Scandium Transition Metal Carbides Sc_3TC_4 with T = Fe, Co, Ni, Ru, Rh, Os, Ir

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The compounds Sc_3TC_4 were prepared by arc-melting cold-pressed pellets of the elemental components. They have the orthorhombic Sc_3CoC_4-type structure. The compounds with T = Ru, Rh, Os, or Ir were obtained for the first time. The crystal structures of Sc_3FeC_4 and Sc_3RuC_4 were refined from single-crystal X-ray data to residuals of R = 0.015 (610 structure factors, 18 variable parameters) and R = 0.022 (248 F's, 18 variables), respectively. The transition metal and carbon atoms form one-dimensionally infinite $[TC_4]_n^{9n-}$ polyanions, where one T atom is linked to the next by two C_2 bridges. The C–C distances in the C_2 pairs of 145.1(1) pm (T = Fe) and 144.1(5) pm (T = Ru) are between the distances for a double and a single bond. Nevertheless, the hydrolyses of Sc_3RuC_4 and Sc_3RhC_4 with dilute hydrochloric acid yield mainly methane, ethane, and propane, and no unsaturated hydrocarbons. All seven title compounds were tested for superconductivity by the induction method and none showed a transition above 2 K. © 1992 Academic Press, Inc.

Introduction

Of the rare earth elements lanthanum has the largest atomic radius and scandium the smallest. Because of the large spread in atomic size it is rare that isotypic compounds are formed with all of these elements. This is especially true for ternary compounds, where there are more possibilities for atomic arrangements than for binary compounds. Among the carbides only those with the perovskite structure RT_3C (R = Sc, Y, the lanthanoids and actinoids, T = transition metals) are known to form such a series (*1*). So far no other ternary scandium-containing carbides were reported to be isotypic with lanthanoid carbides and only one example is known, where scandiumcarbides are isotypic with a corresponding series of actinoid carbides: $ScFeC_2$, $ScCoC_2$, and $ScNiC_2$ (*2*), and $UCoC_2$, $UFeC_2$, and $UNiC_2$, and $PuFeC_2$ (*3*). Sc_2CrC_3 (*4*) and U_2NiC_3 (*5*) have related structures, but they are not isotypic. Some of the scandium carbides form exiting structures, e.g., Sc_3C_4 (*6*) and $Sc_5Re_2C_7$ (*7*) contain linear C_3 groups derived from propadiene. Thus, we thought it worthwhile to explore the structural chemistry of scandium-containing carbides. Here we report on the new ternary scandium platinum metal carbides which we found to be isotypic with the corresponding iron metal carbides (*8*). The results of the structure refinements of Sc_3FeC_4 and Sc_3RuC_4 are discussed together with those of the prototype Sc_3CoC_4 (*8*). A preliminary account of some of this work has been published earlier (*9*).

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Sample Preparation

Starting materials were filings of scandium (99.9%), powders of iron, cobalt, nickel, ruthenium, rhodium, osmium, and iridium (all with stated purities of 99.9%), and graphite flakes (99.5%). They were mixed in the ideal atomic ratio, cold pressed to pellets of about 300 mg, and arc-melted under an atmosphere of purified argon of about 600 mbar. The well-crystallized samples were subsequently annealed in a high-frequency furnace in water-cooled silica tubes slightly below the melting point for about 10 hr. Energy dispersive analyses of the ternary carbides in a scanning electron microscope were in agreement with the ideal composition and did not reveal any impurity elements heavier than sodium.

Properties

The carbides Sc_3TC_4 are grey in powdered form and are stable in air for long periods of time. Hydrolysis with water was not noticeable. At room temperature the well-crystallized samples are even stable for some time in 6 N hydrochloric acid, possibly due to kinetic hindrance. This can be overcome by wrapping the samples in iron foil or by heating. Powders are less stable. Single crystals show metallic luster. Searching for superconductivity we tested the seven Sc_3CoC_4 type carbides in an ac inductivity apparatus. None of these samples showed a transition down to 2 K.

Powdered samples of Sc_3RuC_4 and Sc_3RhC_4 were hydrolyzed in diluted (2 N) hydrochloric acid at about 60°C. The emerging gaseous products were analyzed in a gas chromatograph as described previously (10). In both cases the major hydrolysis products were methane, ethane, and propane, besides hydrogen. There were no unsaturated hydrocarbons.

