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Synthesis, Characterization, and Crystal Structures of Two Scandium Cluster Carbides and a Boride, $Sc_7X_{12}C$ (X = I, Br) and $Sc_7I_{12}B$

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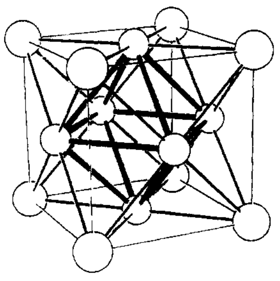
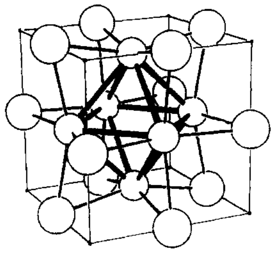
The isomorphous compounds $Sc(Sc_6I_{12}C)$ and $Sc(Sc_6Br_{12}C)$ have been synthesized, and their structures have been successfully refined in the acentric space group $R3$ ($Z = 3$; $a = 14.717$ (1) Å, $c = 9.847$ (2) Å, $R = 0.045$ and $a = 13.628$ (1) Å, $c = 9.203$ (1) Å, $R = 0.034$, respectively). The structure exhibits a significantly asymmetric halogen environment about the isolated scandium atom and a distortion of the cluster from D_{3d} to C_3 symmetry. The changes may reflect the operation of an alternative matrix effect arising from the large halide and the small interstitial. The magnetic susceptibility of the iodide is in agreement with the calculated MO description and the assignment of the isolated atom as scandium(III). The analogous iodide boride was synthesized and characterized by X-ray powder data. A passable but erroneous refinement of the iodide carbide in space group $R\bar{3}$ as $Sc(Sc_7I_{12}C_2)$ ($R = 0.035$) showed some of the same characteristics of earlier structural results for other $M_7X_{12}Z$ compositions.

Introduction

Reduced binary, ternary, and quaternary halides of scandium, yttrium, zirconium, and the lanthanide elements have been studied in this laboratory for a number of years.[1-7] Among the variety of interesting compounds obtained are many consisting of either discrete or condensed metal clusters. In nearly all cases the clusters or their condensation products can be conceptually viewed as originating from either M_6X_8 (6–8) or M_6X_{12} (6–12) units. The few known examples based on 6–8 clusters are normally empty while the 6–12 types for the earlier transition metals usually contain a small interstitial element (Z) in all octahedra.



M_6X_8



M_6X_{12}

Several such compounds are known in scandium–chlorine–interstitial systems, among them the discrete cluster phases $Sc(Sc_6Cl_{12}Z)$ (Z = B, N).[8,9] Herein are reported the first results for this type of chemistry for the heavier bromide and iodide systems with interstitial carbon. These represent not only other examples of discrete carbon- and boron-centered clusters of the early transition elements,[5-7] but their successful refinement in an acentric space group also provides some information regarding apparent disorder and twinning problems that may have affected earlier studies.

Experimental Section

All compounds were manipulated in dryboxes under either a nitrogen or an argon atmosphere. Scandium metal was Ames Laboratory material prepared by metallothermic reduction of ScF_3 with triply distilled calcium and then sublimed. Typical purity has been cited before.[9] Amorphous boron (95%, 325 mesh, Alfa) and powdered graphite (spectroscopic grade, Union Carbide) were utilized. The latter was degassed under high vacuum for several hours at 850 °C prior to use and subsequently stored in stoppered vials in the drybox.

Scandium triiodide was prepared from scandium metal pieces and elemental iodine in an evacuated, sealed fused silica vessel in which the metal was contained in a tungsten crucible.[10] The metal end was heated to 950 °C for several hours and then 850 °C for 3 days, with due precautions being taken to prevent excessive pressure. The product was then sublimed three times under high vacuum in a tantalum apparatus[10] to give the bright yellow ScI_3.

X-ray powder patterns (monochromatic Cu $K\alpha_1$, 1.540562 Å) were obtained with an Enraf-Nonius (FR 552) Guinier camera. Samples were ground in the drybox, mixed with NBS silicon as an internal standard, and mounted between two pieces of cellophane tape to protect them from moisture and oxygen. The samples were maintained in a forepump vacuum within the camera.

Combustion carbon analyses on the iodide carbide were performed by Guelph Laboratories, Ltd., Guelph, Ontario. Magnetic susceptibility data were obtained with the aid of a SQUID magnetometer (Quantum Design, Inc).

