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Synthesis, Structure, and Properties of the Infinite-Chain Compounds Sc_5Cl_8C and Sc_5Cl_8N

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The phases Sc_5Cl_8Z (Z = C, N) are obtained from reactions of Sc, $ScCl_3$, and graphite or NaN_3 at 900–950 °C in sealed niobium tubing. The structures of both have been determined by single-crystal means (space group $C2/m$; $Z = 2$) (for the carbide and nitride, respectively: a = 17.80 (1), 17.85 (1) Å; b = 3.5259 (7), 3.5505 (7) Å; c = 12.052 (7), 12.090 (8) Å; β = 130.11 (4), 130.13 (4)°; R = 0.021, 0.054; R_w = 0.024, 0.085; $2\theta \leq 50, 60°$). The cell dimensions of and distances within the carbide are indistinguishable from those reported earlier from a less satisfactory refinement of the structure of "Sc_5Cl_8". The structures contain infinite pairs of chains composed of $Sc_6Cl_{12}Z$-type clusters sharing both opposite metal edges and chlorine atoms ($Sc_2Sc_{4/2}(Z)Cl_{8/2}Cl_2$) and of $ScCl_6$ cluster units condensed likewise ($\sim ScCl_{4/2}$). The structures fill space effectively, and surprisingly, the carbide exhibits 0.028 Å shorter Sc–Z distances than the nitride. Magnetic susceptibility measurements, Al Kα and He I photoelectron spectra, and extended Hückel band calculations are also reported. Both compounds are predicted to be metallic.

Introduction

The early transition elements, scandium, yttrium, and zirconium in particular, show a remarkable chemistry in their highly reduced halides. Examples of M_6X_{12}-type clusters as well as products of their condensation into infinite metal–metal-bonded chains and sheets have been discovered, for example, in Sc_7Cl_{10},[1] Y_2Cl_3,[2] and ZrCl.[3] A pervasive problem with the synthesis of many other examples, e.g., YCl,[2] Sc_7Cl_{12}, and Zr_6Cl_{15},[4] has been the unpredictable reactions and low yields. Systematic explorations of most of these systems have subsequently shown that many, but not all, of these compounds are in fact stabilized by small interstitial non-metals that must have originated in the early syntheses with adventitious impurities. Thus, the second group of binary phases for instance are now known as $YClH_x$,[5] $Sc_7Cl_{12}Z$ (Z = B, N),[6] and $Zr_6Cl_{15}N$.[7] Many other examples of this class of compounds may be obtained by intentional means as well, viz., Sc_4Cl_6Z (Z = B, N),[6] $Sc_7X_{12}C$ (X = Br, I),[8] M_2Cl_2C (M = Sc, Y, Zr),[9] $Zr_6I_{14}Si$,[10] and Li_yScClH_x.[11]

This study was made in order to clarify the nature of the reported infinite-metal-chain compound Sc_5Cl_8,[12] which was often encountered in low yields of small crystals from gradient reactions at ~940/960 °C. The earlier study of a reasonable-sized diffraction data set from one of the crystals established a new structure type, approximately $^1_\infty[(ScCl_2^+)(Sc_4Cl_6^-)]$, but it resulted in a refinement of only moderate quality (R = 0.115, R_w = 0.136). The final difference map was flat to ≤ 1 e/Å^3, however, including at the center of the cluster. The isostructural phases Gd_5Br_8 and Tb_5Br_8 have subsequently also been obtained in 5–10% yields and their structures refined, the center of the cluster again showing no evident residual.[13] Our more recent experiences have led us to reexamine the scandium compound with the discovery that a dimensionally indistinguishable Sc_5Cl_8C complex can be obtained in high yield as well as a very similar nitride. The greater quantities so afforded have allowed the examination of magnetic susceptibility and the photoelectron spectra of the carbide, and the valence density of states has also been calculated by extended Hückel methods for comparison with the PES result.

