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## Cluster Condensation Reactions. Synthesis and Structure of Pentascandium Octachloride (Sc<sub>5</sub>Cl<sub>8</sub>). An Infinite Chain Structure Derived by Cluster Condensation

Kenneth R. Poepelmeier and John D. Corbett\*

*Contribution from the Ames Laboratory-USDOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011. Received December 30, 1977*

**Abstract:** Single crystals of the phase pentascandium octachloride, Sc<sub>5</sub>Cl<sub>8</sub>, are obtained in several weeks by chemical transport from 940 to 960 °C in a sealed tantalum container starting with powdered metal and ScCl<sub>3</sub>. The role of the lower valent gas-phase species ScCl<sub>2</sub>(g) in the formation of Sc<sub>5</sub>Cl<sub>8</sub> at high temperature is discussed in terms of the postulated transport reaction Sc<sub>5</sub>Cl<sub>8</sub>(s) + 2ScCl<sub>3</sub>(g) = 7ScCl<sub>2</sub>(g). The structure of the green-hued, black crystals has been determined with full-matrix least-squares refinement of all atoms with anisotropic thermal parameters. This phase crystallizes in the monoclinic space group C2/m with *a* = 17.78 (2), *b* = 3.523 (8), and *c* = 12.04 (1) Å, β = 130.10 (6)°, and *Z* = 2; final residuals were *R* = 0.115 and *R<sub>w</sub>* = 0.136 for 486 independent reflections with 2θ ≤ 50° and *I* > 3σ(*I*). Structurally Sc<sub>5</sub>Cl<sub>8</sub> contains separate infinite chains of metal octahedra which share trans edges as in Gd<sub>2</sub>Cl<sub>3</sub>; the common edges contain the shortest Sc-Sc bond yet observed, 3.021 (7) Å. A second, parallel chain consists of edge-shared octahedra of chloride about isolated scandium(III) atoms. The connectivity description [Sc(Cl)<sub>4/3</sub>(Cl)<sub>2/3</sub>]<sub>∞</sub>[Sc<sub>4</sub>Cl<sub>4</sub>(Cl)<sub>2/3</sub>(Cl)<sub>4/3</sub>]<sub>∞</sub> is well approximated by (ScCl<sub>2</sub><sup>+</sup>)<sub>∞</sub>(Sc<sub>4</sub>Cl<sub>6</sub><sup>-</sup>)<sub>∞</sub>, the latter emphasizing the anionic nature of the metal chain. The structure can be considered as arising from the formal condensation of M<sub>6</sub>X<sub>12</sub> clusters such as are found in Sc<sub>7</sub>Cl<sub>12</sub>. The anionic character of the metal chain allows the metal atoms therein to be formally more reduced than in Gd<sub>2</sub>Cl<sub>3</sub>, an effect which is reflected in the relative shortening of the bonds in Sc<sub>5</sub>Cl<sub>8</sub>. The sums of metal-metal bond orders in four structurally diverse scandium chlorides as well as in Gd<sub>2</sub>Cl<sub>3</sub> are found to be a smooth function of the number of delocalized electrons therein. Important in the variety of scandium chloride structures found with small changes in composition is the varied role of halogen atoms serve in connectivity together with the ability of scandium to generate isolated cations and thence strongly metal-metal bonded anionic arrays.

### Introduction

Evidence that any rare-earth metal, yttrium, or scandium would reduce its corresponding trihalide to compositions with X:M < 2.0 has until very recently been limited to the single example of the unusual gadolinium compound Gd<sub>2</sub>Cl<sub>3</sub><sup>1,2</sup> where a remarkable infinite metal chain consisting of edge-shared octahedra is formed. Later McCollum and co-workers<sup>3</sup> were able to reduce scandium trichloride and tribromide to the composition Sc<sub>2</sub>X<sub>3</sub> with scandium foil at elevated temperatures when proper attention was paid to avoiding blockage of the metal surface by product, a condition which also allows the preparation of the monochloride ScCl which contains double metal layers.<sup>4</sup> Recent applications of the technique of chemical transport along a temperature gradient above 880 °C have now allowed kinetic accessibility to several additional scandium phases in the composition range 2.0 > Cl:Sc > 1.0. Among these are Sc<sub>7</sub>Cl<sub>10</sub>,<sup>5</sup> with infinite metal chains composed of double octahedra, Sc<sub>7</sub>Cl<sub>12</sub>,<sup>6</sup> which contains discrete six-atom metal clusters, and the compound of interest in this work, Sc<sub>5</sub>Cl<sub>8</sub>. The chemistry of very reduced rare-earth metal halides (X:M < 2) has also recently been broadened substantially by Simon and coworkers,<sup>7</sup> who have reported the formation of monochlorides for M = Gd, Tb, Er, and Lu together with Tb<sub>2</sub>Cl<sub>3</sub> which is isostructural with Gd<sub>2</sub>Cl<sub>3</sub>. This paper reports on the synthesis, single-crystal x-ray structure, and electron paramagnetic resonance behavior of Sc<sub>5</sub>Cl<sub>8</sub> and relates these results both in terms of architecture and electronic states to those of other polyscandium structures. The formation of

Sc<sub>5</sub>Cl<sub>8</sub> and other transported compositions is considered in terms of transport by the high-temperature species ScCl<sub>2</sub>(g).