Calculations. Noniterative extended Hückel calculations[11] were performed on isolated $(Sc_6I_{12})I_6^{9-}$ and $(Sc_6I_{12}C)I_6^{9-}$ clusters with the dimensions observed in $Sc_7I_{12}C$. The addition of six iodide ligands at appropriate distances to represent terminal atoms on the $Sc_6I_{12}{}^{3-}$ cluster has been shown[6] to be generally important in the correct description of cluster bonding. The Cartesian coordinates used for the atoms in the augmented clusters are available as supplementary material while the orbital parameters have been cited before.[6,9]

Syntheses. The $Sc_7I_{12}C$ was initially obtained from the reaction of Sc (strips), ScI_3, and graphite in a 2.1:1.0:1.0 molar ratio, respectively, that is, ScI_3-limited. The mixture was heated in a sealed niobium tube[10] at 850 °C for 1 week after which it was cooled at ~5 °C/h to 530 °C and then quenched in air. The product consisted of $Sc_7I_{12}C$ as both dark purple parallelepipeds and powder (70% yield visually) plus some black unidentified product, presumably more carbon-rich. The crystal used in the structure determination was obtained from this reaction. Subsequently, more appropriate proportions of ScI_3 and graphite (4.1:1) were heated with excess metal (strips) at 850 °C for 3 days and then cooled to room temperature in ~3 min. This gave the product in quantitative yield based on carbon, i.e., $3Sc + 4ScI_3 + C \rightarrow Sc_7I_{12}C$, the only other product being ScI_x ($x \sim 2.2$)[12,13] and unconsumed metal. The ScI_x reproducibly crystallizes as a blue-black mass that is easily separated from the $Sc_7I_{12}C$. An ScI_3:C ratio of 2.0:1 with excess Sc gave $Sc_7I_{12}C$ in high yield mixed with another unknown product. Excess graphite in general gives a mixture of products that are not easily separated.

Excess scandium strips, ScI_3 (slight excess), and boron heated at 850 °C for 2 weeks gave a purplish powder of $Sc_7I_{12}B$, which is isotypic with $Sc_7I_{12}C$ by Guinier powder photography, together with ScI_x and small scandium crystals (~0.2 mm on edge) mixed with the $Sc_7I_{12}B$. A similar mixture reacted at 850 °C for 1 week and then slowly cooled (~4 °C/h) to 330 °C gave microcrystalline $Sc_7I_{12}B$ but no single crystals suitable for X-ray diffraction.

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Table I. Crystallographic Data for $Sc_7I_{12}C$ and $Sc_7Br_{12}C$

	$Sc_7I_{12}C$	$Sc_7Br_{12}C$
fw	1849.5	1285.6
space group	*R*3	*R*3
a, Å	14.717 (1)	13.628 (1)
c, Å	9.847 (2)	9.203 (1)
V, $Å^3$	1847.0 (4)	1480.2 (4)
n^a	15	30
ρ_{calcd}, g cm^{-3}	5.09	4.33
cryst dimn, mm	0.09 × 0.13 × 0.22	0.11 × 0.15 × 0.20
reflcn measd[b]	$h,\pm k,\pm l$	$h,k,\pm l$; $-h,k,l$; $h,-k,l$
2θ(max), deg[c]	55	50
no. of data collected	2960	1867
obsd	1877	1164
unique ($I > 3\sigma(I)$)	1209	468
R_{av}	0.031	0.029
μ(Mo Kα), cm^{-1}	176.2	263.3
transm coeff	0.17–0.81	0.27–0.75
parameters refined	59	60
R	0.045	0.034
R_w	0.048	0.033
R_I	0.056	0.045
GOF	1.11	0.91
largest residual, e $Å^{-3}$	0.4	0.5

[a] Number of reflections in Guinier powder pattern used for least-squares refinement of lattice constants. [b] In rhombohedral setting. [c] Mo Kα, λ = 0.71073 Å.

Reaction of $ScBr_3$ with excess metal strips and the stoichiometric amount of carbon under a 900/878 °C gradient for 24 days gave a 75% yield of $Sc_7Br_{12}C$ crystals, 20% "mouse fur" (Sc_2Br_3[14]), and a trace of ScOBr.

Crystallography. Single crystals of $Sc_7I_{12}C$ and $Sc_7Br_{12}C$ suitable for a structure determination were sealed in 0.2-mm glass capillaries in a drybox. Three-dimensional diffraction data were obtained at ambient temperatures with a Syntex $P2_1$ four-circle diffractometer equipped with a graphite monochromator. Crystal data are summarized in Table I. Variable scan speeds from 1.0 to 29.3° min^{-1} were employed. Empirical absorption corrections based on four and two azimuthal scans were applied to the iodide and bromide data, respectively. After correction for Lorentz and polarization factors, equivalent reflections were averaged (instrument instability factor 0.05). The data sets were rather different in size since the acentricity and thence a lack of adherence to Friedel's law were not considered when the iodide data set was collected. There was no detectable decay of either crystal according to three reflections that were measured every 100 reflections during data collection. The programs used for data reduction and full-matrix least-squares refinement have been referenced before;[4] the scattering factors employed included the real and imaginary parts of anomalous dispersion.

