tetrabromocuprate(II) appears at ~3000 (s, b) cm^{-1}. This indicates that the presence of hydrogen bonding in the former complexes is stronger than in the latter, as electron density is removed from N—H···X interaction and into the Cu–X bond, and as in all trihalo complexes the NH_2^+ bands appear to be shifted by the same amount, the same hydrogen bonding strength may also be suggested.

As a consequence, hydrogen bonding interactions may be considered to be one of the principal factors responsible for the stereochemistry of our trihalocuprates(II), but the size effect of the cation must also contribute to the reduction of the chlorine–chlorine repulsions. In fact when the dimension and hydrogen bonding ability of the cation are negligible, as in the case of the piperidinium cation,[27] CuX_4^{2-} anions were obtained having "flattened" tetrahedral geometries, while when the hydrogen bonding ability of the cation prevails on its size effect, as in the case of the *N*-phenylpiperazinium dication,[8]

$CuCl_4^{2-}$ ion was obtained having strongly distorted tetrahedral symmetry.

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Study of the Crystal Structures and Nonstoichiometry in the System Cs₃Sc₂Cl₉–CsScCl₃

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The phase Cs$_3$Sc$_2$Cl$_9$ has the Cs$_3$Tl$_2$Cl$_9$ type structure ($R\bar{3}c$, a = 12.707 (2) Å, c = 18.117 (4) Å) rather than the chromium(III) structure type common to the remainder of the 3d elements. The ^{45}Sc NMR spectra of ScCl$_3$ and of Cs$_3$Sc$_2$Cl$_9$, which has been slowly cooled in comparison with that quenched from the melt and annealed, establish that the ternary compound melts somewhat incongruently. Reduction of the scandium(III) phase at elevated temperatures by metal gives CsScCl$_3$ which has the CsNiCl$_3$ structure (hexagonal perovskite, $P6_3/mmc$, a = 7.350 (2) Å, c = 6.045 (3) Å). The close relationship between the two structures, strings of scandium pairs alternating with vacancies in Cs$_3$Sc$_2$Cl$_9$ and fully occupied strings of metal in the reduced limit, allows for an apparent region of nonstoichiometry between the two without X-ray evidence for superstructure ordering of vacancies. Values of R = 0.055 and R_w = 0.064 were obtained by least-squares refinement of 108 independent reflections from a single crystal with a refined average scandium occupancy of 0.79 (3). Limited refinement of $\bar{3}m$-symmetry diffraction data from the same crystal reveals that the scandium atoms are probably unevenly distributed, namely, as fully occupied pairs with random fractional occupancy of the third site. Precise Guinier powder diffraction data suggest that all scandium sites become crystallographically equivalent above about 87–90% average occupancy. The blue CsScCl$_3$ is probably a semiconductor rather than a metallic compound.

Introduction

As a class, ternary phases with the simple formula A$_x$B$_y$X$_{3x}$ include hundreds of compounds related by very useful structural concepts.[2] In particular, the compounds in which A is a large cation, B a transition-metal cation, and X halide or chalcide crystallize in the perovskite or a related structure. Here the large A cations together with the X atoms form close-packed layers in which A atoms are surrounded only by X atoms, and these layers are superimposed so as to generate X$_6$ octahedral sites for the B cation without bringing A cations into direct contact. When A is an alkali metal cation, X a halogen, and B a transition metal in the 2+ oxidation state, the composition is ABX$_3$ and all octahedra are filled. In a similar way the composition A$_3$B$_2$X$_9$ has two-thirds of the octahedral sites filled with B cations which carry a 3+ charge.

Scandium chemistry has traditionally been limited to the 3+ oxidation state, particularly in oxides where attempts to produce new reduced phases have all proven fruitless.[3] Accordingly halometalate(II) compounds ABX$_3$ with perovskite-related structures have been known for all first-row transition metals except scandium.[4-6] However, routes to a variety of reduced scandium chlorides have recently been found,[7] and the thought of an additional stabilization of the close-packed A + 3X layers combined with the possibility of enhanced metal–metal interactions because of a relatively large radial

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extension expected for scandium(II) led us to investigate the ternary $CsCl-ScCl_3-Sc$ system, particularly the region $Cs_3Sc_{2+x}Cl_9$, $0 \leq x \leq 1.0$. Although a simple high-temperature reaction between CsCl(s) and $ScCl_2$(s) cannot be used to synthesize $CsScCl_3$ because of the apparent nonexistence of $ScCl_2$,[7] either more reduced scandium chlorides (Cl:Sc < 2.0) or scandium metal can be used as the reductant. The scandium(III) end member $Cs_3Sc_2Cl_9$ has been identified before and assumed[8] to be isostructural with the series $Cs_3M_2Cl_9$, M = Ti, V, and Cr,[9] rather than with the longer known thallium(III) type.[10,11] In fact the present study shows that the latter arrangement is instead the correct one. The existence of this particular structure type for scandium now allows for the occurrence of an unusual example of nonstoichiometry, apparently a continuous compositional and structural transition between the closely related end members $Cs_3Sc_2Cl_9$ and $CsScCl_3$.

