Supplementary Material Available: For [Ni(dppm)$_2$](BF$_4$)$_2$, [Ni-(dppb)$_2$](BF$_4$)$_2$, and [Ni(dppm)(CH$_3$CN)](PF$_6$)$_2$, Entries 1s–3s, containing text describing X-ray crystallographic experimental procedures, Figures 1s–3s, showing thermal ellipsoid plots with numbering schemes, and Tables 1s–6s, 8s–13s, and 15s–20s, listing atomic coordinates and equivalent isotropic displacement parameters, bond lengths, bond angles, anisotropic displacement parameters, and hydrogen atom coordinates and isotropic displacement parameters (41 pages); Tables 7s, 14s, and 21s, listing calculated and observed structure factors (32 pages). Ordering information is given on any current masthead page.

Contribution from the Anorganisch-Chemisches Institut, Universität Münster, D-4400 Münster, West Germany

Sc$_3$C$_4$, a Carbide with C$_3$ Units Derived from Propadiene

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The title compound was prepared in well-crystallized form by annealing the elemental components in a palladium matrix slightly below the melting point of palladium. It crystallizes in the tetragonal space group $P4/mnc$ with the lattice constants a = 748.73 (5) pm, c = 1502.6 (2) pm, and Z = 10 formula units per cell. The structure was determined from single-crystal X-ray data and refined to R = 0.019 for 476 structure factors and 35 variable parameters. It is the first well-characterized carbide containing C$_3$ units (eight per cell). In addition, two C$_2$ pairs and twelve isolated carbon atoms per cell are present. The C–C bond lengths in the nearly linear (176°) C$_3$ units (2 × 134 pm) and in the C$_2$ pairs (125 pm) correspond to double and nearly triple bonds, respectively. The compound may therefore be considered as a derivative of allene, ethyne, and methane. The C$_3$ units are coordinated to ten scandium atoms, forming bicapped quadratic antiprisms. The C$_2$ pairs and the isolated carbon atoms have octahedral scandium environments. Sc$_3$C$_4$ is a metallic conductor and a Pauli paramagnet. This is qualitatively rationalized by chemical bonding considerations. The compound was previously described with the tentative composition "Sc$_{15}$C$_{19}$" by Jedlicka, Nowotny, and Benesovsky (*Monatsh. Chem.* 1971, *102*, 389). The compounds R$_3$C$_4$ (R = Ho–Lu) are isotypic with Sc$_3$C$_4$. The corresponding yttrium compound could only be obtained by adding 5 atom % boron to the samples.

Introduction

The well-known salt-like carbide Al$_4$C$_3$ and the technically important carbides of the transition metals contain isolated carbon atoms. C$_2$ pairs are known to occur in CaC$_2$ and in the carbides of the rare-earth elements R$_2$C$_3$ and RC$_2$.[1] More recently C$_2$ pairs were found in many ternary carbides of the rare-earth elements with transition metals.[2] The hydrolyses of these and other carbides frequently result in gaseous products containing large amounts of C$_3$, C$_4$, C$_5$, and C$_6$ hydrocarbons.[3] In no case, however, could it be shown by structure determinations that such higher carbon units are present in the solid. Thus, Sc$_3$C$_4$ is the first well-characterized carbide containing C$_3$ units. We obtained a well-crystallized sample of Sc$_3$C$_4$ during an investigation of the ternary system scandium–palladium–carbon. In contrast, from binary samples we have only obtained polycrystalline Sc$_3$C$_4$. A structure proposal for this phase was made on the basis of X-ray film data of a poor-quality crystal some 20 years ago.[4] It resulted in the tentative composition "Sc$_{15}$C$_{19}$". This composition was assumed to be correct in all subsequent investigations of this phase[5] and the isotypic rare-earth carbides.[6-9]

Sample Preparation and Lattice Constants of Sc$_3$C$_4$

Starting materials were scandium chips (>99.9%, no visible contamination by scandium oxide) and graphite flakes (>99.5%). Cold-pressed pellets of the ideal composition were melted in an arc-melting furnace in an argon (99.996%) atmosphere. The argon was further purified by repeatedly melting a titanium button prior to the reaction. The samples were then wrapped in tantalum foil and annealed in silica tubes for 3

Table I. Crystallographic Data for Sc$_3$C$_4$

sp gr: $P4/mnc$ (No. 128)	ρ_{calc} = 3.606 g·cm^{-3}
a = 748.73 (5) pm	μ = 56.4 cm^{-1}
c = 1502.6 (2) pm	transm ratio (highest/lowest): 1.12
V = 0.8424 (2) nm^3	R_i = 0.071
Z = 10	$R(F_o)$ = 0.019
fw = 182.91	$R_w(F_o)$ = 0.018
T = 21 °C	w = 1/σ^2
λ = 0.7107 Å	

weeks at 900 °C. The Guinier powder patterns of these samples showed single-phase Sc$_3$C$_4$. The single crystals used for the structure determination were obtained from a sample containing palladium (>99.9%) with the atomic proportions Sc:Pd:C = 2:1:2. After arc-melting, the sample was annealed in an evacuated, sealed, water-cooled silica tube in a high-frequency furnace 8 h at a temperature slightly below the melting point of the palladium matrix. The single crystals of Sc$_3$C$_4$ were isolated from the crushed button, which was kept under dried paraffin oil. The Guinier powder pattern of this sample showed Sc$_3$C$_4$ as the main phase besides small amounts of ScPd$_3$ and graphite. Energy-dispersive analyses in a scanning electron microscope did not reveal any contamination of the crystals by palladium.