Table II. Atomic Coordinates for $Sc_7I_{12}C$ and $Sc_7Br_{12}C$

atom	*x*	*y*	*z*	B_{iso}, $Å^2$
I(1)	0.0773 (2)	0.3065 (2)	0.0008 (3)	1.87 (4)
I(2)	0.1759 (1)	0.051 (2)	0.66735[a]	1.78 (4)
I(3)	0.3063 (2)	0.2269 (2)	0.0034 (3)	2.00 (4)
I(4)	0.1339 (2)	0.1888 (1)	0.3317 (1)	1.65 (3)
Sc(1)	0	0	0.4752 (7)	2.2 (1)
Sc(2)	0.1045 (3)	0.1462 (3)	0.8708 (6)	1.6 (1)
Sc(3)	0.1419 (3)	0.0406 (3)	0.1374 (6)	1.58 (9)
C	0	0	−0.004[b]	1.7 (7)
Br(1)	0.0772 (3)	0.3088 (3)	0[a]	2.24 (8)
Br(2)	0.1764 (2)	0.0495 (2)	0.6668 (5)	1.88 (7)
Br(3)	0.3100 (3)	0.2276 (2)	0.0062 (3)	1.20 (6)
Br(4)	0.1336 (2)	0.1882 (2)	0.3344 (5)	1.56 (7)
Sc(1)	0	0	0.477 (1)	1.7 (1)
Sc(2)	0.1124 (3)	0.1566 (3)	0.865 (1)	1.6 (1)
Sc(3)	0.1518 (3)	0.0425 (3)	0.149 (1)	1.2 (1)
C	0	0	0.003[b]	1.2 (5)

[a] Fixed coordinate. [b] Coordinate deduced from very fine ΔF map and held constant (see text).

Initial attempts to solve the iodide structure suggested the compound was isotypic with the previously reported $Sc_7Cl_{12}X$ (X = B, N, ?), space group $R\bar{3}$.[8,9] However, a difference map synthesized after the iodine and scandium atoms had been refined anisotropically (and a secondary extinction correction included) suggested a dicarbon unit was centered in the cluster. Conventional refinement with anisotropic thermal parameters for the iodine and scandium atoms and variation of the multiplicity of carbon (B = 1.5 $Å^2$) gave R = 0.095, R_w = 0.103, and GOF = 2.41 (684 reflections; 33 parameters). An acceptable refinement could be obtained if the data were modified by exclusion of 318 weak reflections (R = 0.035, R_w = 0.050, GOF = 1.57, carbon occupancy ~0.7). Although this was an invalid and quite drastic manipulation of the data, similar refinement results could have been obtained by collecting data with a fast scan, by skipping weaker reflections, or by use of a too small crystal. In fact, the first data set was collected with a too small crystal, and this yielded acceptable refinement indices and suggested a dicarbon unit. However, the results had other problems. First, the isolated metal atom exhibited an unusually elongated thermal ellipsoid (B_{33}/B_{11} = 26), although such has nearly always been observed to some degree in other examples of the M_7X_{12} structure.[8,9,15,16] Second, although the final difference map showed no residual electron density greater than 0.7 e/$Å^3$, a Fourier synthesis electron density map showed a peak at the midpoint of the dicarbon unit that was greater than that for the isolated Sc. Attempts to refine a single carbon at the former instead (a fixed B was necessary) produced a small negative occupancy. Third, the occupancy and temperature factors of the isolated scandium atom could not be refined simultaneously.

Laue symmetry $\bar{3}$ seemed clearly indicated by averaging of equivalent reflections while $\bar{3}m$ symmetry gave R_{av} = 0.120. Because of the above problems, a search for higher Laue symmetry was made with a precession camera, but none could be found. This left *R*3 as the only other possible space group even though this had previously been unsuccessfully applied to the isostructural $Sc_7Cl_{12}Z$ (Z unknown).[17]

The initial refinement of the structure in the acentric space group *R*3 gave spectacular results relative to the centric result. Consequently, the data were rereduced to conform to the lower symmetry. Refinement without any carbon atom gave R = 0.050 and R_w = 0.056. A difference map with fine divisions synthesized at this point clearly revealed only one carbon at 0, 0, −0.004 (2) with no indication of a dicarbon moiety. However, refinement of the coordinates and thermal parameters of all atoms gave an unreasonable *z* coordinate for the carbon, and half of the Sc–C distances were too short, the *z* coordinate of the carbon effectively being $^1/_2 + z$ (Sc(1)). The thermal parameter of carbon was also too small. These effects seemed to be artifacts of the least-squares process. Subsequently, the *z* coordinate of the carbon was fixed at −0.004, the value determined from the difference map. The refinement quickly converged to the results given in Tables I and II; the largest shift/error was 0.01. Refinement of the other enantiomorph gave slightly poorer results, R = 0.046 and R_w = 0.049, and the thermal parameters were not as close to spherical. Therefore, the coordinates in Table II were concluded to apply to the enantiomorph studied. Refinement of a secondary extinction parameter was important, as with other well-crystallized cluster iodide carbides.[6]