Experimental Section

The quality of the metal, HCl, and graphite used, the $ScCl_3$ synthesis, reaction procedures in sealed niobium tubing, Guinier powder, and single-crystal diffraction techniques, and the programs, procedures, and parameters for structural studies and extended Hückel calculations have all been described or referenced before.[10,14] NaN_3 (99%, Aldrich) was used as received. Magnetic susceptibility data between 4 and 340 K were obtained at 2.0 and 5.0 kG with a SQUID magnetometer on 25 mg of

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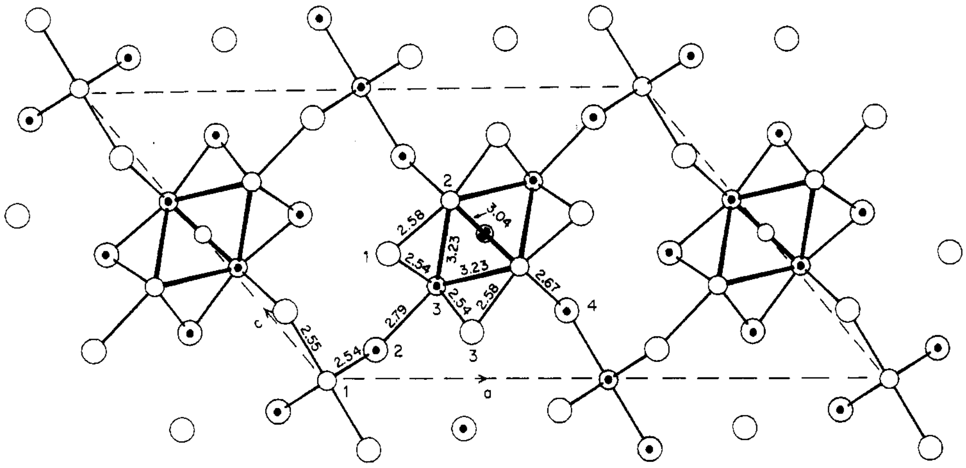

Figure 1. Projection of the structure of Sc_5Cl_8Z (Z = C, N) along [0$\bar{1}$0] plus the atom numbering scheme and the important distances. Small circles are scandium, with those interconnected by heavy lines and centered by Z defining the metal chain; large circles are chlorine. The dotted circles differ from the open ones by $b/2$. The distances shown are for the carbide.

Sc_5Cl_8C sealed in a 3 mm o.d. silica tube under vacuum. The UPS and XPS measurements on Sc_5Cl_8C mounted on indium and cellophane tape, respectively, were made as described before.[14,15] EHMO calculations were carried out with the same parameters as earlier[6] by using 26K points and Gaussian smoothing.

Syntheses. Sc_5Cl_8C is obtained as a single-phase product according to Guinier data and therefore in nearly 100% yield as a green-hued, black powder following the reaction of stoichiometric amounts of Sc, $ScCl_3$, and C powders at 860 °C for ca. 12 days. Larger crystals suitable for diffraction were obtained in the cold end on reequilibration of such a product at 940/900 °C for 18 days. The same phase has also been encountered in studies leading to $Sc_7Cl_{10}C_2$[14] and Sc_2Cl_2C,[9] the yields of these vs. the compound of interest in the presence of excess metal depending primarily on the relative ratio of chlorine to carbon. The preparation of Sc_5Cl_8N suffers from the usual[6] problem of an adequate source of nitrogen in such reaction containers. The compound was encountered in low yields in reactions of N_2, Sc, and $ScCl_3$ that also produced ~10% $Sc_7Cl_{12}N$ (5 weeks, 860/960 °C). A yield of 5–10% Sc_5Cl_8N (based on $ScCl_3$) and the single crystals studied came from a reaction of $ScCl_3$ and NaN_3 (2:1 on a mole basis) with excess scandium strips at 900/950 °C for 4 weeks, the metal being in the hot end and the product (plus Na_3ScCl_6) being found in the cooler portion. The boride was not obtained, $Sc_7Cl_{12}B$ (~85%) and Sc_4Cl_6B (~10%) forming instead at 920 °C. Both Sc_5Cl_8Z compounds appear invariant in the amount of Z, judging from invariant lattice parameters determined by high-precision Guinier methods.

Another whiskerlike phase observed in this work is $ScCl_{1.42}$, which was formed quantitatively from the reaction of either scandium strips and Sc_2Cl_3[16] (1:10) at 877/885 °C or metal powder plus $ScCl_3$ (11:10) at 880/900 °C, each for 2 months, the stoichiometries being chosen in order to prepare Sc_7Cl_{10}. Attempts to make the corresponding $Sc_7Cl_{10}H_{0.5}$ through the addition of stoichiometric amounts of ScH_2 to the same systems gave 85% $ScCl_{1.42}$ plus 3R-$ScClH_x$.[11] The $ScCl_{1.42}$ phase has also been seen in smaller amounts in other reactions. The stated composition was estimated on the basis of electron microscopy (X-ray fluorescence). The powder pattern shows a gross resemblance to that of Sc_7Cl_{10}, but there are additional weak lines. Preparation of the phase in high yield using high-purity metal strips suggests that it does not contain, and is not stabilized by, a significant amount of interstitial. The fibers are too small for normal X-ray studies.

