

Remarkable Metal-Rich Ternary Chalcogenides $\text{Sc}_{14}\text{M}_3\text{Te}_8$ ($\text{M} = \text{Ru}, \text{Os}$)

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In this novel motif, scandium atoms define infinite chains of alternate trans-face-sharing cubes and pairs of square antiprisms in which each polyhedron is also centered by an M atom ($\text{M} = \text{Ru}, \text{Os}$). These chains are further linked into a three-dimensional (3D) structure by $\text{Sc}(\text{Te}_2\text{Te}_{4/2})$ octahedra through strong Sc–Te interactions. Physical property measurements show that $\text{Sc}_{14}\text{Ru}_3\text{Te}_8$ is metallic and Pauli-paramagnetic, consistent with the results of extended Hückel band structure calculations. The Sc–M and Sc–Te interactions are major.

Early transition-metal-rich halides,¹ chalcogenides,² and pnictides^{3,4} have been widely studied. Relative to the present compounds, numerous phases exhibit the well-known W_5Si_3 -type⁵ tetragonal structure $1_{\infty}[(\text{W}_{8/2}\text{Si})(\text{WSi}_{4/2})]$, which in part contains infinite chains of square antiprismatic transition metal T centered by a later element M, generally a transition metal or main group element (Si, etc.). These chains are further interconnected by shared $\text{TM}_{4/2}$ tetrahedra. Other ternary variants exhibit different interconnections between the former chains, as in $(\text{Bi}_4\text{Ru})\text{X}_2$ ($\text{X} = \text{Br}, \text{I}$),⁶ $(\text{Ti}_4\text{M})\text{Br}_2$ ($\text{M} = \text{Cr}–\text{Ni}$),⁷ $(\text{V}_4\text{Si})\text{Sb}_2$,⁸ $(\text{Nb}_4\text{M})\text{Pb}_{0.5}\text{Sb}_2$ ($\text{M} = \text{Cr}, \text{Fe}–\text{Ni}, \text{Si}$),⁴ $(\text{Ta}_4\text{M})\text{Te}_4$ ($\text{M} = \text{Cr}, \text{Fe}–\text{Ni}, \text{Al}, \text{Si}$),⁹ and $(\text{R}_4\text{Os})\text{Br}_4$ ($\text{R} = \text{Y}, \text{Er}$).¹⁰ We have now discovered a novel and quite different structure type that contains chains in which pairs of square antiprismatic scandium alternate with scandium cubes, each cluster being centered by a ruthenium or osmium atom. These compounds were synthesized via typical high-temperature solid-state chemical reactions¹¹ and characterized by single-crystal X-ray diffraction methods in space group $P4/nmc$ for the refined stoichiometries $\text{Sc}_{13.2(2)}\text{Ru}_3\text{Te}_8$ and $\text{Sc}_{13.82(2)}\text{Os}_3\text{Te}_8$.^{13,16}

A [001] projection of the nominal $\text{Sc}_{14}\text{Ru}_3\text{Te}_8$ structure is shown in Figure 1. Scandium metal plays two roles: one as Sc3 in chains of individual octahedral complexes $[\text{Sc}(\text{Te}_2\text{Te}_{4/2})]$ centered at $1/2, 0, z$, etc. ($d(\text{Sc}3–\text{Sc}3) > 4.5 \text{ \AA}$). (It is only here that a Sc deficiency occurs.) The second and principal feature seen in a side view in Figure 2 around $0, 0, z$ consists of infinite chains of confacial clusters, each centered by a Ru or Os atom, in which cubes defined by Sc2 atoms are bonded through common (trans) faces to pairs of square antiprismatic units with Sc1 as the common faces. Each metal unit is connected to four Te-rich bridging chains built of $\text{Sc}-(3)\text{Te}_6$ octahedra to complete the 3D structure. The Te atoms have trigonal prismatic and pentagonal bipyramidal configurations, respectively.

Matrix effects in which the two scandium polyhedra basically “ride on” Ru (Os) interstitials seem evident, especially in the antiprisms (Figure 2). The Ru1–Sc distances in the cube, 2.79 Å, are somewhat longer than for Ru2–Sc in the antiprism, 2.68, 2.73 Å. Twisting of the trans faces in the cube to generate an antiprism diminishes the separation of the faces and crowds the Sc–Ru2 contact, as manifested in the distances. The Sc1–Sc2 distances in the latter side edges are necessarily larger (3.36, 3.41 Å) than the “height” of the cube $d(\text{Sc}1–\text{Sc}1)$, 3.28 Å, and the shared faces are also 0.05 Å larger for the Sc1–Sc1 squares (3.25 Å). The

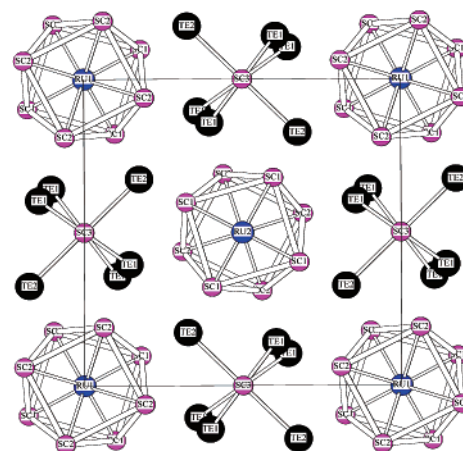


Figure 1. [001] projection of the tetragonal unit cell of $\text{Sc}_{13.2}\text{Ru}_3\text{Te}_8$. Sc1 and Sc2 generate chains of confacial cubes and antiprisms centered by Ru. Sc3 atoms center infinite chains of $\{\text{ScTe}_6\}_n$ octahedra that share trans edges.