### Experimental Section

**Synthesis.** All preparation and analyses of materials were as described in an earlier publication.<sup>4</sup> The best metal available (99.998 atomic % purity) was used and as such had impurity levels in atomic parts per million as follows: H, 401; C, 105; O, 118; F, 14; Fe, 50; Ni, 20; Cu, <20; Ta, 260; W, 160; Gd, <7; La, 6.4; Ho, <4; other rare earths and other metals, <1 each. Typically ca. 0.25–0.50 g of ScCl<sub>3</sub> was placed in one end of a 12 cm, 9 mm o.d. tantalum tube along with two 0.4 × 4 × 110 mm metal strips and the tube welded under a He atmosphere (0.8–0.9 atm). Typical reaction gradients were T<sub>1</sub> → T<sub>2</sub> (850 → 1000 to 1050 °C) and the time of the reaction ranged from 4 to 6 weeks. The temperatures were monitored by thermocouples attached to the outside of the evacuated fused silica jacket in which the tantalum reaction tube had been sealed. The transported phases were identified by powder x-ray diffraction and in addition microprobe analysis was performed on new phases in order to estimate their composition and to ensure absence of other metallic elements. In all cases the products were found condensed in the hotter regions of the reaction tube away from the cold end where the ScCl<sub>3</sub> had been originally placed.

Specifically, in one particular reaction where the gradient was T<sub>1</sub> → T<sub>2</sub> (850 → 1010 °C) three distinct phases were found in separate bands of crystallites loosely attached on both the metal strips and container walls and ordered in increasing degree of reduction. The most oxidized phase Sc<sub>7</sub>Cl<sub>12</sub> (as previously identified from a single-crystal diffraction study<sup>6</sup>) was found in the coolest region of the tube followed by a band of ScCl<sub>1.58±0.04</sub> (Sc<sub>5</sub>Cl<sub>8</sub>) and finally in the middle

portion of the tube, a yet structurally uncharacterized compound  $\text{ScCl}_{1.40 \pm 0.07}$ . Microprobe examination of the latter two phases revealed no significant variation in composition in a particular crystal or between crystals of the same phase and consistently detected only scandium and chlorine among elements beyond the second period. Standard deviations indicated for the compositions were calculated on the basis of 25 independent observations. These reduced scandium chloride compounds all react with water and evolve hydrogen gas, in keeping with their reduced character.

The materials obtained under the above reaction conditions are crystalline but suffer profuse nucleation and growth and result in crystals of very small dimensions. In order to obtain crystals of adequate size for single-crystal x-ray diffraction more control over reaction parameters was necessary. As such, the reaction conditions described in the previous paragraph contrast greatly with minimization of gradients and careful control of the overall stoichiometry necessary to prepare  $\text{ScCl}_4$  or the careful control of the gradient in a narrow range necessary for good crystal growth of the  $\text{Sc}_7\text{Cl}_{10}$  phase. Suitable monocrystals of  $\text{Sc}_5\text{Cl}_8$  were subsequently obtained based on the observation that on several occasions a phase with a unique green hue to otherwise black crystals had been observed to form in small amounts while preparing  $\text{ScCl}_4$ . The phase identified above as  $\text{ScCl}_{1.58 \pm 0.04}$  from the gradient experiment had the same unusual cast, and a comparison of the powder x-ray diffraction patterns from the two experiments showed them to be the same. A composition  $\text{Cl}:\text{Sc} = 1.0$  was prepared as before<sup>4</sup> except that no attempt was made to control the small natural gradient ( $\sim 940 \rightarrow 960$  °C) across the tantalum reaction tube. This was accomplished by positioning the reaction tube within a sealed fused silica jacket in a 2.5-in. bore Marshall furnace without the benefit of a Inconel liner and radiation shields. The desired crystals condensed on the walls in the void end of the tube away from the major product which was a nonequilibrium mixture of metal plus several reduced phases including  $\text{ScCl}$ .

**Crystal Selection and Data Collection.** The crystals were of marginal size ( $0.375 \times 0.04 \times 0.04$  mm) for a single crystal study. Several possible candidates were chosen in the drybox with the aid of a Stereozoom microscope and were mounted and sealed in 0.3-mm i.d. Lindemann glass capillaries under an inert atmosphere. Two possible crystals were chosen on the basis of oscillation and Weissenberg photographs and in the course of this study single-crystal x-ray diffraction data were collected from each.

The data crystal in each case was mounted with the needle axis  $b$  nearly collinear with  $\phi$  on a four-circle diffractometer designed and built in the Ames Laboratory.<sup>8</sup> All procedures used for indexing and orientation of the crystal were as previously described,<sup>9</sup> although the weak diffraction from the very small crystals made the task somewhat tedious. The preliminary film work and the automatic indexing routine both indicated monoclinic symmetry.

**Data Collection.** X-Ray data were collected at ambient temperatures using  $\text{Mo K}\alpha$  radiation monochromatized with a graphite single crystal ( $\lambda 0.70954$  Å). All reflections within a sphere defined by  $2\theta \leq 50^\circ$  in the octants  $HK\bar{L}$  and  $H\bar{K}L$  were examined using an  $\omega$ -scan mode. The scan on the first crystal was over  $\pm 0.5^\circ$  in  $\omega$  from the calculated center peak position, counting 0.5 s per measurement every  $0.01^\circ$  in  $\omega$  and culminating when the count had reached the smaller of the two background count rates. Background was counted for 4 s  $0.5^\circ$  from the peak on each side. This mode proved less than satisfactory because the very small size of the crystal resulted in a relatively large percentage of unobserved reflections. The data set for the second crystal from which all reported parameters were calculated was obtained by increasing the counting time to 1.0 s per step and setting a minimum requirement of either an integrated count of 2000 or a maximum of ten scans across the reflection.

As is customary the peak heights of three standard reflections were remeasured every 75 reflections to check on instrument and crystal stability. These did not show any change over the data collection period. The initial portion of the data was collected based on a primitive monoclinic cell but after sufficient data had been collected the condition for C-centering,  $h + k = 2n$ , was obvious and this Bravais lattice type was imposed. Final cell parameters and their estimated standard deviations were obtained from the same data crystal for which structure parameters are reported, utilizing a least-squares refinement with  $\pm 2\theta$  values from 12 independent reflections for which  $2\theta > 25^\circ$ . The results were  $a = 17.78$  (2),  $b = 3.523$  (8),  $c = 12.04$  (1) Å, and  $\beta = 130.10$  (6)°.