Structural Determination. The crystallographic data are summarized in Table I for both Sc_5Cl_8C and Sc_5Cl_8N. Diffraction data were collected at room temperature on Syntex P2$_1$ (ω–2ω scan) and Datex (ω) diffractometers, respectively, with no indication of intensity decay with time for either crystal. The data were corrected for absorption with the aid of a ψ scan (two for the carbide) as well as for Lorentz and polarization effects. The crystals were recognized as being very similar to those of the previously reported Sc_5Cl_8 on the basis of both lattice parameters and powder patterns, and Weissenberg data for both confirmed the symmetry and the absence of another lattice. The nitride crystal gave distinctly weaker diffraction spots. The refinements started with the previously reported heavy-atom positions. This time a Fourier synthesis map for each phase showed a sizable peak in the special position (0, 0, $^1/_2$) at the center of the cluster unit, and addition of the appropriate atom thereto dropped the R values substantially, for example, from 10.6 to 5.4% for the nitride. The simultaneous variation of the occupancy and thermal parameters for the interstitials gave refined values of the former of 1.07 (2) (B(iso) = 1.0 (2) Å^2) and 0.89 (4) (B(iso) = 0.02 (24) Å^2) for the carbide and nitride, respectively. The latter was thereafter fixed at unity (B = 0.5 (2) Å^2). Data for a smaller crystal of the carbide were also collected earlier and refined; these gave the same results but poorer quality parameters and residuals.

Table I. Crystallographic Data for Sc_5Cl_8Z (Z = C, N)

	Sc_5Cl_8C	Sc_5Cl_8N
space group	$C2/m$	$C2/m$
no. of reflcns[a]	20	21
cell params		
a, Å	17.80 (1)[b]	17.85 (1)
β, Å	3.5259 (7)	3.5505 (7)
c, Å	12.052 (7)	12.090 (8)
β, deg	130.11 (4)	130.13 (4)
V, Å^3	578.6 (4)	585.9 (4)
cryst dimens, mm	0.02 × 0.05 × 0.6	0.02 × 0.03 × 0.4
2θ(max), deg	50	60
octants measd	$\pm h,\pm k,\pm l$	$h,\pm(k,l); -h,\pm(-k,l)$
no. of reflcns measd[c]	2022	1364
no. of reflcns obsd ($I > 3\sigma(I)$)	1557	942
no. of unique reflcns	492	683
R_{av}	0.024	0.030
μ(Mo Kα), cm^{-1}	46	45
trans coeff: min/max	0.89/1.00	0.93/1.00
param refined	53	49
R	0.021	0.054
R_w[d]	0.024	0.085
GOF	0.89	2.69
largest residual, e Å^{-3}	<0.3	<0.4

[a] Guinier data with internal Si standard; λ = 1.54056 Å. [b] For comparison, the cell parameters found for Sc_5Cl_8[12] from diffractometer data were 17.78 (2) Å, 3.523 (8) Å, 12.04 (1) Å, and 130.10 (6)°, respectively. [c] Mo Kα, monochromated. [d] $w = \sigma(F)^{-2}$.

Results and Discussion

The refined positional parameters for Sc_5Cl_8C and Sc_5Cl_8N are given in Table II while the thermal parameter and structure factor data are in the supplementary material. Figure 1 shows a [0$\bar{1}$0] projection of the structure together with the atom-numbering scheme and some distances for the carbide. The dotted atoms therein are at $y = {}^1/_2$ while the remainder are at y = 0. A side view (~[10$\bar{1}$]) of a single pair of chains in this structure is shown in Figure 2 with the thermal ellipsoid data for the carbide. A list of the more important distances and their standard deviations is given in Table III, where they are also compared with those reported earlier for Sc_5Cl_8.

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Table II. Atom Positions in Sc_5Cl_8Z (Z = C, N)

atom	x	y	z
	Sc_5Cl_8C		
Sc1	0.0	0.0	0.0
Sc2	0.48775 (6)	0.0	0.61374 (8)
Sc3	0.33662 (6)	0.5	0.32417 (9)
Cl1	0.29806 (8)	0.0	0.4329 (1)
Cl2	0.13299 (8)	0.5	0.1036 (1)
Cl3	0.32778 (8)	0.0	0.1639 (1)
Cl4	0.52979 (8)	0.5	0.2374 (1)
C^a	0.5	0.5	0.5
	Sc_5Cl_8N		
Sc1	0.0	0.0	0.0
Sc2	0.4875 (1)	0.0	0.6151 (2)
Sc3	0.3346 (2)	0.5	0.3212 (2)
Cl1	0.2973 (2)	0.0	0.4310 (3)
Cl2	0.1324 (2)	0.5	0.1031 (3)
Cl3	0.3271 (2)	0.0	0.1626 (3)
Cl4	0.5300 (2)	0.5	0.2372 (3)
N	0.5	0.5	0.5

^{a}Occupancy = 1.07 (2).