Some other features of the acentric refinement are worth mentioning. The coordintes and anisotropic thermal parameters of the iodine and scandium atoms, the isotropic thermal parameter of the carbon, and the occupancies of both scandium 1 and the carbon could readily be refined simultaneously with rapid convergence. The occupancies of Sc(1) (0.98 (2)) and C (1.29 (10)) were within 3σ of unity and were subsequently fixed at 1.0. Attempts to refine the carbon anisotropically gave a slow divergence, but it could not even be refined isotropically in the centric version. The relative heights of the observed peaks at atomic sites in an electron density map with a very fine scale were in excellent ($\pm$<5%) agreement with the relative atomic numbers (these were in far poorer agreement in the centric case), and most importantly, the electron density and difference maps showed no unusual features. Atomic coordinates from least-squares refinement agreed with peak positions in the electron density map to within the uncertainty with which the latter could be estimated (equivalent to ~0.02 Å), suggesting a highly similar superstructure or an incommensurate structure was not present since either of these might be expected to produce either asymmetric or displaced peaks relative to the least-squares coordinates or distorted thermal ellipsoids. A difference map was featureless with the largest peak of ~0.4 e/$Å^3$ about 1.3 Å from an iodine.

The absence of a complex twinning system for the iodide carbide was also established by both precession measurements and axial photographs taken on the diffractometer while the successful acentric refinement ensured that the crystal did not consist simply of ordered domains with

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opposed c^* axes. Some crystals did show some evidence of twinning, however, with extra spots at nonintegral spacings on axial photographs. The crystals were well faceted and single by optical examination.

Although all the $Sc_7B_{12}C$ specimens had prominent faces, the first three crystals examined were internally twinned. The data crystal showed no unusual features in axial (Polaroid) photographs. Triplicate data were collected (Table I) and reduced as described for the iodide.

Coordinates used initially for the metal and bromine atoms were those of the $Sc_7I_{12}C$ structure. Isotropic refinement (including an extinction parameter) gave $R = 0.047$ and $R_w = 0.050$. After anisotropic refinement of these atoms, a very fine ΔF map revealed a single carbon within the cluster. It was introduced with a fixed thermal parameter and the z coordinate refined. The refinement slowly diverged when both the thermal parameters and z coordinate were varied (along with all parameters for the other atoms). Subsequently, the latter parameter was fixed to place the carbon equidistant from the scandium atoms, and the carbon was refined anisotropically. Simultaneous refinement of the occupancy gave 0.89 (7), which was subsequently fixed at 1.0. The larger absorption coefficient for bromine affected the precision achieved appreciably, particularly in z coordintes. The other enantiomorph gave insignificantly different refinement indicators but did give convergence problems. The final coordinates given in Table II have been inverted from those refined so that these may be compared with data for the iodide.

Results and Discussion

Syntheses. The $Sc_7I_{12}C$ phase may be readily produced by reactions of excess metal strips with stoichiometric amounts of ScI_3 and graphite. The lower limit for formation is ~650 °C, below which the surface of the scandium becomes blocked by $ScI_{2.2}$ and only small amounts of $Sc_7I_{12}C$ form thereon. At 950 °C, the major product is ScI_x with only a trace of $Sc_7I_{12}C$. Most reactions were run at 850 °C, and for the following discussion, this temperature will be assumed unless specified otherwise.

With a moderate excess of either ScI_3 or graphite, $Sc_7I_{12}C$ is the major product as long as excess metal is present. Nearby stoichiometric quantities of all three reactants also give slightly reduced (darkened) ScI_3 and an as-yet-unidentified ternary carbide phase poorer in iodine. Unit cell parameters for $Sc_7I_{12}C$ obtained from Guinier powder data for limiting reactions with excess metal, one with a slight excess of ScI_3 and the other with an excess of graphite and both quenched, were statistically indistinguishable. In the former, $ScI_{2.2}$ was the only other product, while in the latter a trace of the above unknown phase remained intermingled with the $Sc_7I_{12}C$. The former is the preferred synthetic route for $Sc_7I_{12}C$ since $ScI_{2.2}$ forms a crystalline blue-black mass or large crystals that are easily distinguished and separated from the loose, dark purple $Sc_7I_{12}C$. Reactions in which all the metal is consumed yield other carbide compounds, for example, Sc_2I_3C and $Sc_6I_{11}C_2$.[13] It appears that $Sc_7I_{12}C$ has the smallest C:Sc ratio of any phases in the Sc/ScI_3/C system.

The above crystallographic results clearly favor the $Sc_7I_{12}C$ formulation of the new phase and leave only a small ambiguity regarding the composition. However, carbon is a poor X-ray scatterer, especially when compared with iodine, and this is exacerbated in the present case by the low atomic fraction of the light atom. The centric refinement (which gave a formula $Sc_7I_{12}C_2$) was far poorer than that for acentric $Sc_7I_{12}C$. The synthetic experiments corroborate the choice of the formula $Sc_7I_{12}C$ since reaction of stoichiometric ScI_3:C ratios with excess metal give $Sc_7I_{12}C$ in essentially quantitative yield, while those loaded to give the dicarbide formulation give the same product as well as other phases. Even so, the 430 mg:3.0 mg ratio weighed for ScI_3:C was probably known to no better than ±20%. Therefore, a combustion analysis for carbon was also performed on mechanically separated single crystals, and thrice-sublimed ScI_3 was also analyzed to check both the technique and the possibility of adventitious carbon. The latter yielded 0.00% carbon while the $Sc_7I_{12}C$ sample contained 0.59 wt % C vs. 0.65% in theory. Thus, all three techniques are in agreement with the $Sc_7I_{12}C$ formulation.