Experimental Section

Materials. Baker grade 99.9% CsCl was dried under vacuum at 200 °C and then melted. The scandium metal (Ames Laboratory, 99.8 atomic % purity) had individual 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-earth metals and other metals, <1 each. The anhydrous scandium(III) chloride was prepared by reaction of scandium metal and high-purity hydrogen chloride gas and was vacuum sublimed at 650 °C and $<10^{-5}$ torr in a tantalum jacket. The product after sublimation gave Cl:Sc ratios of 2.99 ± 0.01 by wet chemical analytical techniques with typical recoveries >99.5% for both chlorine and metal. All reactions in this study were carried out in tantalum containers which had been sealed by arc welding under helium and which were in turn jacketed in evacuated fused silica containers. Standard vacuum line and drybox techniques were used for storage and manipulation of all starting materials and products.

Preparation of $Cs_3Sc_2Cl_9$. Ground mixtures of 3:2 $CsCl-ScCl_3$ were heated to 700 °C, above the reported melting point,[8] cooled slowly (1.25 °C/h) through the melting transition to 650 °C, and annealed at this temperature for several days. A more satisfactory material was obtained by quenching the homogeneous melt of 3:2 $CsCl-ScCl_3$ from >700 °C to room temperature to give an unsegregated mixture which was then subsequently annealed for 24 h at 650 °C.

Preparation of $CsScCl_3$. The reduction of $Cs_3Sc_2Cl_9$ was accomplished by reaction of a stoichiometric amount of scandium foil or powder above the melting temperature of $Cs_3Sc_2Cl_9$ (695–700 °C) in sealed tantalum tubing. The product is shiny in bulk and blue when ground, in contrast with white $Cs_3Sc_2Cl_9$. The material readily reduces H_2O although its stability in air is relatively good for reduced scandium. The sample from which the crystal for the diffraction study was isolated was an exploratory run in which equimolar amounts of Sc, $ScCl_3$, and CsCl were heated at 690 °C for 17 days and cooled in the furnace.

^{45}Sc NMR. The ^{45}Sc NMR data were obtained as previously described[12] by using a crystal-stabilized radiofrequency source, a conventional crossed-coil NMR probe, and a Torgeson spectrometer.[13] Signal averaging instrumentation has also been described recently.[12] All measurements were made on polycrystalline (powder) samples at temperatures of 77 and 298 K and at resonance frequencies in the range 8–24 MHz, corresponding to magnetic field strengths of approximately 8–23 kOe.

X-ray Data. High-precision powder diffraction data were obtained with an evacuable Model XDC-700 Guinier camera (IRDAB, Stockholm) equipped with a quartz monochromator to provide clean Cu $K\alpha_1$ radiation. NBS Si powder was used as an internal standard for the calculation of all lattice constants. $Cs_3Sc_2Cl_9$ is an extremely hygroscopic material, and in addition the reduced samples are sensitive to oxygen. All samples were mounted between two pieces of cellophane tape in the drybox in order to gain the necessary protection of the
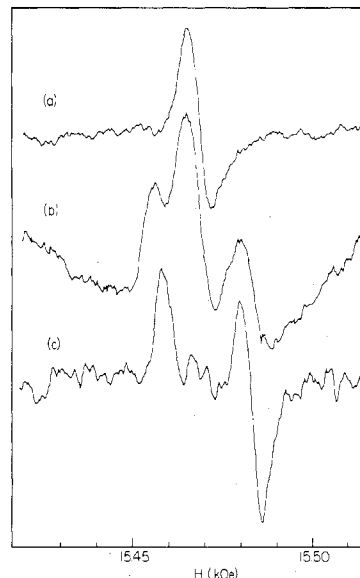
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Figure 1. The central region of the 16 MHz ^{45}Sc NMR spectra of (a) $ScCl_3$ and of $Cs_3Sc_2Cl_9$ which has been (b) slowly cooled from the melt region vs. (c) quenched from the melt and annealed (1.5 and 5.8 Oe modulation used for $ScCl_3$ and $Cs_3Sc_2Cl_9$, respectively).

sample while transferring and mounting it and evacuating the camera (~5 s total).