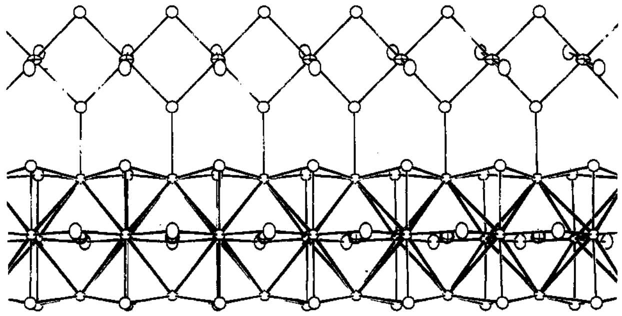

Figure 2. Side view of part of the infinite chains in Sc_5Cl_8Z with the isolated scandium 1 chain at the top and the metal–metal-bonded chain at the bottom. Chlorine is represented by the larger ellipsoids while the isolated scandium and Z atoms are crossed (80% probability ellipsoids for the carbide).

The high-yield preparation of Sc_5Cl_8C when the stoichiometric amount of graphite is included in the reaction and the virtual identity of its cell parameters (Table I) and distances (Table III) with those reported earlier for Sc_5Cl_8 appear to ensure that the two materials are identical and that they contain a carbon atom centered in every octahedral cluster of the metal chain (Figure 2). There appears to be nothing amiss regarding the earlier structural study except that poorer crystal quality limited the refinement resolution ($R = 0.115$, $R_w = 0.136$) and did not reveal the interstitial. The principal axes of the thermal ellipsoids in the present study ($R = 0.021$, $R_w = 0.024$) are with only two exceptions 63–88% as large as before; moreover, the carbon can now be refined anisotropically with an occupancy of 1.07 (2) Å, further indicating something of the quality of the data. The presence of carbide-like carbon in Sc_5Cl_8C was specifically established by the observation of a C (1s) peak shifted by ~3.5 eV to lower binding energy from C (1s) in adventitious carbon. The shift is plausibly a little greater than that for the more oxidized $Sc_7Cl_{10}C_2$ and Sc_2Cl_2C, 3.0–3.1 eV.[9]

It is interesting that "Sc_5Cl_8" was at times obtained earlier along with two other phases that have subsequently been shown to always contain interstitial elements, namely Sc_7Cl_{12}(B, N)[6] and $Sc_7Cl_{10}C_2$.[14] This is analogous to what is now known[10,17] regarding earlier experiments that revealed the first zirconium iodide clusters, again often in low yields. On the other hand, the synthesis of Sc_7Cl_{10}[1] does not seem to show any of these symptoms, and it appears to be a genuine binary compound, although not without some puzzling properties.[18]

Table III. Selected Bond Distances (Å) and Angles (deg) for Sc_5Cl_8Z (Z = C, N) and Sc_5Cl_8

Distances

	Sc_5Cl_8C	Sc_5Cl_8N	Sc_5Cl_8^{a}
Metal Array			
Sc2–Sc2a^b	3.041 (2)	3.090 (4)	3.021 (7)
Sc3–Sc2a	3.229 (2)	3.268 (3)	3.213 (5)
Sc2–Sc3	3.229 (2)	3.275 (3)	3.222 (5)
Sc2–Sc2b^c	3.5259 (7)	3.5505 (7)	3.523 (8)
Chlorine Atoms on Metal Array			
Sc2–Cl1	2.582 (2)	2.596 (4)	2.578 (6)
Sc3–Cl1	2.541 (1)	2.549 (2)	2.530 (3)
Sc3–Cl2	2.791 (3)	2.777 (4)	2.799 (6)
Sc3–Cl3	2.544 (1)	2.552 (2)	2.554 (4)
Sc2a–Cl3	2.575 (3)	2.591 (4)	2.572 (6)
Sc2a–Cl4	2.673 (1)	2.675 (3)	2.667 (4)
Chlorine Atoms around Isolated Metal Atoms			
Sc1–Cl2	2.542 (1)	2.548 (2)	2.538 (4)
Sc1–Cl4e	2.552 (2)	2.555 (3)	2.563 (5)
Nonbonded Distances (<3.6 Å)			
Cl1–Cl1f	3.526 (1)	3.524 (5)	3.517 (7)
Cl1g–Cl4e	3.549 (3)	3.579 (4)	3.541 (6)
Cl1–Cl2	3.531 (3)	3.534 (4)	3.528 (6)
Cl2–Cl3	3.522 (2)	3.538 (4)	3.527 (6)
Cl3–Cl3g	3.526 (1)	3.498 (5)	3.481 (7)
Cl3–Cl4	3.567 (2)	3.589 (4)	3.551 (6)
Cl2–Cl4	3.592 (2)	3.597 (4)	
Interstitial Atoms to Nonbonded Chlorines			
Z–Cl1	3.597 (2)	3.612 (3)	
Z–Cl3	3.594 (2)	3.618 (3)	
Interstitials in Metal Array			
Z–Sc3 (×2)	2.238 (2)	2.273 (1)	
Z–Sc2 (×4)	2.328 (1)	2.353 (1)	