Lattice Constants

The samples were characterized through their Guinier powder patterns. $CuK\alpha_1$ radiation was used with α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as the standard. The lattice constants (Table I) were refined by least-squares fits. To assure proper indexing, the observed patterns were compared with the calculated ones (11) assuming the atomic positions as obtained in the structure refinements for Sc_3FeC_4 and Sc_3RuC_4. The lattice constants of the iron, cobalt, and nickel compounds were in good agreement with the values obtained by Tsokol' et al. (8).

The cell dimensions of these isotypic carbides depend on the position of the T component in the periodic system. The cell volumes change relatively little within one period. The lattice constant a increases from the Fe to the Ni group. This is compensated by the lattice constant c, which shows the inverse behavior. The lattice constant b seems to have a minimum in the Co group.

Structure Refinements

Single crystals of Sc_3FeC_4 and Sc_3RuC_4 were isolated from the crushed buttons after the annealing processes. They were investigated with Buerger precession cameras to establish their symmetry and their suitability for intensity data collections. The precession photographs showed orthorhombic symmetry and had only the systematic extinctions of a body-centered lattice. This led to the space groups $Immm$, $Imm2$, and $I2_12_12_1$, of which the centrosymmetric group $Immm$ (No. 71) was found to be correct during the structure refinements, in agreement with the earlier results for Sc_3CoC_4 (8).

Intensity data were collected on an automated four-circle diffractometer with graphite monochromated $MoK\alpha$ radiation and a scintillation counter with pulse-height dis-

TABLE I

LATTICE CONSTANTS OF THE ORTHORHOMBIC Sc_3CoC_4-TYPE CARBIDES[a]

Compound	a(pm)	b(pm)	c(pm)	V(nm^3)	Reference
Sc_3FeC_4	336.98(5)	438.22(8)	1210.1(2)	0.1787(1)	This work
Sc_3FeC_4	336.36(3)	437.48(3)	1208.7(5)	0.1779(1)	8
Sc_3CoC_4	339.57(9)	437.4(1)	1198.9(3)	0.1781(1)	This work
Sc_3CoC_4	339.33(1)	437.27(1)	1198.9(3)	0.1779(1)	8
Sc_3NiC_4	341.30(4)	439.35(6)	1193.4(1)	0.1790(1)	This work
Sc_3NiC_4	341.18(3)	437.72(3)	1191.6(5)	0.1780(1)	8
Sc_3RuC_4	331.35(4)	448.77(8)	1238.0(2)	0.1841(1)	This work
Sc_3RhC_4	336.74(4)	447.56(5)	1226.8(2)	0.1849(1)	This work
Sc_3OsC_4	332.84(5)	448.24(7)	1235.6(2)	0.1843(1)	This work
Sc_3IrC_4	339.74(6)	445.38(7)	1223.5(2)	0.1851(1)	This work

[a] Standard deviations in the positions of the last listed digits are given in parentheses throughout the paper.

crimination. The crystallographic data and some results are summarized in Table II. The structures of Sc_3FeC_4 and Sc_3RuC_4 were assumed to be isotypic with Sc_3CoC_4 (8), which was confirmed during the full-matrix least-squares refinements with atomic scattering factors (12), corrected for anomalous dispersion (13). A factor accounting for isotropic secondary extinction was refined and applied to the calculated structure factors. Occupancy parameters were also refined as checks for the ideal composition. No significant deviations from full occupancies were found and thus in the