Single crystals of $CsScCl_3$ were mounted and sealed in 0.2-mm i.d. glass capillaries in an inert-atmosphere box constructed with a nearly horizontal window to facilitate the use of a stereozoom microscope. X-ray data were collected on a four-circle diffractometer[14] at ambient temperature using Mo $K\alpha$ radiation monochromatized with a graphite single crystal (λ 0.709 54 Å). A small crystal fragment reasonably equidimensional (0.075 mm) was chosen to avoid absorption effects. The data were collected on a hexagonal cell for which a = 7.345 (2) Å and c = 6.045 (2) Å were calculated from a least-squares refinement involving 12 reflections ($2\theta > 25°$), each of which was tuned on both Friedel-related peaks. All reflections within a sphere defined by $2\theta < 50°$ in octants HKL and $H\bar{K}L$ were examined. Three standard reflections were monitored every 75 reflections to check for instrument and crystal stability during data collection. No evidence for decay was detected. The 649 pieces of data collected were treated as previously described[15] to yield 513 reflections with $I > 3\sigma(I)$. The data were averaged in Laue $6/mmm$ symmetry with no significant loss of data on the basis of rejection criterion $|F_o - \bar{F}|/\bar{F} \geq 0.20$ to yield 108 unique reflections. Here F_o and $\bar{F}$ represent an individual observation and the average of those observations equivalent by the imposed symmetry, respectively. The systematic absence observed, $h,h,2\bar{h},l$ with $l \neq 2n$, limits the choice of space groups in this Laue group to three: $P6_3mc$ (No. 186), $P\bar{6}2c$ (No. 190), $P6_3/mmc$ (No. 194). The structure was successfully refined in the last, the space group known for $CsNiCl_3$.[4] Programs utilized were as referenced earlier.[7]

Data were also collected from the same crystal for the orientation and the cell corresponding to $Cs_3Sc_2Cl_9$ ($R\bar{3}c$, No. 167) again out to $2\theta < 50°$ in octants HKL and $H\bar{K}L$. These averaged to 264 reflections in Laue group $\bar{3}m$ with $I > 2\sigma(I)$.

Results

$Cs_3Sc_2Cl_9$. According to the phase diagram reported for the binary $ScCl_3-CsCl$ system,[8] the 3:2 compound $Cs_3Sc_2Cl_9$ probably melts incongruently at 691 °C. The ^{45}Sc NMR spectra of various samples have proved to be a sensitive measure of the phase composition of $Cs_3Sc_2Cl_9$ samples and thence of the melting character. Representative spectra for $ScCl_3$ and $Cs_3Sc_2Cl_9$ at 298 K and 16 MHz are shown in Figure 1. Although only the central ($-^1/_2 \leftrightarrow +^1/_2$) transition of each spectrum is included (^{45}Sc has spin $I = {}^7/_2$), additional

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Table I. Guinier Powder Diffraction Data for $Cs_3Sc_2Cl_9$ Compared with Data for $Cs_3Tl_2Cl_9$-Type Structure

hkl	d_{obsd}, g/cm³	d_{calcd}, g/cm³	I_{obsd}[a]	I_{calcd}
012[b,c]	6.990	6.994	w	2.7
110[b]	6.350	6.354	vw	1.4
202[b,c]	4.700	4.703	vw	1.0
113	4.387	4.377	s	43.4
104[c]	4.190	4.188	vw	0.8
122[b,c]	3.780	3.780	vw	1.2
300	3.667	3.668	ms	34.0
220	3.180	3.177	mw	12.9
214[b,c]		3.064	vvw	0.7
006	3.019	3.020	m	20.6
312[b,c]		2.892	vvw	0.6
223	2.812	2.812	vs	100.0
116	2.729	2.727	mw	12.1
036	2.332	2.331	mw	5.4
143	2.231	2.231	m	15.7
226	2.189	2.189	m	25.0
330	2.117	2.118	mw	8.0
119[b]		1.919	(Si)	5.4
146	1.880	1.880	mw	8.8
600	1.835	1.834	m	23.5
336[b]		1.734	w	2.7
229	1.700	1.700	m	22.0
253	1.691	1.692	mw	7.6
440[b]		1.588	vw	1.7
066	1.567	1.568	m	18.1

