NMR spectrum of the *trans*-$[ReHD(mhp)_2(PPh_3)_2]^+$ cation[17] shows a hydride resonance that has shifted approximately 0.1 ppm downfield from that of the dihydride complex. As expected, the hydride–deuteride complex does not exhibit resolvable H–D coupling, which would be characteristic of η^2-HD bonding.[18]

We observe an exceedingly slow conversion of the trans isomer to the cis in CD_2Cl_2 at room temperature. The isomerization appears to be an intramolecular process that is independent of added ligand (PPh_3, Hmhp, or Li(mhp)). It proceeds cleanly at room temperature (there are no observable side products) and can be followed conveniently by either ^1H or $^{31}P\{^1H\}$ NMR spectroscopy.[19] A zero-order rate constant $k = (7.9 \pm 0.2) \times 10^{-9}$ M s^{-1} at 20 °C was determined from the $^{31}P\{^1H\}$ spectra.[20] One possible explanation for the remarkable stability of the trans isomer is that the mhp ligands, which lie essentially in a plane with their methyl groups projecting toward each other, provide a barrier to the rotation of the ReH_2 unit that may be necessary to convert it to the cis isomer. This process can only be accomplished by a concomitant twisting of the mhp ligands from this planar arrangement, a process that apparently is not very favorable energetically. We find that the analogous complexes with ligands that do *not* contain methyl groups, i.e., $[ReH_2(L)_2(PPh_3)_2]PF_6$, where L is the anion of 2-hydroxypyridine or 2-mercaptopyridine, appear to exist exclusively in the cis form.[21] Efforts are now being directed toward designing other mixed-ligand sets that will display similar stereochemical characteristics in polyhydride systems.

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Supplementary Material Available: A listing of atomic positional parameters for the structures of *cis*-$[ReH_2(mhp)_2(PPh_3)_2]PF_6\cdot(CH_3)_2CO$ and *trans*-$[ReH_2(mhp)_2(PPh_3)_2]PF_6\cdot C_2H_4Cl_2$ and a figure (Figure S1) showing the ^1H NMR of spectra of these two complexes (9 pages). Ordering information is given on any current masthead page.

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(14) Cis isomer: H(1)–H(2) distance 1.6 (1) Å; H(1)–Re–H(2) angle 61 (3)°. Trans isomer: H(1)–H(2) distance 1.53 (5) Å; H(1)–Re–H(2) angle 56 (2)°.

(15) Cotton, F. A.; Luck, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 5757.

(16) Over the temperature range +25 to −80 °C the Re–*H* resonances remained essentially unchanged although they broadened slightly at the lower temperature limit. For the cis isomer the observed T_1 (min) at 200 MHz was 59 ± 7 ms (−74 °C) while for the trans isomers the observed T_1 (min) was 52 ± 11 ms (−76 °C). For a recent discussion of the T_1 method, see: Crabtree, R. H.; Luo, X. *Inorg. Chem.* **1990**, *29*, 2788.

(17) The deuteride was prepared by the addition of a 10-fold excess of CF_3CO_2D to a CD_2Cl_2 solution of $ReH(mhp)_2(PPh_3)_2$ in a sealed NMR tube, under N_2 gas. Both the acid and the CD_2Cl_2 were deoxygenated prior to use.

(18) For data on a similar shift in a hydride resonance. see: Chinn. M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824.

(19) A comparison was made of the trans → cis isomerization at three temperatures (0, 20, and 40 °C). No detectable amount (by NMR) of the cis isomer had formed after 4 days at 0 °C, while at 20 °C under these conditions the trans to cis isomer distribution was ca. 90:10. After 4 days at 40 °C (refluxing CH_2Cl_2) the cis isomer was now the dominant species (there was very little trans left). but a considerable quantity (ca. 30%) of the deprotonated complex $ReH(mhp)_2(PPh_3)_2$ had also formed under these conditions.