**Structure Determination and Refinement.** Programs for data re-

duction, structure solution and refinement, illustration, and the sources of atomic scattering factors for neutral atoms (including corrections for both real and imaginary parts of anomalous dispersion) were as referenced before.<sup>10,11</sup> Data reduction yielded 563 observed reflections ( $I > 3\sigma(I)$ ), 85% of the total possible. Appropriate averaging of duplicate reflections yielded 513 independent data.

A trial structure was formulated based on structural concepts gained from past work on similar phases, particularly  $\text{Sc}_7\text{Cl}_{10}$ .<sup>5</sup> The observed monoclinic  $\beta$  angle of  $130^\circ$  and the same short  $b$  axis as in  $\text{Sc}_7\text{Cl}_{10}$  implied a possibly similar layered structure in space group  $C2/m$  with all atoms at  $y = 0$  and  $y = 0.5$ . If six atom metal clusters in a chain were again the structural skeleton, the  $\beta$  angle and the length of the  $c$  axis would indicate the metal array to be a single chain of metal octahedra which share edges parallel to the  $b$  axis. Preliminary metal atom coordinates were calculated with appropriate bond distances and with the cluster centered around  $1/2, 1/2, 1/2$  for two orientations of the cluster; that is, with the two apical atoms approximately parallel or perpendicular to the  $(10\bar{1})$  plane (which includes the short diagonal of the  $ac$  face). With the correct choice (the former) an electron density map revealed all of the halogen atoms, and three subsequent cycles of full-matrix least-squares refinement varying the scale factor, positional parameters, and isotropic thermal parameters converged at  $R = 0.154$  where  $R = \sum |F_o| - |F_c| / |F_o|$ . Further refinement with anisotropic thermal parameters for all atoms gave convergence at  $R = 0.144$  and  $R_w = 0.198$  where  $R_w = [\sum \omega(|F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2}$  and  $\omega = \sigma_F^{-2}$ . In this data set the weaker reflections were observed to have larger values of  $\omega \Delta^2$  ( $\Delta = |F_o| - |F_c|$ ) so the data set was reweighted in ten overlapping groups sorted according to  $F_o$  so that  $\omega \Delta^2$  across the groups was constant, yielding converged values of  $R = 0.133$  and  $R_w = 0.165$ . The occupation parameters refined to 1.00 (3) at this stage for all atoms, indicating no significant deviation from the ideal stoichiometry. Two moderately strong reflections were found to be in very poor agreement with the calculated values, with  $|F_o| - |F_c| / |F_o| > 0.85$ . These were remeasured and found to be in error. When this restriction was applied to all the reflections 25 additional reflections were eliminated, all with  $F_c$  less than 10% of  $F_o$  (max), corresponding to those reflections difficult to measure accurately on such a small crystal. Final agreement factors were  $R = 0.115$  and  $R_w = 0.136$ , with a difference Fourier synthesis map flat to  $\leq 1 e/\text{Å}^3$  in all regions. Some of the reason for the size of the residual secured here was that 64% of the observed reflections occurred at  $2\theta > 33^\circ$ .

The first crystal examined (with a faster scan) gave an identical chemical structure with all parameters within  $3\sigma$  of those described above and with the same inherently large residual at first glance,  $R = 0.123$ . Standard deviations obtained in this case for the position and thermal parameters were systematically 30–50% greater than for the result described first, an expected result since the number of reflections per variable was lower for this data set because of the faster scanning mode. But there were no systematic trends suggesting a particular type of disorder or imperfection as was observed earlier with  $\text{Sc}_7\text{Cl}_{10}$ , where weak binding between infinite metal chains composed of double octahedra evidently allowed marked differences in crystal perfection and even in cell volume. Refinement to a residual  $< 10\%$  was possible then but required favorable crystal growth and great patience in searching for that more nearly perfect crystal. We have no reason to suspect that this would not be true with  $\text{Sc}_5\text{Cl}_8$  but our search in this case was only marginally successful.

A comparison of the standard deviations for final positional and thermal parameters of  $\text{Gd}_2\text{Cl}_3$ <sup>2</sup> and  $\text{Sc}_7\text{Cl}_{10}$ <sup>5</sup> with those reported here for  $\text{Sc}_5\text{Cl}_8$  shows that the precision of the atom parameter refinement achieved for  $\text{Sc}_5\text{Cl}_8$  is comparable.

**Electron Paramagnetic Resonance.** The EPR spectrum was obtained at room temperature on a Varian Model E-3 spectrometer utilizing a 20-mg polycrystalline sample from the same reaction product used for the structural determination. This instrument has a frequency range of 8.8–9.6 GHz and a dial-selected magnetic field.

## Results

**Structure Description.** Table I provides final positional and thermal parameters for  $\text{Sc}_5\text{Cl}_8$ , and Table II lists important interatomic distances and selected angles. Structure factor results are available as supplementary material. The spatial arrangement of all atoms in the unit cell is shown in Figure 1