Reactions of excess Sc strips, boron, and ScI_3 in slight excess produce the isomorphous, purplish $Sc_7I_{12}B$ in quantitative yield based on boron. The side product is again $ScI_{2.2}$. The lattice parameters based on 25 lines in the Guinier powder pattern are $a = 14.7341$ (8) Å, $c = 9.9198$ (7) Å, and $V = 1865.0$ (2) Å^3.

Table III. Interatomic Distances in $Sc_7X_{12}C$ Structures (Å)

	I	Br
Sc(1)–Sc(2)	4.342 (8)	4.05 (1)
Sc(1)–Sc(3)	3.812 (8)	3.54 (1)
Sc(1)–X(4)	2.851 (4)	2.635 (3)
Sc(1)–X(2)	2.983 (5)	2.769 (8)
Sc(2)–Sc(2′)[a]	3.324 (6)	3.301 (7)
Sc(2)–Sc(3)	3.235 (7)	3.21 (1)
Sc(2)–Sc(3′)	3.237 (7)	3.22 (1)
Sc(2)–X(1)	2.884 (5)	2.657 (7)
Sc(2)–X(2)	2.920 (5)	2.735 (8)
Sc(2)–X(2′)	2.940 (5)	2.739 (8)
Sc(2)–X(3)	2.901 (5)	2.695 (7)
Sc(2)–X(3′)[b]	3.427 (5)	2.998 (7)
Sc(2)–C[c]	2.32	2.28
Sc(3)–Sc(3′)	3.226 (6)	3.203 (6)
Sc(3)–X(1)	2.950 (5)	2.735 (6)
Sc(3)–X(3)	2.913 (5)	2.700 (6)
Sc(3)–X(4′)	2.933 (5)	2.694 (7)
Sc(3)–X(4)	2.948 (5)	2.723 (7)
Sc(3)–X(1″)[b]	3.456 (5)	3.026 (6)
Sc(3)–C[c]	2.28 (4)	2.28
X(1)–X(4)[d]	3.969 (3)	3.682 (3)
X(3)–X(4)	3.972 (3)	3.723 (5)
X(1)–X(2)	4.059 (3)	3.780 (5)
X(3)–X(2)	4.044 (3)	3.782 (4)
X(2)–X(4)	4.083 (2)	3.791 (6)
X(2)–X(4′)	4.080 (2)	3.769 (6)
X(2)–X(2′)	3.993 (3)	3.719 (5)
X(4)–X(4′)[d]	4.289 (3)	3.958 (5)

[a] Primed atom is related to labeled atom by C_3 operation. [b] Terminal or exo Sc–X distance. [c] Carbon position fixed; $\sigma = 0.04$ was obtained from a coupled refinement of iodide when z(carbon) was allowed to vary. [d] These halogen–halogen distances are the minimum and maximum nearest-neighbor values.

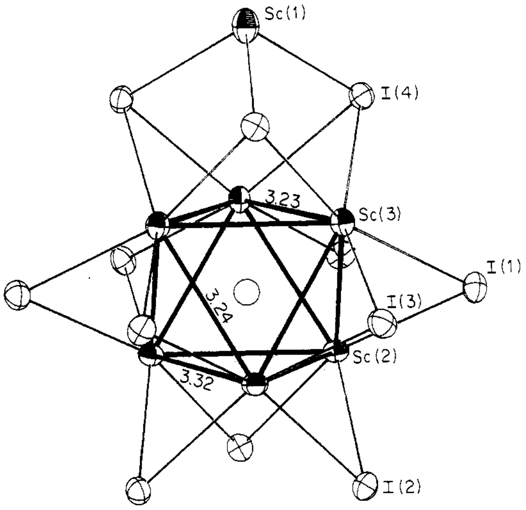

Figure 1. Structure of the independent unit in acentric $Sc(Sc_6I_{12}C)$ (space group $R3$, $R = 0.045$, 50% probability thermal ellipsoids).

Structures. The crystallographic and structural data for the carbides are summarized in Tables I and II, and important bond lengths for $Sc_7I_{12}C$ and $Sc_7Br_{12}C$ are given in Table III. An ORTEP drawing of the acentric $Sc_7I_{12}C$ unit is shown in Figure 1. Anisotropic thermal parameters and angular data are in the supplementary material.