The lattice constants of Sc$_3$C$_4$ (Table I) were obtained from the binary sample with the Guinier technique using Cu Kα_1 radiation and α-quartz (a = 491.30 pm, c = 540.46 pm) as a standard. The identification of the diffraction lines was facilitated by intensity calculations[10] using the positional parameters of the refined structure. The lattice constants of Sc$_3$C$_4$ determined on the four-circle diffractometer were in good agreement with those obtained from the powder.

Properties

Crystals of Sc$_3$C$_4$ have a light gray color with metallic luster; powdered samples are black. They react readily with the humidity of the air; microcrystalline samples are completely decomposed after some hours. The gaseous products of the hydrolyses of "Sc$_{15}$C$_{19}$" samples under different conditions were analyzed previously by gas chromatography.[5] The amounts of the C$_1$, C$_2$, and C$_3$ hydrocarbons obtained agree approximately with those expected from the crystal structure, although minor amounts of higher hydrocarbons were also found.

(1) Atoji, M.; Gschneidner, K., Jr.; Daane, A. H.; Rundle, R. E.; Spedding, F. H. *J. Am. Chem. Soc.* 1958, *80*, 1804. Spedding, F. H.; Gschneidner, K., Jr.; Daane, A. H. *J. Am. Chem. Soc.* 1958, *80*, 4499.
(2) Hoffmann, R.-D.; Jeitschko, W.; Boonk, L. *Chem. Mater.* 1989, *1*, 580.
(3) Jeitschko, W.; Gerss, M. H.; Hoffmann, R.-D.; Lee, S. *J. Less-Common Met.* 1989, *156*, 397.
(4) Jedlicka, H.; Nowotny, H.; Benesovsky, F. *Monatsh. Chem.* 1971, *102*, 389.
(5) Hájek, B.; Karen, P.; Brožek, V. *J. Less-Common Met.* 1984, *96*, 35.
(6) Bauer, J.; Nowotny, H. *Monatsh. Chem.* 1971, *102*, 1129.
(7) Bauer, J. *J. Less-Common Met.* 1974, *37*, 161.
(8) Bauer, J.; Bienvenu, H. C. *R. Seances Acad. Sci. Ser. C* 1980, *290*, 387.
(9) Bauer, J.; Ansel, D. *J. Less-Common Met.* 1985, *109*, L9.

(10) Yvon, K.; Jeitschko, W.; Parthé, E. *J. Appl. Crystallogr.* 1977, *10*, 73.

Table II. Atomic Parameters for $Sc_3C_4{}^a$

atom	$P4/mnc$	occ	x	y	z	B
Sc(1)	2a	1.002 (4)	0	0	0	0.32 (1)
Sc(2)	4e	0.987 (3)	0	0	0.31302 (8)	0.47 (1)
Sc(3)	8h	1.005 (2)	0.4035 (1)	0.1993 (1)	0	0.378 (9)
Sc(4)	16i	0.999 (1)	0.10047 (9)	0.28723 (8)	0.14385 (3)	0.339 (6)
C(1)	4e	1.02 (2)	0	0	0.5417 (4)	0.53 (7)
C(2)	4e	1.03 (3)	0	0	0.1564 (3)	0.43 (7)
C(3)	8h	1.09 (1)	0.6968 (6)	0.1077 (6)	0	0.26 (4)
C(4)	16i	1.04 (1)	0.4041 (6)	0.1933 (5)	0.1676 (1)	0.52 (3)
C(5)	8g	1.05 (1)	0.3507 (5)	0.149 (1)	0.25	0.63 (6)

^{a}Numbers in parentheses are esd's in the least significant digits. The last column contains the isotropic B values of the carbon positions and the equivalent isotropic B values ($\times 100$, in units of nm^2) of the ellipsoidal thermal parameters of the metal positions.
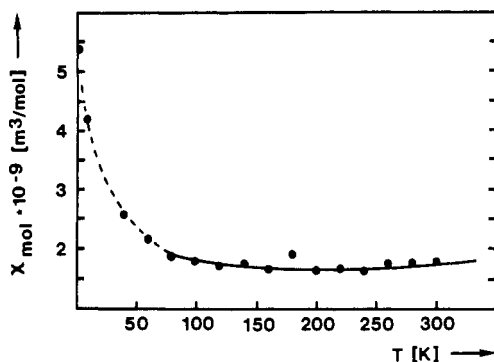

Figure 1. Magnetic susceptibility of Sc_3C_4 as a function of temperature. The upturn below 100 K is attributed to a trace amount of an unknown paramagnetic impurity.