Table I. Crystallographic Data

composition: Sc<sub>5</sub>Cl<sub>8</sub>, Z = 2  
 cell: monoclinic, C2/m (no. 12)  
 lattice parameters: a = 17.78 (2), b = 3.523 (8), c = 12.04 (1) Å, β = 130.10 (6)°  
 refinement: R = 0.115, R<sub>w</sub> = 0.136 (486 reflections, 2θ ≤ 50°)

	x	y	z	Atom Positions			
				B <sub>11</sub> <sup>a</sup>	B <sub>22</sub>	B <sub>33</sub>	B <sub>13</sub>
Sc 1	0.0	0.0	0.0	1.22 (19)	2.12 (21)	0.97 (17)	0.55 (15)
Sc 2	0.4882 (2)	0.0	0.6136 (3)	1.19 (14)	0.96 (14)	0.85 (12)	0.47 (10)
Sc 3	0.3372 (2)	0.5	0.3247 (3)	0.87 (12)	1.22 (14)	0.74 (12)	0.36 (10)
Cl 1	0.2987 (3)	0.0	0.4323 (4)	1.23 (16)	1.35 (16)	1.09 (15)	0.83 (13)
Cl 2	0.1328 (3)	0.5	0.1033 (4)	1.18 (17)	1.27 (15)	1.39 (16)	0.47 (13)
Cl 3	0.3277 (3)	0.0	0.1625 (4)	1.25 (16)	1.27 (17)	0.92 (15)	0.49 (13)
Cl 4	0.5298 (3)	0.5	0.2385 (4)	1.86 (17)	1.67 (17)	1.31 (17)	1.19 (14)

$$^a T = \exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]. B_{12} = B_{23} = 0 \text{ by symmetry.}$$

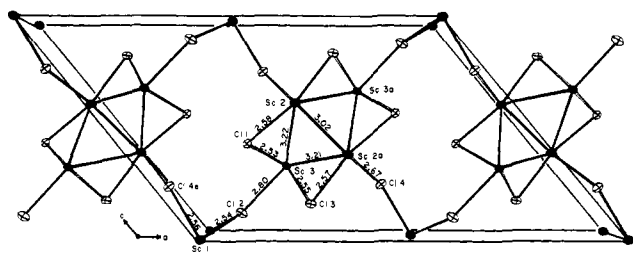
Table II. Selected Bond Distances (Å) and Angles (deg) in Sc<sub>5</sub>Cl<sub>8</sub>

distances		angles	
Metal Array			
Sc 2-Sc 3	3.222 (5)	Sc 2-Sc 3-Sc 2b	66.3 (1)
Sc 3-Sc 2a	3.213 (5)	Sc 3-Sc 2-Sc 2b	56.86 (5)
Sc 2-Sc 2a	3.021 (7)	Sc 2a-Sc 3-Sc 2c	66.5 (1)
		Sc 3-Sc 2a-Sc 2c	56.75 (6)
		Sc 2-Sc 3-Sc 2a	56.0 (1)
		Sc 2-Sc 2a-Sc 3	62.2 (2)
		Sc 3-Sc 2-Sc 2a	61.8 (1)
Chlorine Atoms on Metal Array			
Sc 2-Cl 1	2.578 (6)	Sc 2-Cl 1-Sc 3	78.2 (1)
Sc 3-Cl 1	2.530 (4)	Sc 3-Cl 1-Sc 3d	88.3 (2)
Sc 3-Cl 2	2.799 (6)	Sc 3-Cl 3-Sc 2a	77.6 (2)
Sc 3-Cl 3	2.554 (4)	Sc 3-Cl 3-Sc 3d	87.2 (2)
Sc 2a-Cl 3	2.572 (6)	Sc 2a-Cl 4-Sc 2c	88.7 (2)
Sc 2a-Cl 4	2.667 (4)		
Chlorine Atoms around Isolated Metal Atoms			
Sc 1-Cl 2	2.538 (4)	Cl 2-Sc 1-Cl 2d	87.9 (2)
Sc 1-Cl 4e	2.563 (5)	Cl 2-Sc 1-Cl 4e	89.7 (1)
Nonbonded Distances < 3.6 Å		Bridging Chlorine Atoms	
Cl 1-Cl 1f	3.517 (7)	Sc 1-Cl 2-Sc 3	133.96 (8)
Cl 1g-Cl 4e	3.541 (6)	Sc 2a-Cl 4-Sc 1h	136.16 (9)
Cl 1-Cl 2	3.528 (6)		
Cl 2-Cl 3	3.527 (6)		
Cl 3-Cl 3g	3.481 (7)		
Cl 3-Cl 4	3.551 (6)		
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, 1/2 + y, 1 - z			
g = 1/2 - x, 1/2 + y, -z			
h = x + 1/2, y + 1/2, z			
i = -x, -y, -z			
j = 1/2 - x, y, -z			
k = -x, y, -z			

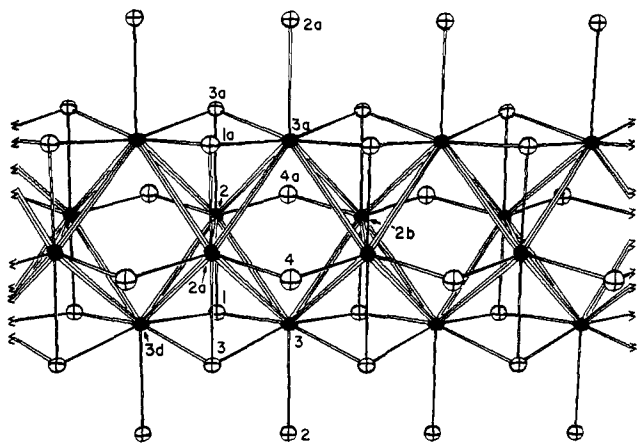
viewed down the short *b* axis, while Figure 2 shows the principal features of the metal array and the chlorine atoms which surround the metal chain approximately from the [1 0 1] direction. As in Gd<sub>2</sub>Cl<sub>3</sub><sup>2</sup> the clustering of metal atoms forms distorted metal octahedra which share trans edges to form scandium chains parallel to the *b* axis. The distortion of the octahedra is principally in the waist (Sc 2, 2a<sup>12</sup>) with two long edges at 3.52 Å (the *b*-axis length) and two short edges at 3.02 Å which comprise those shared between adjacent octahedra. The apical metal sites (Sc 3, 3a) at *y* = 0.5 are centered over the four waist atoms to within experimental error, 3.222 (5)

and 3.213 (5) Å. The isolated Sc 1 atom at (0, 0, 0) forms a chlorine-bridged chain of single metal atoms along *b* with the same 3.52-Å repeat. Both the chlorine-bridged chain and the chain of metal octahedra are related to an adjacent chain by a displacement of *b*/2 in an alternating manner throughout the crystal.