The structure of $Sc_7X_{12}Z$ (X = Cl, Br, I; Z = B, C, N[9]) is closely related to that of $Zr_6I_{12}C$, which has been discussed previously.[6,18] In brief, both consist of cubic-close-packed halogen layers normal to c (hexagonal setting). In every third layer along 0, 0, z one halogen is replaced by a M_6Z cluster, the center of which is taken to be the origin. Halogen atoms bridge all edges of the clusters, and the lateral arrangement of these cluster units generates a R-centered lattice. In the present structure the seventh,

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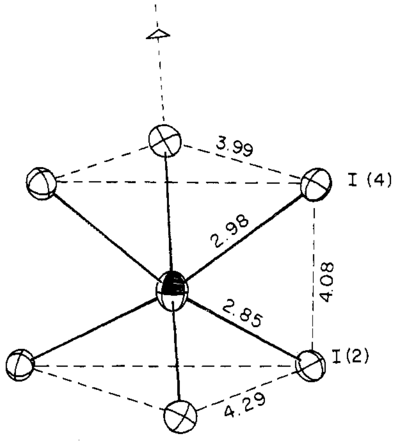

Figure 2. Local environment about the isolated Sc(1) atom in Sc(Sc$_6$I$_{12}$C).

isolated scandium lies approximately halfway between the clusters along *c* (0, 0, ~0.5), within but not always centered in a halogen polyhedron. (The Sc(1) atom in Figure 1 repeats at the bottom of the cluster.) As shown, the six halogens (I(2), I(4)) that form this approximate trigonal antiprism only bridge the edges of a cluster. The six halogens about the waist of the cluster (I(1), I(3), $z \sim 0$) are also more distantly bonded (by ~0.5 Å) to the metal vertices of other metal clusters, and waist halogen atoms in those other clusters are likewise terminal to the cluster of Figure 1 (not shown). Thus, there are discrete but interconnected 6–12 type clusters in the phase.

The Sc–C distances at 2.28 Å are slightly less than the average in Sc$_7$Cl$_{10}$C$_2$, 2.31 Å,[4] in a phase that contains double chains of condensed Sc$_6$Cl$_{12}$-type clusters; the same 2.310 Å is the average of the Sc–Z separations in Sc$_7$Cl$_{12}$B and Sc$_7$Cl$_{12}$N.[9] The most unusual feature of the present structure is the substantial displacement of the isolated Sc(1) atom from the center of the surrounding iodine or bromine polyhedron site (0, 0, $^1/_2$). This is accompanied by a relaxation of the surrounding halogen polyhedron, as shown in Figure 2, and a distortion of the Sc$_6$ antiprism of the cluster, Figure 1. Thus, the edges of one triangular face in the former, I(4)–I(4), lengthen to 4.289 (3) Å, presumarly to accommodate the approaching Sc(1) atom, while the I(2)–I(2) separation on the backside decreases somewhat to 3.993 (3) Å. The former expansion also generates the shortest I–I distances in the structure between I(4) and the waist I(1) and I(3) atoms, 3.97 Å. Within each iodine layer, the atoms about the waist of the cluster, I(1) and I(3), remain essentially fixed in going from $R\bar{3}$ to $R3$. At the same time, the equilateral triangles formed by I(2) and I(4) atoms, each of which have three of the other kind as nearest neighbors, behave in a cooperative manner, alternately expanding and, to a lesser degree, contracting.

The cluster also follows the Sc(1) displacement, the edges of the nearer triangular face (the top in Figure 1) at 3.23 Å being closer to the intertriangle (waist) separations while the edges of the more distant (lower) face of the metal "octahedron" are fully 0.10 (1) Å larger. (The average distance in Sc$_7$Cl$_{12}$(B, N) is 3.267 Å.[9]) Even so, the distance between Sc(1) and Sc(3) in the closer cluster face is a full 0.56 Å greater than the average within the cluster, hardly representative of a significant metal–metal interaction (the bond order is 0.03 (×3)). The iodines largely follow the cluster distortion, and changes accompanying the Sc(1) relaxation are only angular. In other words, the Sc(2,3)–I(2,4) distances are all nearly the same (2.93–2.94 Å) even though these iodines are both members of the distorted polyhedron about the isolated metal atom. The atoms in the enlarged Sc(2) triangle have slightly smaller (2.89 Å average) distances to the waist iodine atoms, while those in the smaller Sc(3) face have what appear to be normal (2.93 ± 0.02 Å) Sc–I separations. Terminal iodine distances similarly reflect the cluster distortion (3.43 and 3.46 Å, respectively).

The displacement of Sc(1) from its ideal trigonal-prismatic configuration in both the iodide and bromide carbides would appear to be the consequence of its presence in an oversized and polarizable cavity defined by the interlinked Sc$_6$X$_{12}$C clusters. The sizeable distortions of the opposite faces of the iodine "antiprism" about it appear to be limited by I(2)–I(2) contacts for the smaller face and I(4)–I(1) for the larger. Even so, the Sc(1) is still 0.13 Å closer to the large triangle of iodines (2.85 Å) and in poor contact with the more distant group (2.98 Å). The distortion of the faces of the metal cluster in the opposite direction that accompanies this displacement of the isolated metal atom is harder to understand, but it may reflect electronic polarization of the cluster by the approaching cation or, alternatively, a different matrix effect (below).