[a] s = strong, m = medium, w = weak, and v = very. [b] Reflections not used in the lattice constant refinement. [c] Only these reflections do not have a counterpart in the hexagonal unit cell of $CsScCl_3$.

measurements made on the sublimed $ScCl_3$ also showed the presence of quadrupolar satellite lines, corresponding to a characteristic quadrupole frequency $\nu_Q = 0.127$ MHz, where ν_Q and the quadrupole coupling constant eQV_{zz} are related by $eQV_{zz} = 14\ h\nu_Q$ for $I = ^7/_2$. The strength of the interaction is insufficient to cause measurable splitting of the central transition in the range of resonance frequencies investigated. The Knight shift (or chemical shift) of this resonance is zero within the experimental uncertainty of an accurate measurement of the line-center position.

The ^{45}Sc quadrupole coupling in $Cs_3Sc_2Cl_9$ is roughly 3.2 times that in $ScCl_3$, as determined both from the splitting of the central transition in Figure 1c and from observation of satellite lines in the full spectrum. At 298 K the characteristic quadrupole frequency is $\nu_Q = 0.408$ MHz. As shown in Figure 1b a superposition of the ^{45}Sc spectra of both $ScCl_3$ and $Cs_3Sc_2Cl_9$ is observed for a sample which has been slowly cooled from the melt, whereas only the $Cs_3Sc_2Cl_9$ spectrum is observed (Figure 1c) when the sample is quenched from the melt and then annealed at 650 °C. This is as expected for an incongruently melting phase. At higher resonance frequencies, the decreased splitting of the $Cs_3Sc_2Cl_9$ resonance causes the left-hand (low field) peak to merge with the $ScCl_3$ resonance, obscuring the resolution of the two spectra. Both samples appeared single phase to X-ray powder diffraction (Guinier) as did the latter sample to DTA (mp 692 ± 3 °C).

As shown in Table I the experimental lattice spacings and intensities for $Cs_3Sc_2Cl_9$ diffraction show very good agreement and no discrepancies when compared with data calculated for the $Cs_3Tl_2Cl_9$ model (space group $R\bar{3}c$).[10,11] The idealized atomic coordinates used to calculate the powder pattern were 18 cesium atoms in the e position with $x \simeq ^2/_3$, 12 scandium atoms in c with $z \simeq ^1/_6$, 18 bridging halogens in e with $x \simeq ^1/_6$, and 36 terminal halogen atoms in the general position f with $x \simeq ^1/_6$, $y \simeq ^1/_2$, and $z \simeq ^1/_4$. Lattice constants of $a = 12.707$ (2) Å and $c = 18.117$ (4) Å (hexagonal axes) were obtained from 16 reflections by least-squares refinement. In contrast, major differences between the observed and calcu-
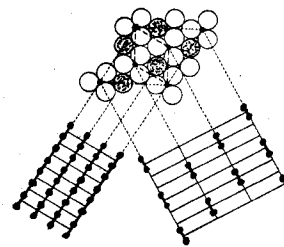

Figure 2. Two perovskite-type structures (after Wells[2]). The top of the figure is close-packed A + 3X layers (A atoms shaded). The bottom of the figure is the ordering of B atoms (solid) in octahedral intersticies: left, ABX_3 (space group $P6_3/mmc$); right, $A_3B_2X_9$ (space group $R\bar{3}c$). The origin in the latter is centered in a vacant octahedron.

lated powder pattern were found on using the $Cs_3Cr_2Cl_9$ model.[9]

There can be absolutely no doubt the A + 3X layers in this phase are stacked in hexagonal ABAB... manner. For later comparisons Figure 2 shows at the top a projection of a close-packed AX_3 layer with the cell outlined and at the right a $(11\bar{2}0)$ view with the occupied B positions, all of which lie in the section shown, marked relative to the AX_3 layers. No displacements from ideal atomic positions were used in the intensity calculations although the scandium(III) ions in the $Sc_2Cl_9^{3-}$ groups doubtlessly repel one another and are displaced outward from the center of the octahedra toward vacancies ($z < ^1/_6$).