As has been the case in all the scandium chloride phases investigated structurally to date<sup>4-6</sup> all halogen atoms have three metal neighbors. Chlorine atoms 1 and 3 cap the outward facing scandium triangles of the cluster but in a manner not seen before, occupying the metal triangles *between* apices of



**Figure 1.** The  $\text{Sc}_5\text{Cl}_8$  structure viewed down the short  $b$  axis. Scandium and chlorine atoms are represented by solid and open ellipsoids, respectively, at 50% probability. Atoms Sc 3, Cl 2, and Cl 4 occur at  $y = 0.5$ ; all others are at  $y = 0$ .



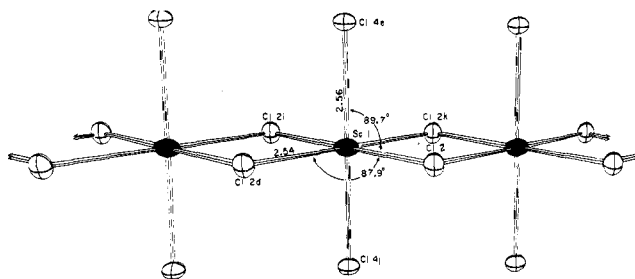
**Figure 2.** The anionic polymetal chain in  $\text{Sc}_5\text{Cl}_8$  with the  $b$  axis horizontal. Solid ellipsoids represent scandium; open, chlorine. The letters in atom identifications refer to symmetry operations, Table II.

the octahedra (e.g., Sc 2-Sc 3-Sc 3d, Figure 2). This allows a higher coordination of the metal chains by chlorine than would result from capping outward facing triangles of the octahedra (2-2b-3) which would thereby crowd the halogen atom Cl 4 situated on the long waist edge of each octahedron. Finally, Cl 2 bonds to the metal cluster at the apices in an exo fashion at a distance which is somewhat longer, 2.80 Å compared with 2.53-2.67 Å for the other metal-chlorine bond distances. These are very typical scandium-chlorine distances relative to 2.58 Å in  $\text{ScCl}_3$ ,<sup>13</sup> 2.59 Å in  $\text{ScCl}_4$ ,<sup>4</sup> and 2.44-2.70 Å in  $\text{Sc}_7\text{Cl}_{10}$ ,<sup>5</sup> which again serves to emphasize the apparent disposition of the reduction electrons within the chains.

The isolated metal sites, Sc 1, presumably consist of tripositive scandium based on both the scandium-chlorine distances and the absence of a detectable EPR transition. The Sc 1 atoms are coordinated by chlorine atoms 2 and 4 to generate only slightly distorted octahedra of halogen atoms which share trans edges parallel to  $b$ , as depicted in Figure 3. Chlorine atoms 2 and 4 serve to connect the two rather different structural environments of the isolated scandium atoms and metal chains and both appear somewhat more tightly bound to the scandium(III) atoms than to the chains based on distances.

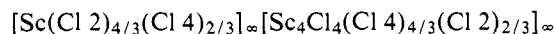
### Discussion

Single-crystal x-ray diffraction has proven to be a valuable tool in unraveling the structural and compositional relationships between the phases in the region  $2.0 \leq \text{Cl}:\text{Sc} \leq 1.0$  where the earliest studies<sup>4,5</sup> indicated what appeared to be an unusually large number of distinct phases unrelated by simple structural principles. The remarkable variety in structure which is achieved with small changes in composition can best be appreciated and understood by considering first the metal substructure and then the arrangement of the halogen atoms around this metal array and the linkages which exist. The atom



**Figure 3.** The chloride-bridged chain about the isolated scandium(III) atoms.

connectivity scheme developed before<sup>14</sup> for discrete clusters also provides a useful description of the  $\text{Sc}_5\text{Cl}_8$  structure, viz.,



where the first portion represents the isolated Sc 1 groups (Figure 3) and the second the metal bonded chain of interest (Figure 2). In this assignment the one long Cl 2-Sc 3 distance, 2.80 Å, is assumed to be equivalent to all other metal-halogen bonds in the sense of formal electron distribution. With consideration of all distances the simple distribution  $(\text{ScCl}_2^+)_{\infty}(\text{Sc}_4\text{Cl}_6^-)_{\infty}$  seems appropriate and is in keeping with the anionic nature of the metal array also found in both  $\text{Sc}_7\text{Cl}_{10}$ <sup>5</sup> and  $\text{Sc}_7\text{Cl}_{12}$ .<sup>6</sup>

The metal array found in  $\text{Sc}_5\text{Cl}_8$  is very much like that in  $\text{Gd}_2\text{Cl}_3$  where  $\text{M}_6$  clusters have also linked through shortened trans edges to form an infinite chain running parallel to the  $b$  crystal axis. The distance between the scandium metal atoms on the shared edges, 3.021 (7) Å, is the shortest metal-metal bond yet observed for scandium and compares with the shortest distance of 3.26 Å in the metal,<sup>15</sup> 3.216 (6) Å in  $\text{ScCl}_4$ ,<sup>4</sup> 3.147 (3) Å in  $\text{Sc}_7\text{Cl}_{10}$ ,<sup>5</sup> and 3.204 (2) Å in  $\text{Sc}_7\text{Cl}_{12}$ .<sup>6</sup> In  $\text{Gd}_2\text{Cl}_3$  the analogous short distance is 3.349 (1) Å vs. 3.604 Å in the metal. In both compounds the presence of the especially short metal-metal bond on the shared trans edge emphasizes the alternate description of the array in terms of parallel dimeric metal units bridged by capping metal atoms.