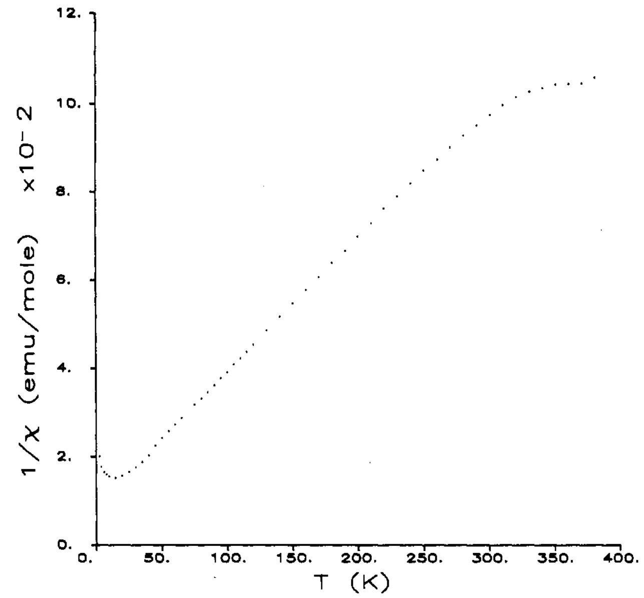

Figure 3. Reciprocal of the molar magnetic susceptibility of Sc$_7$I$_{12}$C vs. absolute temperature.

The distances and distortions observed in Sc(Sc$_6$Br$_{12}$C) parallel those discussed for the iodide in virtually quantitative detail.

Other Properties. The electronic structure of the cluster as observed in Sc$_7$I$_{12}$C was examined by extended Hückel calculations on the cluster unit plus the six terminal iodines. Similar analyses for Zr$_6$I$_{12}$C and Sc$_7$Cl$_{12}$N have recently been oompleted,[6,9] and so only the salient points will be discussed here. Of course, the metal–carbon bonding orbitals designated in O_h symmetry as t_{1u} and the cluster bonding t_{2g} are now split into a and e levels. However, the distortion-generated splittings are all <0.02 eV. As might be expected, the metal-based t_{2g} levels are relatively insensitive to size or shape of the cluster while those important in Sc–C bonding are very sensitive to distance. Assuming the isolated atom is scandium(III), there are 13 cluster-based electrons [7 × 3 (Sc) − 12 × 1 (I) + 4 (C)] and the highest lying group would be derived from t_{2g}^5.

A magnetic susceptibility study confirms the expected parameters and the assignment. A plot of χ^{-1}(cor) vs. T is shown in Figure 3. A least-squares fit of the linear portion to Curie–Weiss law gives $\mu = 1.7\ \mu_B$ ($\theta = -36$ K), in good agreement with theory. The material is EPR-silent at 4 K, as observed also for CsZr$_6$I$_{14}$C.[18] The material seems to undergo an antiferromagnetic transition at ~15 K and shows a deviation from Curie–Weiss behavior about ~300 K, possibly because of thermal population of neighboring levels.

One of the more surprising features of the structural results is the size of the cluster. The average Sc–Sc cluster distance in Sc$_7$Cl$_{12}$B (12 cluster-based electrons) is 3.287 (1) Å, while that in Sc$_7$Cl$_{12}$N (14 e) is 3.246 (1) Å, with both clusters showing a slight (<0.02 Å) compression along the $\bar{3}$ axis.[9] The average Sc–Sc distances in Sc$_7$I$_{12}$C and Sc$_7$Br$_{12}$C (13 e) are very similar, 3.256 (7) and 3.23 (1) Å, respectively. The anion matrices in the latter evidently have the expected effect on the size of the cluster although it is quite small. On the other hand, the 0.04 Å *larger* average Sc–Sc distance in the undistorted chloride boride and nitride phases relative to bromide carbide is unusual. We hypothesize that the distortions in the bromide and iodide represent a means of avoiding a substantial matrix effect[19] and achieving short, strong Sc–C bonds that are about 0.03 Å less than the average in $Sc_7Cl_{12}B$ and $Sc_7Cl_{12}N$.

A number of $M_7X_{12}(Z)$ compounds have been prepared over the years. In addition to the scandium chlorides $Sc_7Cl_{12}(B, N)$, several lanthanide iodides R_7I_{12} have been obtained (R = La–Pr, Gd, Tb, Er, Lu), and three (La, Tb, Er) have been structurally refined in space group $R\bar{3}$.[15,20] None of the lanthanide compounds was recognized as containing an interstitial atom but all gave typical problems associated with a missed interstitial in the form of residual electron density in the center of the clusters, sometimes quite large. Elongated ellipsoids ($B_{33}/B_{11} = 6.5–9$) for the isolated metal atom were again found for the lanthanum and gadolinium examples (but just the opposite for erbium), and the crystals also showed evidence of twinning or disorder. Polydomain twins have also been seen for Sm_7I_{12}.[21]

The above iodides may be less distorted and insufficiently acentric to be refined. We have been unable to refine the data for $Sc_7Cl_{12}(B, N)$[9] in space group $R3$, which gave the correlation problems encountered when a pseudocentric structure is refined by least squares. On the other hand, these structures gave reasonable residuals when refined centrically and only moderate elongation of the Sc(1) thermal ellipsoids (B_{33}/B_{11} = 3.7, 7.5) so that a regular deviation from centricity, if any, is probably small. The analogue without an isolated cation, $Zr_6I_{12}C$,[6] shows none of these problems.