Angles

	Sc_5Cl_8C	Sc_5Cl_8N	Sc_5Cl_8
Metal Array			
Sc2–Sc3–Sc2b	66.18 (5)	65.64 (7)	66.3 (1)
Sc3–Sc2–Sc2b	56.91 (3)	57.18 (4)	56.86 (5)
Sc2a–Sc3–Sc2c	66.18 (5)	65.81 (7)	66.5 (1)
Sc3–Sc2a–Sc2c	56.91 (3)	57.09 (3)	56.75 (6)
Sc2–Sc3–Sc2a	56.18 (4)	56.36 (8)	56.0 (1)
Sc2–Sc2a–Sc3	61.91 (5)	61.94 (7)	62.2 (2)
Chlorine Atoms on Metal Array			
Sc2–Cl1–Sc3	78.14 (5)	79.07 (9)	78.2 (1)
Sc3–Cl1–Sc3d	87.88 (5)	88.3 (1)	88.3 (2)
Sc3–Cl3–Sc2a	78.22 (5)	78.90 (9)	77.6 (2)
Sc3–Cl3–Sc3d	87.73 (5)	88.2 (1)	87.2 (2)
Sc2a–Cl4–Sc2c	82.52 (5)	83.1 (1)	82.7 (2)
Chlorine Atoms around Isolated Metal Atoms			
Cl2–Sc1–Cl2d	87.81 (6)	88.33 (9)	87.9 (2)
Cl2–Sc1–Cl4e	89.67 (5)	89.63 (8)	89.7 (1)
Bridging Chlorine Atoms			
Sc1–Cl2–Sc3	134.01 (3)	133.82 (6)	133.96 (8)
Sc2–Cl4a–Sc1h	136.28 (3)	135.95 (6)	136.16 (9)
Interstitial Atoms in Metal Array			
Sc2–Z–Sc2a	81.55 (4)	82.07 (8)	
Z–Sc2–Sc2a	49.22 (2)	48.97 (4)	

^{a}Data from ref 12. ^{b}Symmetry operations: a = $1 - x, y, 1 - z$; b = $x, 1 + y, z$; c = $1 - x, 1 + y, 1 - z$; d = $x, y - 1, z$; e = $x - {}^1/_2, y - {}^1/_2, z$; f = ${}^1/_2 - x, {}^1/K + y, 1 - z$; g = ${}^1/_2 - x, {}^1/_2, -z$; h = ${}^1/_2$ at x, ${}^1/_2$ at y, $1 + z$. ^{c}All atoms in the structure have like atoms at ±b, but this is listed here only once as the edge of the metal octahedron.

The Sc_5Cl_8Z structure exhibits some of the characteristic features of condensed clusters; the shortest Sc–Sc distance is in the shared Sc2 edge (3.041 Å in carbide) with a longer separation between these and the apex Sc3 atoms (3.229 Å). The repeat along the chain is 3.526 (1) Å, the b axis. All but the shared edge