$CsScCl_3$. The composition $CsScCl_3$ appears stoichiometric in that the metal added cannot be found or discerned in the Guinier pattern of the powder. Moreover the X-ray powder diffraction patterns of blue $CsScCl_3$ and white $Cs_3Sc_2Cl_9$ are *extremely* similar but with two important differences. First, the powder pattern of $CsScCl_3$ lacks six weak reflections which are observed (Table I) for $Cs_3Sc_2Cl_9$, and, second, the hexagonal cell lattice parameters of $CsScCl_3$, $a = 7.350$ (2) Å and $c = 6.045(3)$ Å, are related to those of the larger hexagonal cell of $Cs_3Sc_2Cl_9$ (which is required by these weak reflections) by factors of $1/3^{1/2}$ and $1/3$, respectively, together with a small expansion. These data are consistent with a $CsScCl_3$ structure containing the A + 3X layers hexagonally close packed as in $Cs_3Sc_2Cl_9$, and the absence of these particular weak reflections (or any new ones) and the unit cell expansion indicate that all scandium B sites in $CsScCl_3$ are now crystallographically equivalent and that no ordered vacancies occur along the columns of face-shared chloride octahedra as they did in $Cs_3Sc_2Cl_9$. Not surprisingly, such a structure corresponds to that of the parent type $CsNiCl_3$ ($P6_3/mmc$).[4] The relationship between the two structures is depicted in Figure 2.

This structure was confirmed in detail by a single-crystal study, which also provided the first evidence for nonstoichiometry. Refinement with Cs and Sc atoms in fixed positions, types d and a, respectively, and Cl in h, that is, x, $\bar{x}$, $^1/_4$ starting with the ideal close-packed value $x = ^1/_6$, proceeded readily to an unweighted residual $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.099$. Variation of only the scale factor and occupation parameters for all atoms at this stage indicated the scandium position was not fully occupied. An electron density map was computed with the observed data and refined positions, and an occupation parameter of 0.82 for scandium was determined by peak integration scaled to that for a chlorine atom. The occupancy of the scandium site was constrained to this value until the final stage. With anisotropic temperature factors for all atoms, three cycles of least-squares refinement gave $R = 0.057$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.065$ with the maximum shift in any variable in the final cycle of less than 1% of its estimated standard deviation. The occupation parameter of scandium was independently varied at
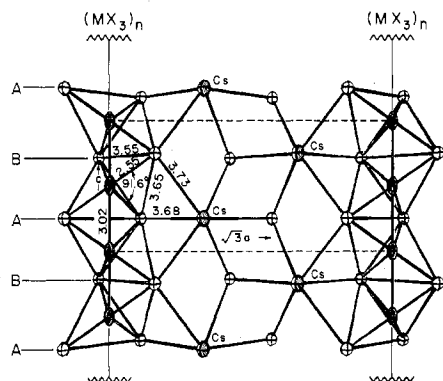
Figure 3. The (11$\bar{2}$0) section of CsScCl$_3$. The scandium occupation parameter is 0.79 (3).

Table II. Positional and Thermal Parameters for CsScCl$_3$[a]

atom	position	x	y	z	β_{11}[b]	β_{33}	β_{12}
Cs	d	$^1/_3$	$^2/_3$	$^3/_4$	174 (5)[c]	298 (9)	87 (3)
Cl	h	0.1611 (3)	−0.1611	$^1/_4$	155 (9)	205 (13)	87 (9)
Sc	a[d]	0.0	0.0	0.0	101 (15)	376 (34)	51 (8)

[a] Space group $P6_3/mmc$. [b] The general form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Restrictions on the thermal parameters are $\beta_{11} = \beta_{22}, \beta_{13} = \beta_{23} = 0$, and, for Cs and Sc, $\beta_{12} = ^1/_2\beta_{11}$. [c] All β's $\times 10^4$. Numbers in parentheses are estimated standard deviations. [d] Occupation parameter = 0.79 (3).

this stage and in two cycles led to a final value of 0.79 (3), with $R = 0.055$ and $R_w = 0.064$. A comparable value of 0.079 for R_w was obtained with the scandium fixed at unit occupancy, a model which can be rejected at the 0.005 significance level.[16]

The final positional and thermal parameters for CsSc$_{0.8}$Cl$_3$ in the $P6_3/mmc$ cell are listed in Table II. Figure 3 is an ORTEP drawing of the (11$\bar{2}$0) section of the cell with the atoms behind the mirror plane included. Some important distances and angles are Sc–Cl = 2.548 (3) Å, Cl–Sc–Cl = 91.60 (8)°, Cs–Cl(intralayer) = 3.6759 (2) Å, Cs–Cl(interlayer) = 3.734 (2) Å, Cl–Cl(shared face) = 3.552 (7) Å, and Cl–Cl(between faces) = 3.654 (2) Å. Final calculated and observed structure factors are available as supplementary material.