Magnetic susceptibility measurements taken with a SQUID magnetometer between 2 and 300 K are compatible with Pauli paramagnetism. Between 100 and 300 K the susceptibility of our Sc_3C_4 sample had a value of about $\chi = 1.75 \times 10^{-9}$ m^3/mol (Figure 1). This value is of the same magnitude as the value of $\chi = 2.43 \times 10^{-9}$ m^3/mol calculated[11] for 1 mol of Sc_3C_4 from the molar susceptibilities of the metal scandium ($\chi = 1.21 \times 10^{-9}$ m^3/mol obtained by interpolation of the values $\chi = 0.55 \times 10^{-9}$ m^3/mol and $\chi = 1.87 \times 10^{-9}$ m^3/mol for the metals Ca and Ti) and compacted, randomly oriented graphite ($\chi = -0.30 \times 10^{-9}$ m^3/mol). Below 100 K the magnetic susceptibility of our Sc_3C_4 sample increases, probably because of a minor amount of a paramagnetic impurity.

Electrical conductivity measurements with a two-probe device resulted in a specific conductivity of about $\sigma = 300$ (± 100) Ω^{-1} cm^{-1} at room temperature. The conductivity increased to $\sigma = 360$ (± 100) Ω^{-1} cm^{-1} when the sample was cooled to 90 K. The temperature dependence indicates metallic conductivity, in agreement with the magnetic susceptibility measurements. The absolute value of the electrical conductivity, however, is rather low, when compared to the values for silver or bismuth with $\sigma = 628 \times 10^3$ Ω^{-1} cm^{-1} and $\sigma = 9.36 \times 10^3$ Ω^{-1} cm^{-1}, respectively.[12]

Crystal Structure of Sc_3C_4

The crystals of Sc_3C_4 used for the structure determination were isolated from the sample prepared in the palladium matrix. They were enclosed in evacuated thin-walled silica tubes to prevent hydrolysis. Precession diagrams of the first crystal investigated taken with Mo radiation could be interpreted with the tetragonal cell reported for $Sc_{15}C_{19}$.[4] Additional reflections could be assigned to twin domains. The twinning was such, that the 4-fold axes of the two twin orientations coincided, and the 550 reflection of the one twin domain was exactly superimposed on the 710 reflection of the other twin domain. Thus, the matrix that transforms the indices hkl of the one domain to the indices of the other domain is (0.8, 0.6, 0/−0.6, 0.8, 0/0, 0, 1), and the angle needed to rotate

one domain around the common 4-fold axis into the orientation of the other is 36.86°.

Fortunately, already the second crystal of Sc_3C_4 investigated did not show this twinning. It was used for the structure determination in an automated four-circle diffractometer (CAD4) with graphite-monochromated Mo $K\alpha$ radiation. The crystallographic data are summarized in Table I and in a more detailed table of the supplementary material. An empirical absorption correction was made from ψ-scan data.

The structure was refined with the starting parameters as given for "$Sc_{15}C_{19}$" by Jedlicka et al.[4] in space group $P\bar{4}2_1c$. However, strong parameter correlations indicated that this space group might not be correct. The crystal had the high Laue symmetry, and the systematic extinctions ($0kl$ observed only with $k + l = 2n$; hhl only with $l = 2n$) led to the space groups $P4/mnc$ and $P4nc$. The structure was eventually successfully refined in the space group with the highest symmetry, $P4/mnc$-D_{4h}^6. The difference Fourier syntheses indicated that one of the carbon positions of the structure proposed earlier had to be substituted by the acetylide group C_2. Thus the proper composition is $Sc_{15}C_{20}$, i.e. Sc_3C_4.

The structure was refined by full-matrix least-squares cycles. The atomic scattering factors[13] were corrected for anomalous dispersion.[14] Weights were assigned according to the counting statistics. A parameter accounting for isotropic secondary extinction was refined and applied to the calculated structure factors. To check for deviations from the ideal composition, we also refined the occupancy parameters along with the thermal parameters, while the scale factor was held constant. The lowest and highest occupancies (in %) were as follows: Sc(2), 98.7 (3); Sc(3), 100.5 (2); C(1), 102 (2); C(3), 108.5 (8). Thus the largest deviation from the ideal values was for the C(3) position. It seems possible that any nitrogen impurity accumulates on that (isolated) carbon position. However, when we refined this position with the scattering factor for nitrogen, it was occupied to only 86.4 (6)%. Thus, even if nitrogen were present at this position, it could only be a fraction of the total occupancy, and we do not believe that nitrogen is necessary for the formation of the compound. In the last cycles the ideal occupancies were assumed with ellipsoidal thermal parameters for the scandium atoms and isotropic thermal parameters for the carbon atoms. The final conventional and weighted residuals are $R = 0.019$ and $R_w = 0.018$ for 35 variable parameters and 476 structure factors. A difference Fourier synthesis gave no indication for the occupancy of additional atomic sites (highest value 1.0 e/$Å^3$). The atomic parameters and the interatomic distances are listed in Tables II and III. The anisotropic thermal parameters and the structure factor tables are available as supplementary material. A stereoplot[15] of the structure is shown in Figure 2.