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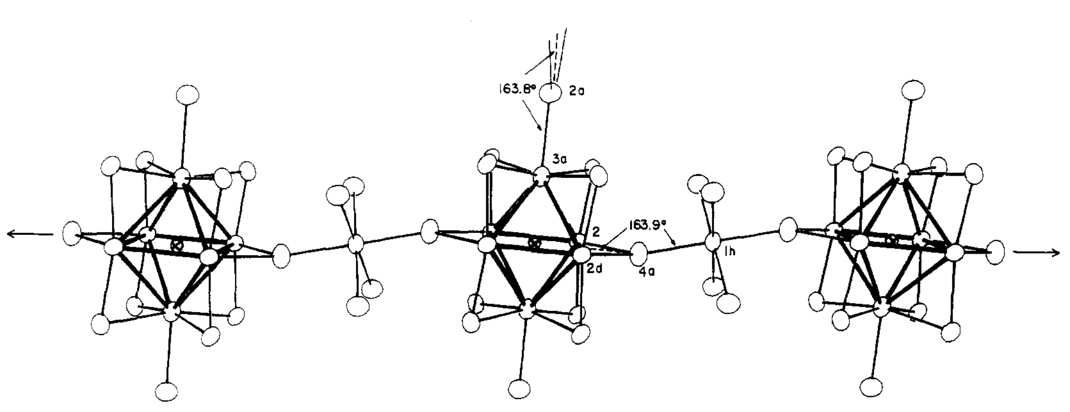

Figure 3. Bridging between the two types of chains viewed along 0, *y*, $^1/_2$ with the *c* axis horizontal. The infinite chains run normal to the figure, and only one member of each is shown. The atom identification scheme is given in Figure 1 and Table II (data for the nitride; 90% probability ellipsoids).

of the M_6X_{12}-type parent clusters are still bridged by chloride in the chain; Cl1 and Cl3 atoms are shared between adjacent clusters in this function while Cl4 bridges the side edges and also serves as apices in the parallel condensed chains of $Sc^{III}Cl_6$ octahedra. The last can be approximated as $(Sc1)(Cl2)_{4/2}(Cl4)_2$ when the connections to the metal chain are neglected. The last function is more easily seen in Figure 3, a [010] view down the chain axis that shows a single unit in each of three chains bridged by $(Sc1)(Cl2)_{4/2}$ units along the *c* axis. The Cl2 atoms bonded at longer distances to the metal vertices at the top and bottom of each Sc_6Cl_{12} cluster unit are those that are shared along the condensed $ScCl_6$ chain (Figure 2).

The structure of and the interconnectivity in the reported[6] Sc_4Cl_6Z phase is achieved by replacing the isolated $(Sc1)(Cl2)_{4/2}$ units (Figure 3) by a second chain of condensed Sc_6Cl_{12} clusters rotated by about 70° so that the edge-bridging Cl4 atoms that are vertices in the isolated Sc1 chain here are bonded to the open vertices in the added metal cluster chain. The bridging angle at Cl4 and Cl2 defined in Figure 3 is near 164° in both the carbide and nitride; this compares with 167.4° in Sc_4Cl_6Z with some small differences in packing requirements.

The chlorine sheathing of the metal chain and the packing of these units in the Sc_5Cl_8Z structure seem to be quite effective, judging from Cl–Cl separations. All such contacts around, between, and along the chains in the carbide fall in a narrow range of 3.52–3.57 Å except for the slightly longer Cl2–Cl4 separation within the shared $ScCl_6$ units (3.59 Å). This chlorine packing limitation alone is sufficient to account for the elongation of the metal octahedra along the chain. Also, restrictive Cl2–Cl3 interactions are presumably responsible for the longer Cl2–Sc3 separation, 2.79 Å, at the somewhat protected metal vertex of the chain (Figure 1) although this may amount to a mutual accommodation since halogens at cluster vertices are always observed to be bound at greater distances (more weakly) than are the inner halogen atoms.

The chain of isolated and evidently scandium(III) atoms has been described as a source of additional electrons for the electron-poor metal chain. This is also indicated by the approximate formulation $\frac{1}{\infty}[(ScCl_2^+)(Sc_4Cl_6C^-)]$, which is obtained by neglecting the long Sc3–Cl2 interchain separation and by assigning the edge-bridging Cl4 to the metal chain. It was noted before[6] that such a charge transfer seems to be indicated by the average Sc–Sc distance in the $\frac{1}{\infty}[Sc_4Cl_6C^-]$ chain, 3.210 Å (weighted for the two types of metal atoms in the chain), since this is appropriately shorter than the equivalent 3.295 Å value in the same type of cluster chain in Sc_4Cl_6Z when the data for the compounds with interstitial (Z) boron and nitrogen are averaged. However, an unfortunate choice of examples appears to have been involved.