An ordering of the vacancies in the particular crystal studied seemed plausible in view of both the close relationship apparent between the CsScCl$_3$ structure and that of Cs$_3$Sc$_2$Cl$_9$ (Figure 2) as well as the observed dependence of lattice constants on composition (below). One particularly obvious mode would be with the dimer groups (see Figure 2) at full occupancy plus the remaining octahedral sites at ca. 40% occupancy. No anomalous diffraction intensity could be detected in 2θ–ω step scans ($\Delta\omega = 0.05°$) over axial and nonaxial directions with the crystal in the above orientation, and no evidence for any of the weak reflections characteristic of the Cs$_3$Sc$_2$Cl$_9$ supercell (Table I) could be found even at the 2$\sigma(I)$ level in the data set collected with the orientation of the larger $R\bar{3}c$ cell. Nonetheless an uneven occupancy of sites at this composition was explicitly indicated by the observed diffraction data for the larger cell. In this case a regular least-squares refinement was, as expected, not possible because of coupling of the shifts in especially the positional parameters of atoms which are identical in the $P6_3/mmc$ cell. But limited, cyclic refinement among the variables of independent chlorine position, the temperature factors, and the occupancy parameters for the scandium atoms was sufficient. With isotropic temperature parameters an initially uniform distribution of scandium atoms
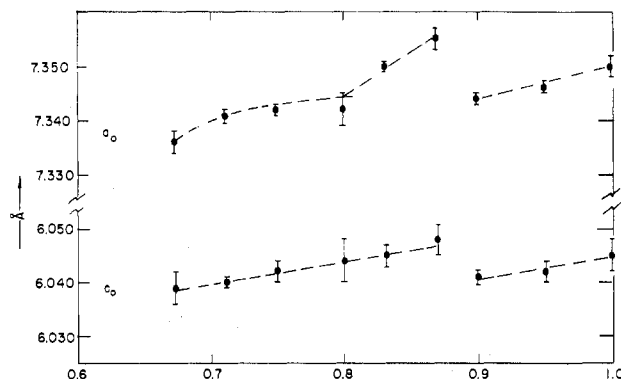
(16) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

Figure 4. Lattice constants for CsSc$_x$Cl$_3$ (0.667 ≤ x ≤ 1.0) samples, calculated on the basis of the $P6_3/mmc$ cell.

Table III. Lattice Constants (Guinier Data) for the CsSc$_x$Cl$_3$ System (0.67 ≤ x ≤ 1.00)[a]

x	a	c
0.667	7.336 (2)	6.039 (3)
0.706	7.340 (1)	6.040 (1)
0.750	7.342 (1)	6.042 (2)
0.800	7.342 (3)	6.044 (4)
0.816	7.350 (1)	6.045 (2)
0.870	7.355 (2)	6.048 (3)
0.900	7.344 (1)	6.041 (1)
0.950	7.346 (1)	6.042 (2)
1.000	7.350 (2)	6.045 (3)

[a] Calculated on the basis of the $P6_3/mmc$ cell.

readily refined to 1.03 (dimer, type c) and 0.26 (at origin, b) occupation parameters ($R = 0.094$, $R_w = 0.111$). Then with fixed unit occupancy of the former and anisotropic thermal parameters for all but the extra scandium atom at the origin the occupancy of the latter alone refined to 0.31 (4) and $R = 0.064$ and $R_w = 0.079$. A uniform distribution with no refinement increases each residual by 0.004. Among the anisotropic temperature parameters (subsets of which did not couple badly), the values of β_{33} for the pairs of scandium atoms and β_{11} (and the related β_{22} and β_{12}) for the chlorine atoms defining the octahedron about the fractional atom at the origin were somewhat ($\sim$30%) larger, consistent with a partial occupancy of that site. The chlorine parameter equivalent to that given in Table II was 0.1593 (9) before oscillation set in. The overall composition found for the $R\bar{3}c$ cell is thus CsSc$_{0.77}$ $_{(2)}$Cl$_3$, in good agreement with CsSc$_{0.79}$ $_{(3)}$Cl$_3$ found for a uniform distribution. Thus although strong coupling of some parameters prevented a conventional least-squares refinement of all variables, an unequal distribution of scandium does seem very likely.