Isotypic Compounds

The carbides "$R_{15}C_{19}$" (R = Y, Ho–Lu) were reported[6-9] to be isotypic with "$Sc_{15}C_{19}$",[4] for which our structure determination resulted in the ideal composition Sc_3C_4. We confirm these results

(11) Roth, W. A.; Scheel, K. In *Landolt-Börnstein, Physikalisch-Chemische Tabellen*; Springer: Berlin, 1923; Vol. 2.
(12) Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 59th ed.; CRS Press, Inc.: Boca Raton, FL 33431, 1978.
(13) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321.
(14) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
(15) Keller, E. Schakal 86. Kristallographisches Institut der Albert-Ludwigs-Universität Freiburg, 1988.

Table III. Interatomic Distances (pm) in the Structure of $Sc_3C_4{}^a$

Sc(1) Distances			
2 C(2) 235.1 (5)	8 Sc(4) 314.1 (1)	4 Sc(3) 336.9 (1)	
4 C(3) 241.0 (5)			

Sc(2) Distances			
1 C(1) 218.3 (5)	4 C(4) 242.4 (4)	4 Sc(4) 345.1 (1)	
1 C(2) 235.3 (5)	4 Sc(4) 341.4 (1)	4 Sc(3) 367.2 (1)	

Sc(3) Distances			
1 C(3) 230.0 (5)	2 C(4) 251.9 (2)	1 Sc(3) 331.5 (1)	
1 C(3) 234.7 (5)	2 Sc(4) 320.2 (1)	2 Sc(3) 334.4 (2)	
1 C(3) 241.8 (5)	2 Sc(4) 323.5 (1)	1 Sc(1) 336.9 (1)	
2 C(1) 244.7 (2)	2 Sc(4) 325.3 (1)	2 Sc(2) 367.2 (1)	

Sc(4) Distances			
1 C(3) 216.6 (1)	1 C(5) 266.9 (3)	1 Sc(3) 325.3 (1)	
1 C(2) 228.6 (1)	1 Sc(1) 314.1 (1)	1 Sc(4) 340.4 (1)	
1 C(4) 239.4 (4)	1 Sc(3) 320.2 (1)	1 Sc(2) 341.4 (1)	
1 C(4) 240.6 (4)	2 Sc(4) 322.2 (1)	1 Sc(2) 345.1 (1)	
1 C(4) 244.0 (4)	1 Sc(3) 323.5 (1)	1 Sc(4) 352.4 (1)	
1 C(5) 250.3 (3)			

C(1) Distances			
1 C(1) 125.3 (7)	1 Sc(2) 218.3 (5)	4 Sc(3) 244.7 (2)	

C(2) Distances			
4 Sc(4) 228.6 (1)	1 Sc(1) 235.1 (5)	1 Sc(2) 235.3 (5)	

C(3) Distances			
2 Sc(4) 216.6 (1)	1 Sc(3) 234.7 (5)	1 Sc(3) 241.8 (5)	
1 Sc(3) 230.0 (5)	1 Sc(1) 241.0 (5)		

C(4) Distances			
1 C(5) 134.2 (3)	1 Sc(4) 240.6 (4)	1 Sc(4) 244.0 (4)	
1 Sc(4) 239.4 (4)	1 Sc(2) 242.4 (4)	1 Sc(3) 251.9 (2)	

C(5) Distances			
2 C(4) 134.2 (3)	2 Sc(4) 250.3 (3)	2 Sc(4) 266.9 (3)	

^{a} All distances shorter than 430 ppm (Sc–Sc), 300 pm (Sc–C), and 260 pm (C–C) are listed. Standard deviations, computed from those of the positional parameters, are given in parentheses. If the standard deviations of the lattice constants are also considered, the standard deviations of this table have to be increased by about 0.2 pm.
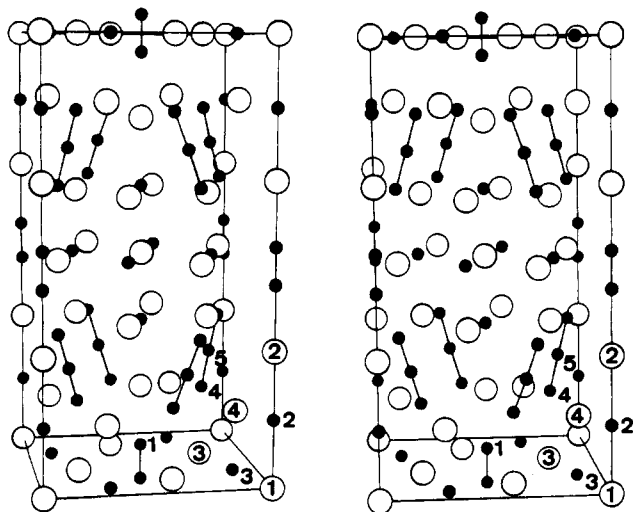
Table IV. Lattice Constants for Tetragonal Sc_3C_4 Type Carbides^a