If two chlorines are formally allocated to the isolated scandium(III) the anion chain in this compound and the metal chain in  $\text{Gd}_2\text{Cl}_3$  have the same X:M ratio ( $\text{M}_4\text{X}_6$ ). But because of the presence of the isolated scandium(III) ion the average number of valence electrons per metal site in the chain in  $\text{Sc}_5\text{Cl}_8$  is greater than in  $\text{Gd}_2\text{Cl}_3$  even though the average oxidation state in the gadolinium compound is less. The simplest manifestation<sup>14</sup> of a greater effective reduction should be found in the  $\Delta d/d$  ratio where  $\Delta d$  is the relative shortening of a bond compared with the average metal-metal distance  $d$  in the 12-coordinate metal. The  $\Delta d/d$  value of 0.07 for the short bond in  $\text{Gd}_4\text{Cl}_6$  compares with 0.08 for the corresponding bond in  $(\text{ScCl}_2^+)(\text{Sc}_4\text{Cl}_6^-)$ , a small difference which is at least in the right direction in terms of electron count. More strikingly, the apical to waist atom distances in the gadolinium compound are both slightly longer than the average distance in the element, while in  $\text{Sc}_5\text{Cl}_8$  these distances are less,  $\Delta d/d = 0.02$ .

Surprisingly, this sort of comparison may be extended fairly well to all of the reduced scandium compounds as well as to  $\text{Gd}_2\text{Cl}_3$  in spite of the diversity of bonding arrangement and electronic structures. Table III lists for the phases  $\text{ScCl}$ ,  $\text{Sc}_7\text{Cl}_{10}$ ,  $\text{Gd}_4\text{Cl}_6$ ,  $\text{Sc}_5\text{Cl}_8$ , and  $\text{Sc}_7\text{Cl}_{12}$  the average number of bonding electrons per metal atom together with all significant metal-metal distances and their multiplicity per metal atom. Finally the Pauling bond orders  $n$  (where  $d_n = d_1 - 0.60 \log n$ ) summed over all distances are listed. As shown in Figure 4, the marked irregularities and contrasts now all disappear, and

**Table III.** Stoichiometry and Bonding Electrons, Bond Distances, and Bond Orders in Scandium and Gadolinium Metal–Metal Bonded Arrays

	ScCl	Sc <sub>7</sub> Cl <sub>10</sub>	Gd <sub>4</sub> Cl <sub>6</sub>	Sc <sub>5</sub> Cl <sub>8</sub>	Sc <sub>7</sub> Cl <sub>12</sub>
Cl:M	1.00	1.43	1.50	1.60	1.71
bonding electrons per M in sheet, chain, or cluster	2.00	1.83 <sup>a</sup> (1.50 <sup>b</sup> )	1.50	1.75 <sup>a</sup>	1.50 <sup>a</sup>
M–M distances, Å (frequency per M)	3.22 (×3) 3.47 (×6)	3.15 (× <sup>4</sup> / <sub>3</sub> ) 3.26 (× <sup>8</sup> / <sub>3</sub> ) 3.41 (× <sup>4</sup> / <sub>3</sub> )	3.35 (× <sup>1</sup> / <sub>2</sub> ) 3.74 (×4)	3.02 (× <sup>1</sup> / <sub>2</sub> ) 3.22 (×4)	3.20 (×2) 3.23 (×2)
Σ Pauling bond order <sup>c</sup>	1.70	1.51	1.37	1.63	1.32

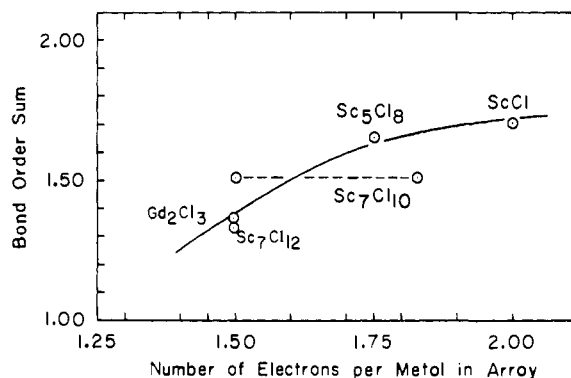
<sup>a</sup> One isolated Sc(III) ion per formula unit is presumed to have donated three electrons to the metal–metal bonded unit. <sup>b</sup> Alternate value assuming 2 of 11 electrons per six metal atoms in the metal–metal bonded repeating unit are localized and nonbonding. <sup>c</sup>  $d_n = d_1 - 0.60 \log n$ ,  $n$  = bond order;  $d_1$  (Sc) = 2.924 Å,  $d_1$  (Gd) = 3.264 Å (ref 15).

the total bond order per metal is seen to closely parallel the number of bonding electrons, including for Gd<sub>2</sub>Cl<sub>3</sub>! Even the status of Sc<sub>7</sub>Cl<sub>10</sub> is clarified. This compound has been found to exhibit a sharp EPR signal and a magnetic moment which closely corresponds to two separate d<sup>1</sup> states per formula unit (Sc<sub>7</sub>Cl<sub>10</sub>) if Curie–Weiss behavior is assumed. The correlation shown in Figure 4 supports this in the sense that the bond order sum found appears too low when compared with that expected for all 11 electrons per repeating unit whereas fewer bonding electrons (but >9) would be more consistent.

