

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: OH1090). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Re₄S₄Te₄

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Abstract

The structure of the tetrahedral cluster compound tetrarhenium tetrasulfide tetratelluride, Re₄S₄Te₄, has been determined using X-ray diffraction data collected on a single crystal grown by the high-temperature reaction of stoichiometric amounts of rhenium and sulfur in molten tellurium. The compound contains tetrahedral

Re₄ clusters with S atoms capping each of the four faces; the Te atoms bridge the [Re₄S₄] units to form a three-dimensional structure.

Comment

Chalcogenides of rhenium are of fundamental interest because of their significance as catalysts, their material properties and their occurrence as minerals (Halbert, Ho, Stiefel, Chianelli & Daage, 1991; Korzhinsky, Tkachenko, Shmulovich, Taran & Steinberg, 1994). All structurally characterized chalcogenides of rhenium are cluster compounds. The participation of Re atoms in the formation of metal–metal bonds results in the formation of Re₄ parallelograms in ReS₂ and ReSe₂ (Murray, Kelty, Chianelli & Day, 1994; Wildervanch & Jellinek, 1971) or Re₆ octahedra in Re₆Te₁₅ (Klaiber, Petter & Hullinger, 1983). It is conceivable that the amorphous compound Re₂S₇ also contains Re₄ cluster fragments (Müller, Krickemeyer, Bögge, Ratajczak & Armatage, 1994). Recently, we prepared the first non-molecular tetrahedral cluster compound of rhenium, Re₄S₄Te₄, and also partly substituted phases such as Re_{4-x}Mo_xS₄Te₄ and Re₃MoS_{4-y}Se_yTe₄ (Fedorov, Mironov, Fedin & Mironov, 1994). The structure of Re₄S₄Te₄ was determined by the Rietveld method from powder diffraction data. Reported in this communication are the preparation and determination of the structure of single crystals of the title compound. These crystals can be obtained by the high-temperature reaction of a stoichiometric powder mixture of rhenium and sulfur in molten tellurium. Using a large excess of tellurium does not cause substitution of sulfur by tellurium, and the product of the reaction has the composition Re₄S₄Te₄.

The Re₄S₄Te₄ structure is characterized by the presence of tetrahedral Re₄ clusters with an Re–Re distance of 2.785 (3) Å, similar to the Re–Re distances in the molecular tetrahedral cluster compounds of Re^{IV}, [Re₄S₄(CN)₁₂]⁴⁻ (Laing, Kiernan & Griffith, 1977) and [Re₄S₄(S₃)₆]⁴⁻ (Müller, Krickemeyer & Bögge, 1986). Each triangular face of the regular Re₄ tetrahedron is capped symmetrically by triply bridging sulfide ions with an Re–S distance of 2.337 (10) Å. Each Re atom is further coordinated by three bridging Te atoms at a distance of 2.790 (2) Å.

This structure is isotopic with those of the chalcogeno halides of niobium and molybdenum, M₄Y₄X₄ (M = Nb, Mo; Y = S, Se; X = Cl, Br, I) (Fedorov, Evstaf'ev, Kirik & Mishchenko, 1981; Perrin, Chevrel & Sergent, 1975). These structures have been described as a NaCl-type arrangement of M₄Y₄ clusters and tetrahedral X₄ fragments. In Re₄S₄Te₄, the Te–Te distance within a Te₄ tetrahedron is 3.62 Å with the centre of the Te₄ tetrahedron at (½, 0, 0). The structure can also be envisaged as a zinc-blende-type arrangement of Re₄S₄ clusters and Te₄ tetrahedra. In this description, the Te₄ tetrahedron is centred at (¼, ¼, ¼) and the Te–Te distance