compd	a, pm	c, pm	c/a	V, nm³	ref
Sc_3C_4	748.73 (5)	1502.6 (2)	2.007	0.8424 (2)	b
"$Sc_{15}C_{19}$"	750.0	1500.0	2.000	0.8437	4
$Y_3C_{4-x}B_x$	804.9 (1)	1603.7 (3)	1.992	1.039 (2)	b
"$Y_{15}C_{19}$"	794.0	1588.0	2.000	1.001	6
Ho_3C_4	804.96 (9)	1586.9 (2)	1.971	1.0282 (2)	b
"$Ho_{15}C_{19}$"	800.4 (2)	1585.7 (3)	1.981	1.0159 (2)	9
Er_3C_4	798.8 (1)	1578.5 (3)	1.976	1.0073 (2)	b
"$Er_{15}C_{19}$"	798.9 (1)	1579.4 (2)	1.977	1.008 (1)	7
Tm_3C_4	793.0 (1)	1573.0 (4)	1.983	0.9892 (2)	b
"$Tm_{15}C_{19}$"	794.1 (2)	1573.4 (3)	1.984	0.9919 (2)	9
Yb_3C_4	790.96 (9)	1552.1 (4)	1.962	0.9707 (2)	b
"$Yb_{15}C_{19}$"	790.6 (2)	1553.9 (5)	1.965	0.9712 (2)	8
Lu_3C_4	784.96 (9)	1563.3 (2)	1.992	0.9633 (2)	b
"$Lu_{15}C_{19}$"	787.3 (2)	1551.8 (4)	1.971	0.9619 (2)	8

^{a} Standard deviations in the least significant digits are given in parentheses. ^{b} This work.

higher ytterbium content in a sealed tantalum tube under argon. The excess ytterbium was condensed at colder parts of the tube.

The samples were characterized through their Guinier powder patterns as described above. The observed patterns agreed well with the calculated ones, assuming the positional parameters of the Sc_3C_4 structure. The lattice constants are in good agreement with those determined earlier (Table IV). Small differences are possibly due to homogeneity ranges.

We have not (yet?) reproduced the yttrium compound, either in the arc-melted and quenched samples or in the samples subsequently annealed for 4 weeks at 850 °C in sealed silica tubes. The samples were also equilibrated at 1500 °C (1–8 h) in water-cooled silica tubes with use of a high-frequency furnace, without success. Bauer and Nowotny[6] have obtained this phase in pure form only by adding 5–10 atom % boron. This we can confirm. We have obtained this phase with a yield of about 90% in samples containing 5 atom % boron. The boron atoms probably occupy some carbon positions. The powder pattern reported by Carlson and Paulson[16] for a sample where Y:C = 45:55 is probably multiple phase and gives no unambiguous evidence for a carbide with the Sc_3C_4 structure. Our samples with this composition give a powder pattern that we have not yet identified. In samples with a slightly lower carbon content, we find another phase with a powder pattern similar to that given by Storms[17] for "Y_5C_6".

Discussion

The present structure determination of Sc_3C_4 shows two main differences from the earlier suggested structure of "$Sc_{15}C_{19}$": Sc_3C_4 contains a C_2 pair at the place of an isolated carbon atom in "$Sc_{15}C_{19}$", and Sc_3C_4 contains a nearly linear C_3 unit instead of a C_2 pair with an "isolated" carbon atom further away (at a distance of about 200 pm). The scandium positions are essentially identical in the two refinements; however, because the structure of Sc_3C_4 is refined in a higher symmetry space group, there are fewer atomic positions. The atomic positions of Sc(1), Sc(2), Sc(3), C(2), C(3), and C(5) of Sc_3C_4 correspond to the positions of the Sc(5), Sc(4), Sc(1), C(5), C(1), and C(3) atoms in "$Sc_{15}C_{19}$". The 16-fold positions of the Sc(4) and C(4) atoms of Sc_3C_4 correspond to two 8-fold scandium and two 8-fold carbon positions in "$Sc_{15}C_{19}$", and finally the C(1) atoms of Sc_3C_4 form pairs at the positions of the isolated C(6) atoms of the structure proposed previously.

The structure is best described as derived from the well-known NaCl structure, which is also the structure of $ScCl_{1-x}$.[18] A cutout of the Sc_3C_4 structure is shown in Figure 3. The atomic layers ABC and DEF have distorted NaCl type structure. They extend two-dimensionally and infinitely, perpendicular to the c direction. One-fifth of the carbon atoms in layers B and E are replaced by C_2 pairs. In layers A, C, D, and F one-fifth of the carbon atoms

Figure 2. Stereoplot of the Sc_3C_4 structure. The scandium and carbon atoms are shown as large open and small filled circles, respectively. The atom designations are indicated at the lower right corner of the plot.

for the compounds R_3C_4 (R = Ho–Lu). Starting materials were powders of the elements (R, >99.9%; C, 99.5%). The carbides Ho_3C_4, Er_3C_4, Tm_3C_4, and Lu_3C_4 were obtained by arc-melting cold-pressed pellets of the ideal composition with subsequent annealing in evacuated, sealed silica tubes (4 weeks at temperatures between 850 and 900 °C) and quenching. The ytterbium compound has a higher vapor pressure and is more difficult to prepare by arc-melting. We have obtained Yb_3C_4 by high-frequency melting (1 h at about 2000 °C) of a pellet with a somewhat