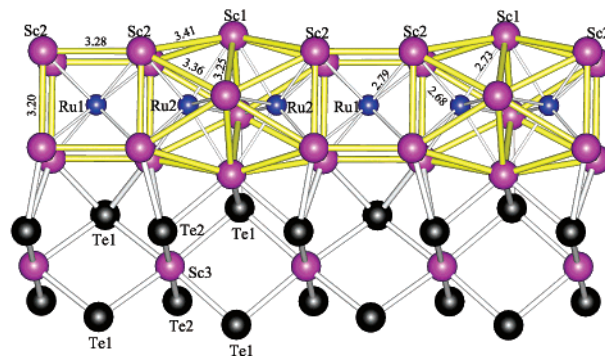


Figure 2. Segment of condensed $\{\text{Sc}_4\text{Ru}\}_n$ infinite chain of trans-face-sharing cubic (Sc1) and square antiprismatic (Sc1 and Sc2) polyhedra centered by Ru1 and Ru2, respectively. Distances in Å.

substitution of Os for Ru affects all distances by 0.03 Å or less, generally as a decrease.

Extended Hückel band structure calculations¹⁷ for $\text{Sc}_{14}\text{Ru}_3\text{Te}_8$ yield the densities-of-states (DOS) data shown in Figure 3 (left). As is usual for such scandium-rich chalcogenides,^{19–22} the Fermi level (–5.07 eV) is located on the low-energy side of a high DOS region that is dominated by Sc 3d orbitals, with small Ru 4d contributions around E_F . The crystal orbital overlap population (COOP) data in Figure 3 (right) show that most Sc–Sc bonding levels are occupied and that the Sc–Ru bonding is optimal, but there are insufficient electrons to utilize all Sc–Sc bonding states. The Mulliken overlap population (MOP) make clear that Sc–Sc interactions within the cubes, namely, Sc2–Sc2, 3.20 Å, MOP 0.071 and 3.28 Å, 0.059, are greater than in the square antiprismatic polyhedra: Sc1–Sc1, 3.25 Å, 0.045; Sc1–Sc2, 3.36 Å, 0.042; Sc1–Sc2; 3.41 Å, 0.032. (MOP values for Sc–Sc bonds among binary as well as ternary Sc–Te phases with small 3d interstitials

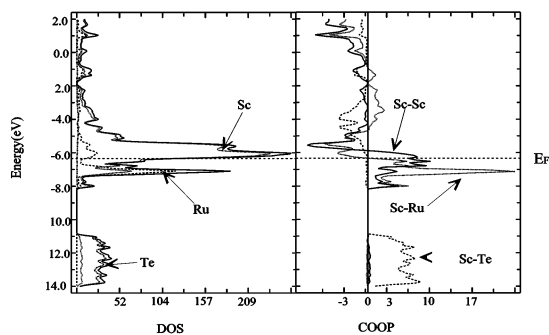


Figure 3. DOS and COOP plots from extended Hückel band calculations on $\text{Sc}_{14}\text{Ru}_3\text{Te}_8$. In the DOS (left), the solid, dotted, dashed, and dot-dashed lines refer to total and partial DOS for Sc, Ru, Te, respectively. In COOP (right), the solid, dotted, and dashed lines represent weighted overlap populations as a function of energy for all Sc–Sc, Sc–Ru, and Sc–Te contacts within 3.5, 3.0, and 3.1 Å, respectively.

usually fall in the range of 0.1–0.37,^{18–21,23,24} also attesting to the matrix effects from the larger Ru, Os here.) The ruthenium 4d states spread over a wide energy range (–6.1 to –3.5 eV) with a pronounced peak at –5.7 eV just below E_F . Ru 5s states make small contributions over –6.0 to –5.0 eV. The Ru–Ru interactions (not shown) are weakly bonding. The Te 5p states fall between –6.0 and –8.0 eV. E_F is marginally lower for the observed $\text{Sc}_{13.2}\text{Ru}_3\text{Te}_6$ stoichiometry, and only some slightly antibonding Sc3–Te states are emptied.