The Homogeneity Range. The obvious implication of the foregoing is that a substantial range of nonstoichiometry connects the end members CsSc$_{0.67}$Cl$_3$, and CsScCl$_3$ more or less continuously, with an implied order–disorder transition in B site occupancy with a change in composition somewhere in the upper part of the range. This indeed appears to be the case to the extent present information defines such subtleties. The blue-gray color is basically unchanged between a reduction of 12%, the smallest amount investigated, and CsScCl$_3$. The weak reflections characteristic of the ordered vacancies in the oxidized limit weaken but persist in the Guinier patterns well into the range, ultimately disappearing beyond CsSc$_{0.8}$Cl$_3$. Actually this point depends somewhat on the history of the sample as do the lattice constants, especially since the overall change in the latter is small.

Figure 4 illustrates the lattice constants listed in Table III for samples which had been held at 695 °C for several hours and then cooled at 1.25 °C/h to 300 °C. The numerical values

were obtained by least-squares refinement of 12–20 indexed reflections on each Guinier film, where each θ value was the average of three to five measurements. For comparison purposes the reflections were all indexed on the smaller $P6_3/mmc$ cell, thus omitting only the weak reflections which require the $R\bar{3}c$ cell of $Cs_3Sc_2Cl_9$. No definite evidence for a two-phase region such as line broadening or splitting was encountered. Although the changes in cell parameters are all small, the internal consistency among the samples is good. The same results ($\pm 1\sigma$) were obtained with $CsSc_{0.8}Cl_3$ and $Cs Sc_{1.0}Cl_3$ samples which had been quenched from 750 °C and annealed 2 days at 650 °C.

The data in the figure together with the earlier single-crystal results are consistent with an initial reduction stage where vacant sites in $Cs_3Sc_2Cl_9$ are statistically occupied up to somewhat over 40% while the dimeric scandium(III) groups originating with the oxidized end member persist. An increase in a just beyond the composition $CsSc_{0.8}Cl_3$, if real, may result from interchain coupling. But the most significant break in the data, especially in a (5σ), occurs at an average scandium occupancy of 0.87–0.9, corresponding to an occupation of the third B site of 60–70% or just above where the weak supercell reflections can no longer be detected. This may well be the point of the implied disorder–order transition where all scandium atoms become crystallographically equivalent on reduction.

The fully reduced compound appears to melt incongruently at 704 ± 3 °C with the production of scandium metal which can be detected in both the Guinier pattern and the NMR spectrum. Some semicrystalline fragments exhibit a moderately low resistance ($\geq$10 Ω by two-probe measurements across small crystalline fragments) while other portions (and compressed powders) exhibit very high resistances (10^3–10^6 Ω). Similarly, the more reduced samples do not charge under irradiation in the XP spectrometer whereas the less reduced ones do. A broad EPR signal observed at room temperature ($g \approx 2.0$) for the reduced samples is presently under further investigation. Thus although quantitative data are not yet available, present evidence suggests that even the fully reduced $CsScCl_3$ is not a metallic conductor, contrary to earlier expectations[17] and in contrast to the behavior of the isostructural $BaVS_3$.[18]

Discussion

Crystal Structure of $Cs_3Sc_2Cl_9$. $Cs_3Sc_2Cl_9$, like $Cs_3Cr_2Cl_9$, contains confacial double chlorine octahedra about the two transition-metal ions, which provides for maximum anion polarization, and both maintain a uniform spatial distribution of these $M_2Cl_9^{3-}$ groups, octahedral B-site vacancies, and cesium ions. But in the scandium salt the A + 3X layers are hcp (alternatively, (h)₆) and all the B sites occur in chains parallel to c with every third site empty (Figure 2), the two atoms of the dimer doubtlessly being displaced outward from one another and toward the vacancy. On the other hand the $Cr_2Cl_9^{3-}$ groups in that system together with the B-site vacancies are distributed in a spatially more uniform manner between A + 3X layers arranged ...ABCACB... or (hcc)₂.

The rhombohedral structure for the thallium and scandium salts clearly provides an energetically feasible alternative to the hexagonal structure of the chromium compound. Some reasons for this difference can be perceived. First, it can be imagined that a higher positive charge on the B atom would occur with the scandium salt, in which case the observed arrangement leaves room for these ions to repel one another

and to move toward the octahedral vacancies along the chains. On the other hand the chromium salt has cesium ions positioned outward along threefold axis from both ends of the confacial double octahedra, resisting separation of the chromium pair therein. This is doubtlessly a more favored arrangement when the B atom carries a lower charge, and a covalent description has in fact been applied to the $Cs_3Cr_2Br_9$ analogue.[19] In addition there is an increasingly close approach of the halogens which comprise the common face of the two shared octahedra as one proceeds from $Cr_2Cl_9^{3-}$ to $Ti_2Cl_9^{3-}$,[20] and one can imagine that this distance could become excessively short were the scandium salt to adopt the same arrangement.