(16) Carlson, N. O.; Paulson, W. M. *Trans. Met. Soc. AIME* **1968**, *242*, 846.
(17) Storms, E. K. *High Temp. Sci.* **1971**, *3*, 99.
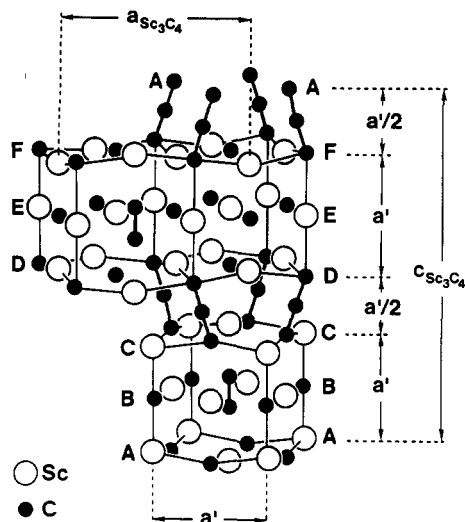(18) Rassaerts, H.; Nowotny, H.; Vinek, G.; Benesovsky, F. *Monatsh. Chem.* **1967**, *98*, 460.

Figure 3. Cutout of the tetragonal Sc_3C_4 structure. It consists of two-dimensionally infinite NaCl-like layers formed by the atomic layers ABC and DEF. Adjacent triple atomic layers ABC and DEF are connected by C_3 units. The lattice constant a' corresponds to a NaCl type lattice, which actually exists for the defect carbide ScC_{1-x}.[18]
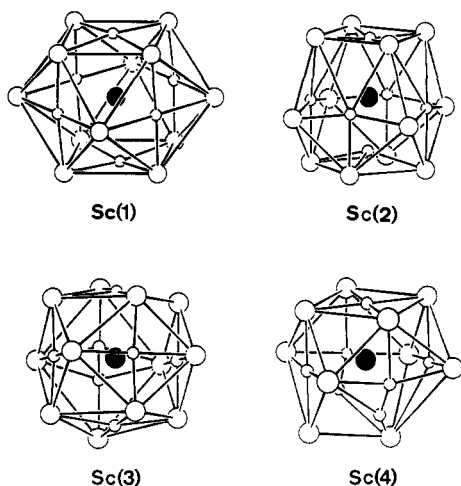

Figure 4. Coordination polyhedra of the scandium atoms in Sc_3C_4. The central scandium atoms are shown as filled circles, and the neighboring scandium and carbon atoms are represented by large and small open circles, respectively.

are isolated, while the other four-fifths of the carbon atoms belong to C_3 units, which connect the adjacent NaCl-like layers. Figure 3 also shows the relation of the lattice constants of the NaCl type and the Sc_3C_4 structure: $a(Sc_3C_4) \sim (5/2)^{1/2}a(NaCl)$ and c-$(Sc_3C_4) \sim 3a(NaCl)$. If we take the lattice constants for the carbon-rich side of ScC_{1-x} with NaCl type structure[18] as $a = 472$ pm, we obtain the values of $a = 746$ pm and $c = 1416$ pm for a "NaCl-like" Sc_3C_4, as compared to the actually observed values of 749 pm and 1502 pm.

The scandium atoms occupy four different atomic sites. The Sc(1) and Sc(2) atoms have six carbon neighbors; the Sc(3) and Sc(4) atoms have seven carbon neighbors (Figure 4). The Sc–C distances vary between 216.6 and 266.9 pm; the average Sc–C distances are 239.0 and 237.2 pm for Sc(1) and Sc(2) and 242.8 and 240.9 pm for Sc(3) and Sc(4), thus reflecting the different number of carbon neighbors. The Sc–Sc distances cover the range between 314.1 and 367.2 pm. The average Sc–Sc distances vary considerably: they are 321.7, 351.1, and 334.1 pm for the Sc(1), Sc(2), and Sc(3) atoms, which have twelve scandium neighbors. For the Sc(4) atom with ten scandium neighbors, the average Sc–Sc distance is 330.7 pm. The greatly varying average Sc–Sc distances indicate that the scandium–scandium bonding is considerably less important than the scandium–carbon bonding, in agreement with the following discussion of the chemical bonding.
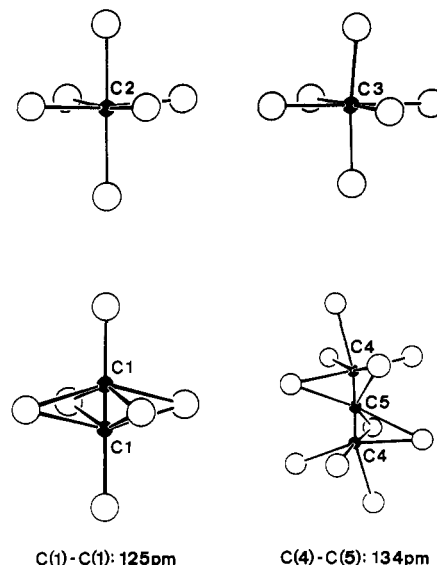

C(1)-C(1): 125pm   C(4)-C(5): 134pm

Figure 5. Atomic environments of the carbon atoms in Sc_3C_4.