In these chain structures the halogen atoms complete the structure in a remarkably versatile fashion and ultimately determine the traditional definition of the degree of reduction X:M. In order to generate the anionic chain in Sc<sub>5</sub>Cl<sub>8</sub>, octahedral sites for the isolated scandium(III) cation must be created in the anion sublattice. The M<sub>4</sub>X<sub>6</sub> chain units in Sc<sub>5</sub>Cl<sub>8</sub> have separated in relation to those in Gd<sub>4</sub>Cl<sub>6</sub> so that half the halogen atoms on triangular faces of the chain are no longer exo to a waist metal atom in a neighboring M<sub>6</sub> chain cluster. Moreover the capping halogen atoms occur over the triangular face situated *between* apices of the condensed clusters, and as such belong wholly to the chain. Now the exo positions are occupied by the apical Cl 2 and, in a sense, by Cl 4 bridging the long edge of the octahedra, and both of these simultaneously complete the anion sublattice and create the octahedral interstice necessary for the isolated metal atom. Another important difference is the decrease in chlorine–chlorine repulsion relative to those in Gd<sub>4</sub>Cl<sub>6</sub>. There the shortest distances between face capping and bridging halogen atoms are 3.22 and 3.34 Å vs. 3.48 Å here, the rearrangement being dictated in part by the smaller size of the triangular faces with the scandium compound.

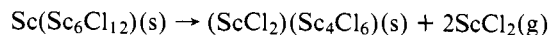
We now begin to understand the ways the metal and anion sublattices adapt to one another to create new structures with slightly different compositions. There are clearly major electronic requirements in the metal bonded arrays as well, as witnessed by the strong proclivity to form anion states, but we are well short of understanding these. The versatility of scandium in creating these new structures certainly must depend at the very minimum on both its ability to readily form the relatively low charged scandium(III) counteranion, thereby allowing the generation of anionic chains, and a sufficient radial extension of the valence orbitals to form shortened metal–metal bonds. To date neither titanium nor zirconium appears capable of generating (or needing) isolated M(IV) cations, and we have not succeeded in generating strongly metal–metal bonded or metallic examples of titanium halide systems. Zirconium does form both ZrCl<sup>10</sup> analogous to ScCl and (Zr<sub>6</sub>Cl<sub>12</sub>)Cl<sub>3</sub><sup>6</sup> which is isoelectronic with Sc<sub>7</sub>Cl<sub>12</sub>.

The disposition of halogen in the anion chain in Sc<sub>5</sub>Cl<sub>8</sub> (Figure 2), namely, edge bridging rather than face capping as found in the extended chains in Gd<sub>2</sub>Cl<sub>3</sub> and Sc<sub>7</sub>Cl<sub>10</sub>, provides a new perspective for the *hypothetical* cluster condensation reactions. Edge bridging by halide in isolated clusters such as



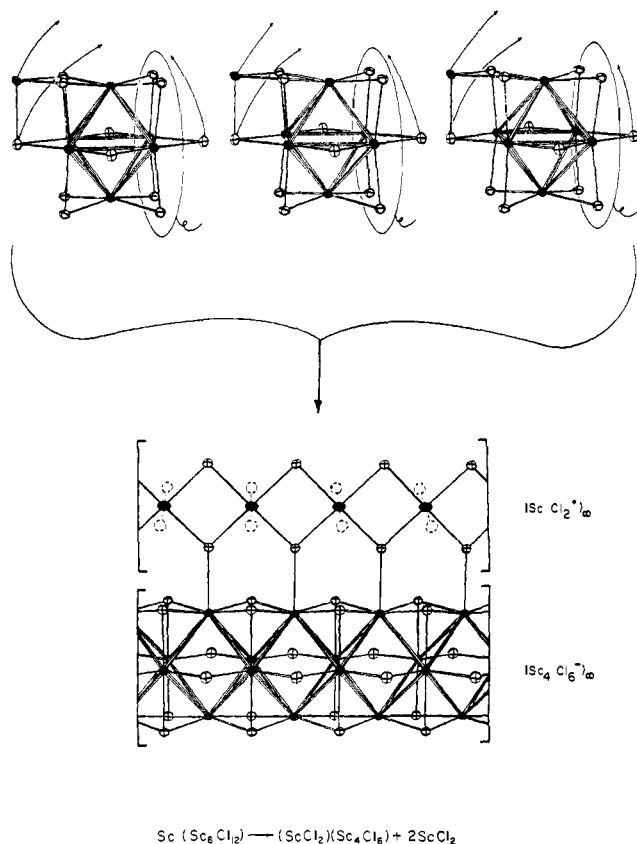
**Figure 4.** The number of electrons per metal atom in the cluster, chain, or sheet vs. the sum of Pauling bond orders for all metal–metal bonds. The dotted line for Sc<sub>7</sub>Cl<sub>10</sub> represents the range possible, corresponding to 11 (right) or 9 (left) electrons per repeating unit (see text).

Ta<sub>6</sub>Cl<sub>14</sub><sup>2+</sup> is well known,<sup>14</sup> and a structurally comparable anion is known in Sc(Sc<sub>6</sub>Cl<sub>12</sub>).<sup>6</sup> In all of these the presence of a polar solvent, a basic group, or condensation into the solid state invariably causes occupation of secondary exo or outward pointing orbitals of the octahedron. A similar behavior is also observed in the present structure with Cl 2 as well as in Sc<sub>7</sub>Cl<sub>10</sub>, and in Sc(Sc<sub>6</sub>Cl<sub>12</sub>) half of the bridging halide in one cluster occupies exo positions in neighboring clusters, that is M<sub>6</sub>X<sub>6</sub><sup>i</sup>X<sub>12/2</sub><sup>i-a</sup>.<sup>16</sup> In Sc<sub>5</sub>Cl<sub>8</sub> the particular arrangement of Cl 1, Cl 3, and Cl 4 only over *edges* of the scandium chain seems particularly significant in that the anion (Sc<sub>4</sub>Cl<sub>6</sub>)<sub>∞</sub> can be viewed as the first example of the condensation of *edge*-bridged M<sub>6</sub>X<sub>12</sub> polyhedra. The corresponding condensation of face-capped M<sub>6</sub>X<sub>8</sub> clusters (as found in MoCl<sub>2</sub> and Nb<sub>6</sub>I<sub>11</sub>) to yield the infinite chain in Gd<sub>2</sub>Cl<sub>3</sub> has been described by Simon,<sup>17</sup> and Sc<sub>7</sub>Cl<sub>10</sub> also provides a further example. The cluster condensation to yield both the cation and anion chain in Sc<sub>5</sub>Cl<sub>8</sub> can be accomplished structurally in a particularly simple way from the phase Sc(Sc<sub>6</sub>Cl<sub>12</sub>), as depicted in Figure 5. Stoichiometrically the conversion amounts to the reaction