The corresponding nitrides Sc_5Cl_8N and Sc_4Cl_6N show effectively identical average Sc–Sc distances, 3.253 and 3.255 Å, respectively, and these are also very close to that in the isolated cluster compound $Sc(Sc_6Cl_{12}N)$, 3.246 Å.[6] There is considerable evidence that relatively constant Sc–Z distances and hence effective radii for Z can be developed with the aid of a crystal (or some other) empirical radius of scandium, e.g., 0.885 Å.[19] The asymmetric environment about Z in the condensed cluster chain compounds makes the use of the shorter pair of Sc3–Z distances more appropriate than the average. This procedure gives a 1.44-Å radius for boron from both Sc_4Cl_6B and $Sc_7Cl_{12}B$[6] and 1.39, 1.39, 1.41, and 1.38 Å values for nitrogen in Sc_5Cl_8N, Sc_4Cl_6N, $Sc_7Cl_{12}N$, and Sc_2Cl_2N,[9] respectively, the latter two having a symmetric environment about the interstitial. In these respects it is Sc_5Cl_8C that exhibits anomalously small values for the shorter Sc–C distances (2.238 Å) and therefore a smaller radius for carbon, 1.35 Å. The corresponding carbon radii in the distorted acentric $Sc_7X_{12}C$ (X = Br, I) are 1.40 and 1.42 Å,[8d] while that in Sc_2Cl_2C (possibly with some nitrogen impurity) is 1.42 Å.[9] Relatively short metal–carbon distances are also found in $Zr_6I_{12}C$ compared with those in other zirconium iodide cluster carbides, but in this case specific enhanced bonding resulting from weaker interactions of terminal iodine at the metal vertices has been identified as the source.[17] Of course, this does not apply here in a comparison with the isostructural nitride. Although this particular problem with the carbide has not been pursued further, we suspect a specific effect related to the electron count in the carbide chain may be responsible.

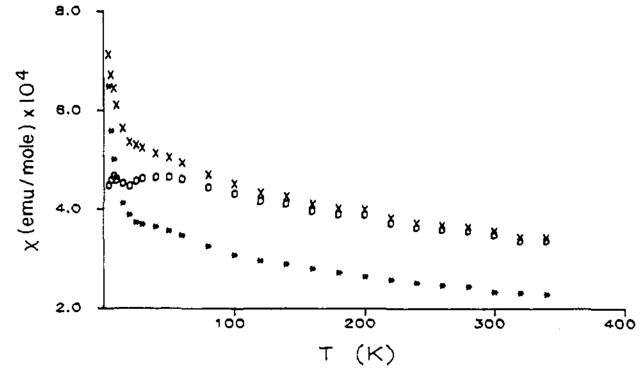

Figure 4. Molar magnetic susceptibility of Sc_5Cl_8C as a function of temperature and field: ×, 2 kG; *, 5 kG; O, 2 kG data corrected for the Curie tail.

Magnetic susceptibility measurements were carried out on Sc_5Cl_8C with the intention of clarifying the bonding features. The data at two field strengths are shown in Figure 4. Data at lower temperatures suggest a paramagnetic impurity, and fitting the 2-kG data below 50 K to a Curie–Weiss expressive gives $C = 2.13 \times 10^{-3}$ emu K mol^{-1}, $\Theta = -4$ K, and $\chi_0 = 4.58 \times 10^{-4}$ emu mol^{-1}. The probable paramagnetic impurity corresponds to the equivalent of only 13 at. ppm of gadolinium. The corrected data over the 4–340 K range, shown with open circles, suggest a phase transition occurs at ~75 K and possibly also at ~200 K. More importantly, the dependence of the data on both temperature and field suggests the presence of a possible incommensurate behavior. In comparison, the susceptibility and other properties of the double-chain

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(19) Shannon, R. D. *Acta Crystallogr., Sect. A.: Found Crystallogr.* **1976**, *A32*, 751.

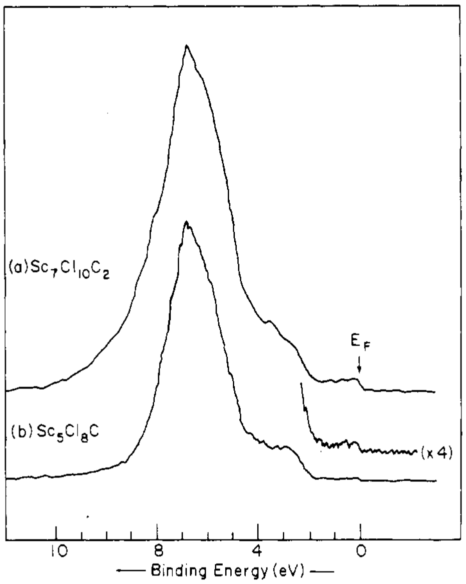

Figure 5. Helium I photoelectron spectra of (a) $Sc_7Cl_{10}C_2$ and (b) Sc_5Cl_8C ($E_F = 0$).