TABLE II

CRYSTALLOGRAPHIC DATA FOR Sc_3FeC_4 AND Sc_3RuC_4

	Sc_3FeC_4	Sc_3RuC_4
Lattice constants	Table I	Table I
Formula units/cell	$Z = 2$	$Z = 2$
Space group	*Immm* (No. 71)	*Immm* (No. 71)
Formula weight	238.76	283.98
Calculated density [g/cm^3]	$\rho_c = 4.44$	$\rho_c = 5.12$
Absorption coefficient [cm^{-1}]	$\mu(MoK\alpha) = 92.5$	$\mu(MoK\alpha) = 90.6$
Crystal dimensions [μm^3]	$20 \cdot 20 \cdot 180$	$5 \cdot 15 \cdot 45$
$\theta/2\theta$ scans up to	$2\theta = 115°$	$2\theta = 90°$
Range in hkl	$\pm 8, \pm 10, \pm 28$	0 to 6, ± 8, ± 24
Total no. of reflections	4470	1678
Absorption correction	From psi scans	From psi scans
Transmission coefficient (highest/lowest)	1.083	1.039
Unique reflections	745	469
Inner residual	$R_i = 0.022$	$R_i = 0.042$
Reflections with $I > 3\sigma(I)$	610	248
No. of variables	18	18
Conventional residual	$R = 0.015$	$R = 0.022$
Weighted residual	$R_w = 0.021$	$R_w = 0.017$
Weights	$w = 1/\sigma^2$	$w = 1/\sigma^2$

TABLE III

ATOMIC PARAMETERS OF Sc_3FeC_4 AND Sc_3RuC_4[a]

Atom	Immm	Occupancy	x	y	z	B_{eq}
			Sc_3FeC_4			
Sc(1)	2d	0.994(1)	$\frac{1}{2}$	0	$\frac{1}{2}$	0.302(3)
Sc(2)	4i	0.999(1)	0	0	0.18893(2)	0.288(2)
Fe	2b	1.004(1)	0	$\frac{1}{2}$	$\frac{1}{2}$	0.353(3)
C	8l	1.014(3)	0	0.1656(2)	0.37493(6)	0.371(8)
			Sc_3RuC_4			
Sc(1)	2d	1.001(4)	$\frac{1}{2}$	0	$\frac{1}{2}$	0.39(2)
Sc(2)	4i	0.994(3)	0	0	0.18992(6)	0.36(1)
Ru	2b	1.001(2)	0	$\frac{1}{2}$	$\frac{1}{2}$	0.410(8)
C	8l	1.039(9)	0	0.1606(8)	0.3712(2)	0.49(4)

[a] The last column contains the equivalent isotropic thermal parameters B_{eq} ($\times 100$, in units of nm^2). The occupancy parameters were refined in separate least-squares cycles. In the final cycles the ideal occupancies were assumed.

final least-squares cycles the ideal occupancies were assumed. Final difference-Fourier analyses gave no indications for the occupancy of additional atomic sites. The positional parameters and the interatomic distances of both structures are listed in Tables III and IV. Listings of the structure factors and the anisotropic thermal parameters are available from the authors (14).

Discussion

The interaction of the Sc atoms with the transition metal and carbon atoms may in a first approximation be considered as ionic and we may write the formula $[3Sc^{3+}]^{9+}[TC_4]^{9-}$. The T and C atoms form a one-dimensionally infinite $[TC_4]_n^{9n-}$ polyanion, where one T atom is linked to the next by two C_2 bridges, as can be seen in the upper right-hand corner of Fig. 1. The C–C distance in the three Sc_3TC_4 structures with T = Fe, Co, Ru, which were refined, varies only between 144.1 pm and 146.4 pm and thus it is halfway between the C–C single-bond distance of 154 pm and the double-bond distance of 134 pm in hydrocarbons.

It is therefore surprising that the hydrolysis products consisted only of methane, ethane, and propane, with no unsaturated hydrocarbons. In U_2NiC_3 (5), where the C–C distance is 143 pm, 15 wt.% ethylene was found under similar hydrolysis conditions.

Chemical bonding within the transition-metal carbon polyanion of the Sc_3CoC_4-type structure was already briefly discussed together with other low-dimensional polyanions of similar composition (10). It was shown that this polyanion is favored over other one-dimensionally infinite transition-metal carbon polyanions for an electron count of 34, i.e., T = Co. The interatomic distances in Sc_3FeC_4 and in the previously determined structure of Sc_3CoC_4 (8) are very similar. The greatest differences occur for the Sc–Sc distances. However, these distances are rather large and therefore these interactions are all of less importance. The differences in the Sc–C distances are all less than the combined standard deviations. The Co–C distances are 2.1 pm shorter than the Fe–C distances. This is practically the same difference as the difference of the metallic radii for the coordination number 12

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TABLE IV

INTERATOMIC DISTANCES (pm) IN THE STRUCTURES OF Sc_3TC_4 (T = Fe, Co, Ru)[a]