where conceptually two ScCl<sub>2</sub> groups as well as two bridging chlorine atoms split off what will become the common face and shared metal edge, with the latter combining with the isolated scandium(III) ion to form the infinite ScCl<sub>2</sub><sup>+</sup> chain. To generate the rest of the structure one has only to pack these (1 0 1) sheets (the short diagonal in Figure 1) together so that Cl 4 atoms which edge bridge the metal chain also form the apices of the chlorine octahedra in the ScCl<sub>2</sub> chain in another sheet (the dotted atoms in Figure 5).

The preparative methods available are only beginning to allow the characterization of phase-pure metal-rich scandium halides by methods other than x-ray crystallography. As a result the nature of the electron distribution in these highly

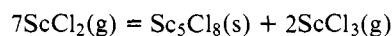


**Figure 5.** A hypothetical representation of the condensation of  $\text{Sc}(\text{Sc}_6\text{Cl}_{12})$  to yield a section of the  $[1\ 0\ 1]$  sheet in the structure of  $\text{Sc}_5\text{Cl}_8$ . The overall reaction is  $\text{Sc}(\text{Sc}_6\text{Cl}_{12}) \rightarrow \text{Sc}_5\text{Cl}_8 + 2\text{ScCl}_2$ ; the  $\text{ScCl}_2$  units removed at the condensation points are circled. The structure is completed by packing these sheets so that Cl 4 atoms which bridge the long edges of the octahedra in the  $(\text{Sc}_4\text{Cl}_6^-)_\infty$  chain also comprise the apices of the shared octahedra in the  $(\text{ScCl}_2^+)_\infty$  chain (dashed circles).

anisotropic materials is by no means clear and additional physical measurements are needed. The phase  $\text{Sc}_7\text{Cl}_{10}$  provides an interesting comparison with  $\text{Sc}_5\text{Cl}_8$  as only the former gives a detectable EPR signal. This and the nearest-neighbor distances clearly support the assignment of scandium(III) to the isolated scandium atoms (0, 0, 0) contained in the edge-shared chloride octahedra which are found in both phases, a distribution consistent with the effective reduction of the metal array as in  $\text{Sc}_5\text{Cl}_8$  shown by the relative shortening of the metal distances ( $\Delta d/d$  ratios and Figure 4). The weak, temperature-dependent paramagnetism measured for  $\text{Sc}_7\text{Cl}_{10}$ <sup>5</sup> appears to arise from localized nonbonding paramagnetic centers associated with some but not all of the metal atoms in the metal array.  $\text{Sc}_2\text{Br}_3$ <sup>3</sup> also has been found to have a similar susceptibility. Judging from its lack of a detectable EPR signal  $\text{Sc}_5\text{Cl}_8$  may be expected to behave in a more conventional fashion, with a simple temperature-independent Pauli paramagnetism, although this has not been verified to date experimentally.

One of the most fascinating aspects of the chemistry in the reduction of  $\text{ScCl}_3$  has been the formation of the new solid-state compounds  $\text{Sc}_7\text{Cl}_{10}$ ,  $\text{Sc}_7\text{Cl}_{12}$ , and, in particular,  $\text{Sc}_5\text{Cl}_8$  by vapor-phase transport. The molecular transporting species

is probably  $\text{ScCl}_2(\text{g})$ . Hastie and coworkers<sup>18</sup> have reported the formation of  $\text{ScCl}_2(\text{g})$  from reaction of gaseous  $\text{ScCl}_3$  with Sc metal at 1450 °C followed by isolation in a solid argon matrix and IR examination. In our synthesis work isothermal and stoichiometric reactions involving metal and  $\text{ScCl}_3$  under solid-liquid or solid-gas conditions have all been unsuccessful routes to compositions Cl:Sc > 1.5. The formation of compounds which are very incongruent melting from either a melt or the metal by a reaction requiring substantial diffusion certainly is kinetically hindered, although thermodynamically the compounds appear quite stable. The disproportionation of a lower valent vapor species such as  $\text{ScCl}_2$  would, on the other hand, provide a direct and facile transport reaction, viz.,



Empirical evidence based on observation suggests that there are several competing processes and that, depending on conditions, compounds as oxidized as  $\text{Sc}_7\text{Cl}_{12}$  and as reduced as the metal itself will deposit. Simple condensation of a stable dichloride has not been observed. A possible structure for  $\text{ScCl}_2(\text{s})$  would be the neutral cluster  $\text{Sc}_6\text{Cl}_6^i\text{Cl}_{12/2}^{i-a}$ , isostructural with the recently characterized  $\text{Zr}_6\text{I}_{12}$ ,<sup>6</sup> and an energetically more favorable alternative to the layered  $\text{CdI}_2$  or  $\text{CdCl}_2$  types common to the majority of the transition metal dihalides. However, only the nine-electron cluster  $[\text{Sc}^{3+}]_6\text{Cl}_6^i\text{Cl}_{12/2}^{i-a}]^{3-}$  has been prepared to date, and the stoichiometric dichloride with only six bonding electrons may be too electron deficient to be stable.

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**Supplementary Material Available:** Tables of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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