Consistent with band structure calculations, $\text{Sc}_{13.2}\text{Ru}_3\text{Te}_8$ exhibits metallic behavior. Magnetic measurements²² show a Pauli paramagnetic susceptibility with only a small temperature dependence above 100 K and $\chi_{298} = 7.0 \times 10^{-4}$ emu/mol, comparable to those in binary Sc–Te compounds.²⁴ The metallicity of $\text{Sc}_{13.2}\text{Ru}_3\text{Te}_8$ is clearly shown by polycrystalline resistivity data, $\rho_{298} = 10$ m Ω ·cm; $\rho_4 = 8.2$ m Ω ·cm (see Supporting Information).

The $\text{Sc}_{14}\text{M}_3\text{Te}_8$ phases represent a new and remarkable structure-type among metal-rich ternary chalcogenides. The condensed chains built of centered cubes and square antiprisms have only a distant relationship to the condensed antiprisms in W_5Si_3 -type phases and others.²⁵ Replacement of Sc3 with other elements, e.g., Pt, Au, or a vacancy (to resemble V_4SiSb_2 more closely) would be novel. Although wide ranges of M atoms can be substituted in W_5Si_3 -type phases and in related variants, our first attempts here have been widely unsuccessful.¹¹ Likewise, appreciable variabilities of M among the sizable collection of ternary scandium tellurides have not been achieved except to some degree among hexagonal Sc_6MTe_6 phases (Fe_2P type).¹²

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Supporting Information Available: Tables of X-ray data collection and refinement results, structural parameters and distances, and plots of magnetic and resistivity data (PDF). X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) $\text{Sc}_{14}\text{Ru}_3\text{Te}_8$ was first encountered from a Sc:Ru:Te = 3:1:1 reaction in a carbon-heated vacuum furnace to 1300 °C for 48 h. The Guinier powder pattern of the dark-grey product revealed 90% $\text{Sc}_{14}\text{Ru}_3\text{Te}_8$ and ~10% ScRu. The rutheride was then synthesized quantitatively from the stoichiometric reaction mixture once the composition was established crystallographically. The Ru phase can be prepared in high yields (>90%) over a wide temperature range from 1050 to 1300 °C or higher. The Os phase also forms on target. Single crystals of the latter phase were isolated along with Sc_6OsTe_2 (Fe_2P type)¹² after annealing the arc-melting product from a 6:1:2 stoichiometry. Similar stoichiometries and reaction conditions have yielded no isotopic tetragonal phases for M = Rh, Ir, Pd, Pt, Fe, Ag, Cu, Mo, or W.
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- (13) Single-crystal data were collected on a Bruker SMART 1000 CCD-based X-ray diffractometer, from which space group $P4/mnc$ (No. 128) was indicated. Absorption effects were corrected by SADABS.¹⁴ Lattice parameters for $\text{Sc}_{13.21(2)}\text{Ru}_3\text{Te}_8$ were obtained from calibrated Guinier camera data with 40 lines indexed, $a = b = 11.3332(4)$ Å, $c = 9.0793(5)$ Å, $V = 1166.17(9)$ Å³, and for $\text{Sc}_{13.82(2)}\text{Os}_3\text{Te}_8$, $a = b = 11.4008(9)$ Å, $c = 9.074(1)$ Å, $V = 1179.5(1)$ Å³ with 28 indexed lines (23 °C). The structures were solved by direct methods and refined with SHELXTL¹⁵ by full-matrix least-squares to anisotropic convergence at R [$I > 2\sigma(I)$] = 2.75%, wR_2 (F^2) = 4.33% for $\text{Sc}_{13.21(2)}\text{Ru}_3\text{Te}_8$ and 1.69%, 3.69% for $\text{Sc}_{13.82(2)}\text{Os}_3\text{Te}_8$. Parameters and distances are given in the Supporting Information.
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- (15) SHELXTL, version 5.1; Bruker AXS, Inc.: Madison, WI, 1998.
- (16) The reductions in total scandium content below the idealized $\text{Sc}_{14}\text{M}_3\text{Te}_8$ result entirely from a refined substoichiometry of Sc3 that centers the nominal tellurium octahedra, 61(1) and 91(1)% for M = Ru, Os, respectively. The Sc3 content in the former evidently does not represent the lower end of an appreciable nonstoichiometry region; rather, each appears to be an intrinsic and essentially fixed value. Guinier-based lattice dimensions of similarly synthesized compositions $\text{Sc}_x\text{Ru}_3\text{Te}_8$ for $x = 13, 14, 15$ all fell within a range of $\Delta a = 0.007$ Å (10 σ), $\Delta c = 0.01$ Å (8 σ), $\Delta V = 2.63$ Å³ (29 σ), and for $\text{Sc}_x\text{Os}_3\text{Te}_8$, within $\Delta a = 0.014$ Å (2 σ), $\Delta c = 0.034$ Å (6 σ), $\Delta V = 1.5$ Å³ (15 σ) We suspect that the different amounts of the more oxidized Sc^{III} at the Sc3 sites probably arises largely with differences in the stability of other products observed in equilibrium with $\text{Sc}_{-14}\text{M}_3\text{Te}_8$, namely ScTe (NiAs type) and ScRu (NaCl type); or ScTe and ScOs_2 (MgZn₂ type).
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