		Sc_3FeC_4	Sc_3CoC_4[b]	Sc_3RuC_4
Sc1	8C	237.82(8)	237.8(3)	241.0(3)
	4T	276.40(4)	276.87(7)	278.9(2)
	4Sc2	316.67(5)	314.07(12)	325.0(2)
	2Sc1	336.98(5)	339.57(9)	331.3(2)
Sc2	4C	236.31(10)	236.2(3)	235.7(4)
	2C	236.48(11)	236.2(3)	237.4(3)
	2T	284.00(5)	282.21(12)	287.6(2)
	4Sc2	313.44(6)	314.23(12)	316.1(2)
	2Sc1	316.67(5)	314.07(12)	325.0(2)
	2Sc2	336.98(5)	339.57(9)	331.3(2)
T	4C	210.68(12)	208.6(3)	220.5(4)
	4Sc1	276.40(4)	276.87(7)	278.9(2)
	4Sc2	284.00(5)	282.21(12)	287.6(2)
	2T	336.98(6)	339.57(9)	331.3(2)
C	1C	145.1(2)	146.4(4)	144.1(6)
	1T	210.68(12)	208.6(3)	220.5(4)
	2Sc2	236.31(10)	236.2(3)	235.7(4)
	1Sc2	236.48(11)	236.2(3)	237.4(3)
	2Sc1	237.82(8)	237.8(3)	241.0(3)

[a] All distances shorter than 433 pm (Sc–T), 410 pm (Sc–Sc), 345 pm (Sc–C), 331 pm (T–T), 327 pm (T–C), and 291 pm (C–C) are given.

[b] These distances were calculated assuming the positional parameters from Tsokol' et al. (8) with the lattice constants obtained in the present work.

given by Teatum et al. (15) for Fe (r = 127.4 pm) and Co (r = 125.2 pm). One may wonder where the additional valence electron of the cobalt atom is accomodated. A similar observation was made in comparing the structure refinements of the isotypic series $ScTC_2$ (T = Fe, Co, Ni) (16). There it was rationalized that two trends seem to counterbalance each other. One is the decreasing electron count in going from the Ni to the Fe compound and the other is the increasing electropositivity of the T element component in the same direction. Band structure calculations for such carbides (17, 18) have shown that the antibonding C–C orbitals are at the Fermi level. Thus, a decrease in the number of valence electrons in going from the Ni to the Fe compound

should result in a decrease of the C–C distances. This is balanced by the higher electropositivity of the iron atoms, which raises the energy of all bands involving Fe interactions and thus the C–C antibonding levels are filled again.
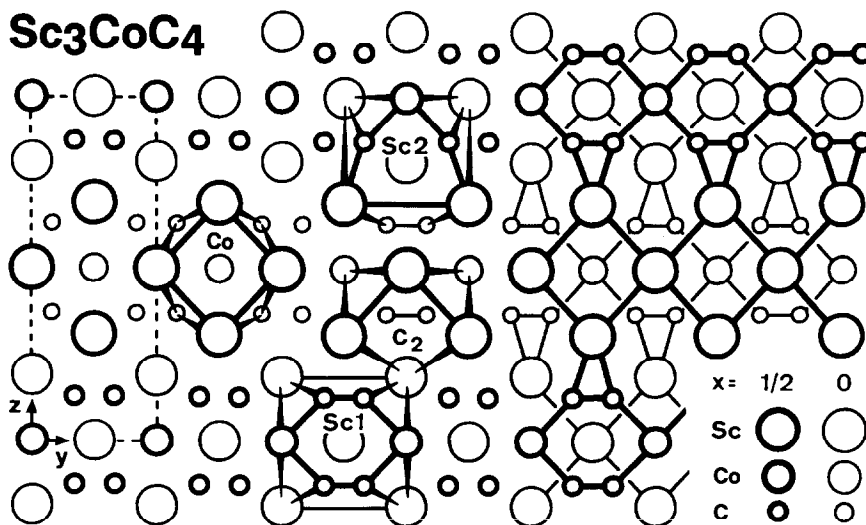
Acknowledgments

FIG. 1. Crystal structure and coordination polyhedra of the Sc₃CoC₄-type carbides. Atoms connected by thin and thick lines are separated by half a translation period of the projection direction. For the coordination polyhedra of the metal atoms the atoms one translation period above and below may be counted as additional neighbors.

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