compound Sc_7Cl_{10} are more complex than might be suggested by the structure.[18]

Photoelectron spectra measured with ultraviolet radiation for numerous related compounds have been found to be particularly useful in identifying features of the valence region, namely fairly well-resolved chlorine, interstitial, and conduction bands.[20] Those for ZrCl and the M_2Cl_2C (M = Sc, Zr) derivatives have in addition been found to show good correspondence (allowing for differences in photoionization cross sections) with densities of states calculated by using extended Hückel methods.[15] The UPS results for Sc_5Cl_8C together with that for $Sc_7Cl_{10}C_2$,[21] which has been measured subsequent to the earlier publication,[14] are shown in Figure 5. Both exhibit the familiar chlorine band ~7 eV below E_F and a clear shoulder associated with the carbon 2p at ~3 eV. In addition, $Sc_7Cl_{10}C_2$ shows a sufficient shoulder at or near E_F to indicate that it is metallic or a small-gap semiconductor, in spite of the relatively high average oxidation state for scandium therein, +2.57. On the other hand, this result for Sc_5Cl_8C is more problematical, and it is difficult to make a prediction from these data.

Extended Hückel calculations have been carried out for Sc_5Cl_8C to provide better evidence regarding the last point. The total density of states is shown in Figure 6. Because of the great similarity of this to earlier results,[6,15] only the most general features will be noted, particularly those regarding the bands identified in the PES data. The chlorine band is again found to contain an appreciable scandium 3d contribution reflecting covalent Sc–Cl interactions, the remainder representing nonbonding chlorine 3p states. The carbon 2s band is off-scale near −22 eV as is the chlorine 3s band at ~−18 eV, although the calculated energy for neither is expected to be particularly accurate.[15] The nominal carbon 2p band peaks near −3.2 eV, close to that seen experimentally (Figure 5), and these states also contain appreciable scandium 3d contributions reflecting the strong polar Sc–C covalent bonding. Finally, the conduction band is again effectively only scandium 3d in character, and metallic conduction is clearly predicted. As in Sc_4Cl_6Z chains, the distribution of AO's within the metal band is consistent with the results described for $NaMo_4O_6$,[22] given the addition of the interstitial and the chain elongation associated with the larger chlorine.

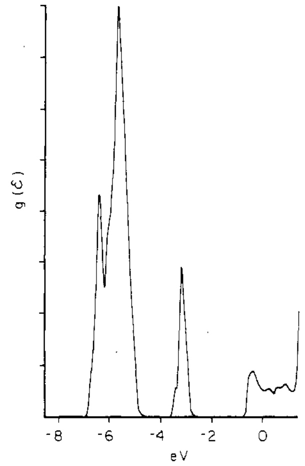

Figure 6. Density of state calculated for Sc_5Cl_8C by extended Hückel methods (26K points, smoothed, $E_F = 0$). See text for the details of the atom contributions to, from left to right, the nominal chlorine 3p, carbon 2p, and scandium 3d bands.

This report together with others recently published appears to complete the description of the scandium chloride phases for which there is some hope of a structural solution, although one can never rule out the discovery of successful reactions at lower temperatures that generate new phases or better crystals. Three structurally undefined phases remain. One is Sc_2Cl_3 (and Sc_2Br_3), for which preparation in good yields and analysis are available but for which the appellation "mouse fur" aptly identifies the diffraction problem.[16] A similar material in habit and yield is $ScCl_{1.42}$, the synthesis of which is described in some detail in the Experimental Section. Their characteristics and previous experience suggest, but do not guarantee, that both chlorides are binary phases. A third phase with some unusual reaction characteristics is $ScCl_{1.45(3)}$, according to direct analysis.[1] However, its evidently unique powder pattern was never encountered during the present and related investigations.[6,9,14] We have been generally unsuccessful in binding other interstitials such as Be, O, F, Al, or Si into scandium chloride cluster or condensed phases.

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Supplementary Material Available: A table of anisotropic thermal parameters (1 page); listings of observed and calculated structure factors for Sc_5Cl_8C and Sc_5Cl_8N (3 pages). Ordering information is given on any current masthead page.

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(20) Corbett, J. D.; Marek, H. S. *Inorg. Chem.* **1983**, *22*, 3194.

(21) $Sc_7Cl_{10}C_2$[14] is structurally distinct from Sc_7Cl_{10}, as it has edge-bridging rather than face-capping chlorine functions on the metal framework, but both contain double chains of distorted scandium octahedra sharing edges.

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