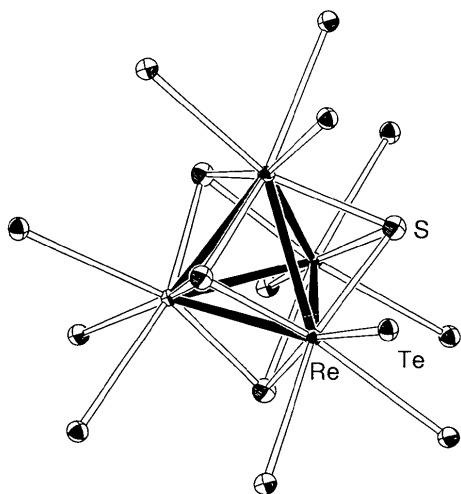


Fig. 1. The structure of the Re₄S₄Te₁₂ unit showing 90% probability displacement ellipsoids.

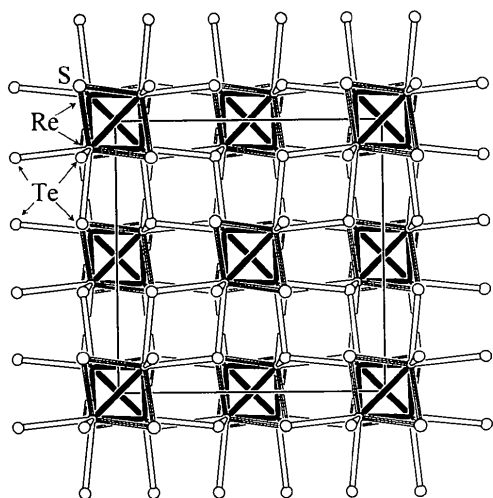


Fig. 2. The unit cell of Re₄S₄Te₄. Re—Te bonds are represented by thick lines and Re—S bonds are represented by thin lines.

is 3.49 Å. The Te₄ tetrahedron is surrounded by four Re₄S₄ clusters and each Te atom bridges three of the surrounding clusters.

The structure of Re₄S₄Te₄ can also be viewed as a variation of the spinel structure. In this interpretation, the chalcogen atoms (S and Te) form a cubic close-packed arrangement with Re atoms in the octahedral interstices. The arrangement of the ReS₃Te₃ octahedra is the same as that of the MO₆ octahedra in the spinel structure TM₂O₄, where T is a tetrahedrally coordinated metal atom and M is an octahedrally coordinated metal atom. Although the M atom is at the centre of the O₆ octahedron in the spinel structure, the Re atom is shifted from the centre of the S₃Te₃ octahedron to form an Re₄ cluster. The sites which are occupied by T atoms in the spinel structure are empty in Re₄S₄Te₄. Filling

half of the T sites with metal atoms gives the GaMo₄S₈ structure, found for GaM₄Y₈ (M = Nb, Mo; Y = S, Se) and TMO₂Re₂S₈ (T = Fe, Ni) (Ben Yaich *et al.*, 1984; Perrin, Chevrel & Sergent, 1976).

Experimental

Single crystals of the title compound were obtained from the elements (Re:S:Te = 1:1:6). The reaction was carried out in an evacuated sealed quartz ampoule at 1173 K. After three weeks at this temperature, the excess tellurium was evaporated off *in vacuo* at 773 K, allowing the isolation of tetrahedral crystals. Analysis: calculated for Re₄S₄Te₄ Re 53.54, S 9.27, Te 36.89%; found Re 53.55, S 9.33, Te 36.75%.

Crystal data

Re₄S₄Te₄
M_r = 1383.4
 Cubic
F $\bar{4}3m$
a = 10.044 (3) Å
V = 1013.1 (8) Å³
Z = 4
D_x = 9.069 Mg m⁻³

Mo Kα radiation
 λ = 0.7107 Å
 Cell parameters from 20 reflections
 θ = 17.44–21.55°
 μ = 60.37 mm⁻¹
T = 296 K
 Tetrahedron
 0.2 × 0.2 × 0.2 mm
 Black (metallic)