Some of the twinning and disorder problems with the above lanthanide M_7I_{12} phases may originate with the preparation method as all were obtained from melts. There is also the possibility that the twinning results during the descent from a high-symmetry supergroup, a disordered cubic structure in $I23$, for example. The fact that all of the $Sc_7X_{12}Z$ phases we have studied were grown by vapor-phase transport may be important in obtaining better crystals with fewer problems. Of course, different and unknown interstitials may also be responsible in the former cases.

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Registry No. $Sc_7I_{12}C$, 103437-35-0; $Sc_7Br_{12}C$, 103368-85-0; $Sc_7I_{12}B$, 103368-86-1.

Supplementary Material Available: Tables of anisotropic thermal parameters, angles, and the EHMO parameters used (3 pages). Ordering information is given on any current masthead page.

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Photoelectrochemistry of Dianionic Maleonitriledithiolate Complexes of Nickel and Platinum in Ion-Exchange Films on Transparent Tin Oxide Electrodes

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The water-insoluble compounds of the dianionic bis(maleonitriledithiolate) complexes of Ni and Pt were ion-exchanged into films of quaternized poly(vinylpyridine) that had been deposited onto transparent tin oxide electrodes. The electrochemistry of these films in contact with aqueous electrolyte is analogous to that of the anions in acetonitrile solution. On irradiation with visible light, photocurrents are observed that are larger than the currents for the corresponding complexes in acetonitrile solution. The Pt complex, after irradiation, catalyzes the cathodic solvent wave. Recrystallization of the oxidized monoanionic complex occurs in the film so that its behavior is not stable in time. The rates of processes and currents in the film tend to be sensitive to anions from the supporting electrolyte.

Introduction

The square-planar complexes of the formula $M(mnt)_2^{n-}$ where M is Ni, Pd, Pt, or Cu, mnt is the maleonitriledithiolate ligand, $(CN)_2C_2S_2^{2-}$, and *n* ranges from 0 to 3, are of interest for photoelectrochemistry for several reasons. First, they exhibit absorption with charge-transfer character in the visible spectral region. Second, they have several available oxidation states in an interesting potential range. Third, their structures are very similar in the various oxidation states, which should favor rapid, facile electron transfers with minimal inner-sphere reorganization barriers. We have reported some solution photoelectrochemistry of these complexes.[1] The study was limited by two factors. One is that the complexes are insoluble in water so that the homogeneous photoelectrochemistry was limited to organic solvents. (We used acetonitrile.) The other is that the lifetime of states found to be active following excitation in the visible region appeared to be rather short.

There is reason to believe that mounting of these chromophores in a polymer film on an electrode can mitigate both problems. The film may be utilized in contact with an aqueous electrolyte, and in this context, the insolubility of the complexes in water may be advantageous in preventing leaching. Also, a complex localized on a binding site in a film may acquire a longer lifetime by way of reduction of vibrational degrees of freedom, and as well, it may be possible to organize reaction partners in the film so as to utilize short-lived states more effectively. To test these concepts, we have prepared films from poly(vinylpyridine) that has been quaternized by reaction with benzyl chloride to produce a cationic polyelectrolyte. These films can incorporate the dianionic mnt complexes from acetonitrile solution to occupy up to 30% of the ion-exchange capacity of the film. We report some electrochemistry and photoelectrochemistry of such films doped with $Ni(mnt)_2^{2-}$ and $Pt(mnt)_2^{2-}$. The films are mounted on transparent tin oxide electrodes so that the films may be efficiently irradiated.

Experimental Section

Materials. The complexes were prepared and characterized as described in ref 1. Electrode materials are also described in ref 1. Poly(4-vinylpyridine-10%-*co*-styrene) was obtained from Aldrich Chemical Co. Dichlorodimethylsilane was purchased from Petrach Systems, Inc.

Poly(4-vinylpyridine-10%-*co*-styrene) (PVP) was quaternized with benzyl chloride from Fisher. A 2.5-g sample of PVP estimated to contain approximately 0.02 mol of vinylpyridine units was dissolved in 150 mL of spectrograde methanol in a three-neck flask fitted with a condenser and a gas bubbler. The solution was deaerated with N_2, and 12 mL (0.1 mol) of reagent grade benzyl chloride was added to the solution, which was heated to 60 °C. The pressure in the flask was then lowered and the temperature reduced to 55 °C. The sample was maintained at this

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