The C(1) atoms form pairs that are situated in elongated octahedral voids (Figure 5), like the C_2 pairs in CaC_2. The C-(1)–C(1) bond distance of 125.3 (7) pm is close to that of a triple bond. In CaC_2 the C–C distance was determined by neutron powder diffraction data to 119.1 (9) pm,[19] in good agreement with the C–C distance in C_2H_2 of 120.4 (1) pm determined from IR spectroscopic data.[20] The C(2) and C(3) atoms do not form carbon–carbon bonds. They occupy octahedral voids of the metal atoms. This is the usual environment of carbon atoms in carbides of the earlier transition metals, including the carbon atoms in ScC_{1-x}.[18]

A novel feature for a solid-state carbide is the C_3 unit formed by the C(4) and C(5) atoms. The C(4)–C(5)–C(4) bond angle is 175.8 (3)° and the C(4)–C(5) distances are 134.2 (3) pm, indicating double bonds. This C_3 unit thus corresponds to the carbon skeleton of propadiene, C_3H_4. It is located in a distorted bicapped square antiprism of scandium atoms.

Chemical bonding in Sc_3C_4 can be discussed best by starting from an idealized ionic model. We *count* the electrons of the scandium–carbon interactions at the carbon atoms and assume that the carbon atoms obey the octet rule. This is certainly justified, since the carbon atoms are the more electronegative component and there are enough valence electrons in the compound to fill all 2s and 2p orbitals. In the first approximation we assume triple C–C bonds for the C(1) pairs and two double bonds for each C_3 unit. For the cell content of $Sc_{30}C_{40}$ we then obtain a formula, where the superscripts indicate oxidation numbers: $[30Sc^{3+}]^{90+}[2(C(1)-C(1))^{2-}]^{4-}[4C(2)^{4-}]^{16-}$- $[8C(3)^{4-}]^{32-}[8(C(4)-C(5)-C(4))^{4-}]^{32-}$·6e. Thus, in this formula there are six valence electrons, which do not participate in Sc–C or C–C bonding. We note that the C–C distance of the C_2 pairs is somewhat longer (125 pm) than the ideal distance for a triple bond (120 pm). However, even if we assume the C_2 pairs to contain a double bond (i.e. we assume C_2^{4-} instead of C_2^{2-} "anions"), we are left with two valence electrons per cell content, which cannot be accounted for in this way. In the extended solid, it is possible to have transitions between double and triple bonds. By linear interpolation for the observed bond distance of 125 pm between the triple (120 pm) and double bond (134 pm), we obtain a formal charge of 2.8– per C_2 unit, which corresponds to about four additional valence electrons per cell content. The occupancy factor of the C(3) position was found to be somewhat high, and we have speculated that some nitrogen could be present at this position. This, however, would only increase the number of excess electrons.

The excess electrons can be accounted for in two ways. One likely possibility is their accommodation in Sc–Sc bonding "crystal"

(19) Atoji, M. *J. Chem. Phys.* **1961**, *35*, 1950.
(20) Allen, P. W.; Sutton, L. E. *Acta Crystallogr.* **1950**, *3*, 46.

orbitals. There are numerous Sc–Sc interactions in Sc_3C_4 with about the same distances as observed in elemental scandium (hcp;[21] each Sc atom has six neighbors at an average distance of 328 pm; the ionic radius of Sc^{3+} is only about 100 pm though!). Since there are only about 4 "excess" electrons per 30 scandium atoms, they certainly could not fill all Sc–Sc bonding states. This rationalization is in agreement with the metallic conductivity and the Pauli paramagnetism of the compound.

Another (additional) possibility to account for the excess electrons concerns the bonding of the scandium atoms to the C(5) atoms. So far we have assumed that the C(5) atoms form two double bonds with their two C(4) neighbors within the C_3 units. This leaves no possibility whatsoever for the C(5) atoms to form bonds to the scandium atoms. The C(5) atoms have two Sc neighbors at 250 pm and two at 267 pm. Even though these distances are considerably greater than the shortest Sc–C distances of 217 pm, one cannot exclude the possibility for weak Sc–C(5) bonding. This can only be achieved if the C(5)–C(4) bonds have a bond order of less than 2. Even small deviations from the full double bonds create many low-lying additional states in the cell (The Lewis formula for propadiene has 16 valence electrons; for propane it has 20.) The C(5)–C(4) bond length of 134.2 pm is indeed slightly greater than the bond lengths of 131.1 and 133.5 pm observed in gaseous propadiene by electron diffraction[22] and

by IR spectroscopy,[23] respectively. It is also greater than the average bond length of 130.3 pm observed in six organometallic allenylidene complexes by Berke et al.[24] Thus, in summary the valence electron count agrees rather well with the observed bond lengths.

(21) Donohue, J. *The Structures of the Elements*; Wiley: New York, 1974.
(22) Almenningen, A.; Bastiansen, O.; Traetteberg, M. *Acta Chem. Scand.* **1959**, *13*, 1699.