Data collection

Rigaku AFC-6S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
T_{min} = 0.631, *T_{max}* = 1.000
 422 measured reflections
 103 independent reflections

101 observed reflections
 [*F* > 3σ(*F*)]
R_{int} = 0.032
 θ_{\max} = 30.0°
h = 0 → 14
k = 0 → 14
l = 0 → 14
 3 standard reflections monitored every 150 reflections
 intensity decay: 0.12%

Refinement

Refinement on *F*
R = 0.0286
wR = 0.0224
S = 4.27
 101 reflections
 11 parameters
 Weighting scheme based on measured e.s.d.'s
 $(\Delta/\sigma)_{\max}$ < 0.001
 $\Delta\rho_{\max}$ = 12.95 e Å⁻³
 $\Delta\rho_{\min}$ = -6.85 e Å⁻³

Extinction correction: Zachariasen (1967)
 Extinction coefficient: 1.78 (9) × 10⁻⁷
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Re	0.09805 (9)	<i>x</i>	<i>x</i>	0.0030 (4)
Te	0.3727 (2)	<i>x</i>	<i>x</i>	0.0050 (7)
S	-0.1302 (8)	<i>x</i>	<i>x</i>	0.006 (2)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Re—Re ^I	2.785 (3)	Te—Te ^{II}	3.486 (6)
Re—Te ^{II}	2.790 (2)	Te—Te ^{III}	3.616 (6)
Re—S ^I	2.337 (10)		
Re ^I —Re—Re ^{II}	60	S ^I —Re—S ^{II}	104.6 (3)
Te ^{II} —Re—Te ^I	77.35 (11)	Re ^{II} —Te—Re ^I	101.36 (9)
Te ^{II} —Re—S ^{II}	87.3 (2)	Re ^I —S—Re ^{II}	73.2 (4)
Te ^{II} —Re—S ^{II}	160.2 (2)		

Symmetry codes: (i) $-x, -y, z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} - z$; (iii) $1 - x, y, 1 - z$; (iv) $-x, y, -z$; (v) $\frac{1}{2} - x, y, \frac{1}{2} - z$; (vi) $x, -y, -z$.

Refinement of the inversed geometry gave $R = 0.048$, $wR = 0.036$ and $S = 6.82$, confirming that the absolute configuration chosen here is correct.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *EQVRFL* (Imoto, 1992). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *ANYBLK* (Imoto, Hayakawa, Morita & Saito, 1990). Software used to prepare material for publication: *ANYBLK*.

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Copper–Zinc Oxide Catalysts. III. Structure of $[\text{Zn}(\text{NH}_3)_3][\text{Cu}(\text{CN})_2]_2$

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Abstract

The structure of the new Cu–Zn bimetallic compound triamminezinc(II) bis[dicyanocuprate(I)] is built up from infinite —Cu—AA—Cu—AA— (where AA represents a disordered CN group) helical chains with 2_1 symmetry. Terminal cyano groups and —CN—Zn(NH₃)₃ groups are bonded alternately to the Cu atoms of the chains. Both crystallographically independent Cu^I atoms are trigonally coordinated by three cyano groups. The Zn^{II} atom is tetrahedrally coordinated by three ammonia molecules and one nitrogen-bonded cyano group. The intra- and interchain CN···HN hydrogen bonds contribute to the stabilization of the structure.

Comment

Copper–zinc bimetallic compounds can be used as precursors for the unconventional preparation of model catalysts for the methanolization of syngas (CO + H₂). The advantage of such precursors is the intimate presence of both metals at the first stage of catalyst preparation (Chinchen, Denny, Jennings, Spencer & Waugh, 1988). Our goal is to study the preparation, characterization and crystal structure of such bimetallic compounds. In previous papers we described the preparation and thermal properties of new Cu–Zn bimetallic compounds (Černák, Chomič, Kappenstein, Brahmi & Duprez, 1995) and the crystal structures of two, Zn(NH₃)₂Cu(CN)₃ (ZCA) and

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