(20) A CD_2Cl_2 solution of the trans isomer was sealed in an NMR tube (under N_2 atmosphere), and the integrated intensity of the $^{31}P\{^1H\}$ signal was monitored over a period of several weeks to ca. 90% conversion. A CD_2Cl_2 solution of PPh_3 was used as an external standard.

(21) Leeaphon, M.; Walton, R. A., unpublished results. The mechanism of this zero-order isomerization is under further study, but it does not appear to be photochemical in origin.

$Nb_{1.72}Ta_{3.28}S_2$: A Novel Phase in the Ta–Nb–S Ternary System with a Layered Structure

Xiaoqiang Yao and Hugo F. Franzen*

Department of Chemistry and Ames Laboratory—DOE
Iowa State University, Ames, Iowa 50011

Received November 5, 1990

The structures of the metal-rich sulfides of Nb and Ta differ markedly. In $Nb_{21}S_8$[1] and $Nb_{14}S_5$,[2] the metal coordinations are capped pentagonal prisms and capped distorted cubes, while Ta_2S[3] and Ta_6S[4,5] contain linear chains of facing-sharing Ta pentagonal antiprisms.

High-temperature preparative studies have recently yielded two compounds: $Nb_{4.92}Ta_{6.08}S_4$[6] and $Nb_{6.74}Ta_{5.26}S_4$.[7] Both ternaries have unique structure types with coordinations similar to the Nb-rich sulfides. Here we report a new compound $Nb_{1.72}Ta_{3.28}S_2$ (*I4/mmm* $a = 3.320$ Å, $c = 21.619$ Å), with a layered structure reminiscent of Ta_2Se[8] found by high-temperature techniques.

The initial reactant, Ta_2S, was synthesized from the elements in an out-gassed silica tube at 800 °C for 3 days. By the same procedure "Nb_2S" was synthesized. A pellet of Ta_2S and "Nb_2S" (n_{Ta_2S}:n_{Nb_2S} = 3:1) was arc-melted on a copper plate under Ar by using a tungsten electrode. The arc-melted sample exhibits the facile shearing characteristic of layered compounds. The powder pattern of the arc-melted sample arose principally from the title compound. The full width of the 002 diffraction ($2\theta = 8.17°$) in the Guinier pattern is 0.13°. The widths of the diffraction lines indicated that the sample was poorly crystallized. When the sample was annealed at 1350 °C for several hours the new phase disproportionated. The major remaining phase was $Nb_xTa_{11-x}S_4$ ($x \simeq 5$).[6]

Intensity data were obtained from a crystal (0.02 × 0.02 × 0.25 mm^3) obtained from the arc-melted sample by using a Rigaku AFC6 single-crystal diffractometer employing monochromatic Mo Kα radiation and the 2θ–ω scan technique up to 60° (2θ). Data were obtained for 124 unique reflections with $F^2 > 3\sigma(F_o^2)$. Calculations were performed with the program package TEXSAN. The crystal was also examined by the Weissenberg technique and some streaking was observed. Thus, the crystal was not of optimum quality for refinement and the precision of the results could be adversely effected. However, the *R* factor was indicative of satisfactory refinement.

The structure was solved in the space group *I4/mmm* by the direct method. The formula was determined from the refinement to be $Nb_{1.72}Ta_{3.28}S_2$. The DIFABS absorption correction was applied. The results are given in Table I. Each metal position is occupied by both Nb and Ta. The arc-melted sample was checked by EDAX. The major phase consists of Ta, Nb, and S elements with minor amounts of W and Cu originating from the arc-melting and therefore probably on the sample surface.

The structure (Figure 1) can be viewed as *bcc*-type elemental Nb or Ta structure in which two neighboring layers in every seven are replaced by sulfur and thus some distortions relative to *bcc* are observed; e.g., the cube consisting of eight M2 contracts along the *c* axis while the cube of four M1 and four M3 expands along the *c* axis, with M2 deviating slightly from the center of the cube. This novel layered structure is reminiscent of Ta_2Se,[8] which is composed of six layers in the sequence Se–Ta–Ta–Ta–Ta–Se, also in *bcc*-type packing. In ZrCl[9] the sequence of the layers is Cl–

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