(23) Lord, R. C.; Venkateswarlu, Putcha. *J. Chem. Phys.* **1952**, *20*, 1237.
(24) Berke, H.; Härter, P.; Huttner, G.; Zsolnai, L. *Z. Naturforsch., B* **1981**, *36*, 929. Berke, H.; Huttner, G.; von Seyerl, J. *Z. Naturforsch., B* **1981**, *36*, 1277. Berke, H.; Härter, P.; Huttner, G.; von Seyerl, J. *J. Organomet. Chem.* **1981**, *219*, 317. Berke, H.; Härter, P.; Huttner, G.; Zsolnai, L. *Ber. Dtsch. Chem. Ges.* **1982**, *115*, 695. Berke, H.; Härter, P.; Huttner, G.; Zsolnai, L. *Ber. Dtsch. Chem. Ges.* **1984**, *117*, 3423. Berke, H.; Grössmann, U.; Huttner, G.; Zsolnai, L. *Ber. Dtsch. Chem. Ges.* **1984**, *117*, 3432.

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Zirconium Chloride Cluster Phases Centered by Transition Metals Mn–Ni. Examples of the Nb₆F₁₅ Structure

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Reactions of Zr, $ZrCl_4$, chlorides of Mn–Ni (Z), and LiCl where appropriate in sealed Ta tubing at 750–900 °C yield the dark purple $Li_2Zr_6Cl_{15}Mn$, $LiZr_6Cl_{15}Fe$, $Zr_6Cl_{15}Co$, and $Zr_6Cl_{15}Ni$, all with the basic Nb_6F_{15} structural framework. The structures of all four have been refined by single-crystal X-ray means in the cubic space group $Im\bar{3}m$, $Z = 2$. The a dimensions (Å) and R and R_w (%) are, respectively, as follows: Mn, 10.3459 (4), 2.4, 3.4; Fe, 10.2645 (4), 3.3, 4.2; Co, 10.186 (4), 2.4, 2.0; Ni, 10.1907 (4), 2.1, 3.1. Transition-metal-centered clusters in this structure type are interconnected at all vertices by linear chlorine bridges into three-dimensional ReO_3-like networks $[Zr_6(Z)Cl^i{}_{12}]Cl^{a-a}{}_{6/2}$, and two such networks interpenetrate but are unlinked. The relative sizes of the clusters and bridging halogens are critical for this disposition. The lithium atoms in $Li_2Zr_6Cl_{12}Mn$ were refined in an internetwork, six-coordinate site of D_{2h} symmetry, consistent with the solid-state NMR spectrum observed for ^7Li. The expansions of the networks about $Zr–Cl^{a-a}$ necessary to accommodate the lithium ions correspond to volume increments of 12–13 $Å^3$ for each ion. The effective sizes of the metal interstitials Z increase slightly from Mn to Ni.

Introduction

Among the many centered zirconium chloride cluster compounds,[1] those with the Zr_6Cl_{15} stoichiometry have the greatest structural versatility. These all share a common cluster connectivity, $[Zr_6Cl^i{}_{12}]Cl^{a-a}{}_{6/2}$, in which Cl^i is solely edge-bridging within a single cluster while Cl^{a-a} atoms bridge between cluster vertices to generate three-dimensional networks. Four distinctly different architectures are found within this category in terms of both local geometries at the shared Cl^{a-a} and the long-range connectivities of the cluster frameworks.[2–4] Earlier work has provided numerous Zr_6Cl_{15} compositions centered by second-period elements that are distributed among the structure types Ta_6Cl_{15},[5] $KZr_6Cl_{15}C^3$ or $CsNb_6Cl_{15}$,[6] $K_2Zr_6Cl_{15}B$, and $K_3Zr_6Cl_{15}Be$.[4] The

first three contain unrelated frameworks, while $K_3Zr_6Cl_{15}Be$ contains a modification of that in $K_2Zr_6Cl_{15}B$. With the aid of these structure types, the relationships between structure type and the size and number of the countercations that must be accommodated in the cluster framework have been well delineated.[4]

Recent successes in incorporating transition metals into the Zr_6Cl_{12} cluster cores have provided more unique cluster compounds.[7] Because of the significant expansion of the clusters that is associated with the change of interstitial from a second-period element to a transition metal, many of these new phases exhibit novel structural features. Differences in the structural behaviors of these two groups of centered clusters are especially obvious in the Zr_6Cl_{15} systems. For instance, with the same stoichiometry but different interstitial elements, $Zr_6Cl_{15}N^2$ adopts the Ta_6Cl_{15} structure whereas $Zr_6Cl_{15}Co$ is based on the novel Nb_6F_{15}

(1) Ziebarth, R. P.; Corbett, J. D. *Acc. Chem. Res.* **1989**, *22*, 256.
(2) Ziebarth, R. P.; Corbett, J. D. *J. Less-Common Met.* **1988**, *137*, 21.
(3) Ziebarth, R. P.; Corbett, J. D. *J. Am. Chem. Soc.* **1987**, *109*, 4844.
(4) Ziebarth, R. P.; Corbett, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 1132.
(5) Bauer, D.; von Schnering, H.-G. *Z. Anorg. Allg. Chem.* **1968**, *361*, 259.

(6) Imoto, H.; Simon, A. Unpublished research.
(7) Rogel, F.; Zhang, J.; Payne, M. W.; Corbett, J. D. *Adv. Chem. Ser.* **1990**, *226*, 369.