Qualitatively, the substantial increase in the ^{45}Sc quadrupole coupling strength which occurs between $ScCl_3$ (ccp YCl_3 structure[2]) and $Cs_3Sc_2Cl_9$ must be associated with the occurrence of scandium(III) dimers in the latter case. A sensible quantitative comparison of the two compounds would entail an analysis of electric field gradient (EFG) contributions resulting from both point-charge (ionic) and covalent-bonding contributions. However, it is evident even without detailed calculation that the presence of the near-neighbor scandium(III) on the symmetry axis of the EFG tensor (i.e., the crystalline electric field) will contribute much more strongly to the net EFG than will the off-axis chloride and cesium ions.

Crystal Structure of $CsScCl_3$. The refined structural model deduced for $CsScCl_3$, Figure 3, consists of similar A + 3X layers in hcp packing. Here the shared face of the chlorine octahedra is only slightly compressed from the ideal value, with $x_{obsd} = 0.1611$ (3) vs. the ideal coordinate 0.1667. The indices of the set of *observed* reflections are consistent only with a model of high symmetry ($P6_3/mmc$) in which a random distribution of scandium atoms is required on equivalent B sites when the occupancy factor for the B site is less than unity. Notwithstanding, a refined average B-site occupancy of 0.79 (3) is found combined with a noticeable elongation of the thermal ellipsoid parallel to c (Figure 3). Some disorder is doubtlessly responsible, presumably the displacement of scandium atoms when adjacent to a vacancy. However, the *intensities* of the reflections do contain further information regarding the vacancy distribution in the larger $R\bar{3}c$ cell, namely, that the dimers in $Cs_3Sc_2Cl_9$ remain and that the third site only is fractionally occupied (0.31 (4)). Details regarding subtle atom displacements which must occur around this site are obscured by parameter coupling during refinement owing to the higher pseudosymmetry relating different types of scandium and chlorine atoms.

Nonstoichiometry. The occurrence of the scandium(II) and scandium(III) end members of the series in closely related structures (Figure 2) is a fortunate circumstance as far as the existence of a homogeneity range is concerned. The present X-ray evidence suggests that metal addition on reduction of $Cs_3Sc_2Cl_9$ proceeds by fractional occupation of the B-site vacancies in a random way up to about 60–70%, whereupon all B sites become equivalent to X-rays. Though the final answers are not in, available information indicates that the system contains localized and therefore mixed oxidation states, which do not order even in samples which have been very slowly cooled from 695 to 300 °C. This is comparable to the situation found for the presumed tetravalent tantalum compound $BaTaS_3$.[21,22] Careful compositional studies[23] subsequently showed this was the diamagnetic compound $BaTa_{0.8}S_3$

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in which no ordering of the vacancies could be detected. Although the fully oxidized $Cs_3M_2Cl_9$ phases for 3d elements other than scandium have a different structure, it would not be particularly surprising to find that the $CsMCl_3$ salts for at least titanium and vanadium may be significantly substoichiometric on the B sites. Evidence for the presence of voids and mixed oxidation states on the B sites in perovskite-related ABX_3 phases has been obtained by McPherson and co-workers[24] in systems containing small amounts of paramagnetic gadolinium(III) or chromium(III) cations in, for example, a $CsMgCl_3$ host. In this case the trivalent B ions occur in pairs around a cation vacancy, a reasonable situation based on local lattice interactions. At least in the scandium system such effects do not take place with long-range order until somewhat more than 30% of the sites are vacant. Work is continuing by using EPR and NMR techniques as more sensitive probes of short-range order: at the present time NMR data do not appear to provide any particular clarification of the reduction process.

Complete occupation of the octahedral sites at the limiting composition $CsScCl_3$ is achieved in a single-phase product with only small changes in lattice constants. This scandium salt completes the series for dipositive 3d elements, as this structure

is already known for Ni, Co, Fe, V, and Ti and, in distorted form, for Cu, Mn, and Cr.[4,5] The packing of the Cs + 3Cl layers so dominates these structures that the metal–metal distances along the chains parallel to c are all 3.01 or 3.02 Å for elements from Sc through Co while the a parameters show a 1.7% decrease over the same range. The fully reduced $CsScCl_3$ is isoelectronic and isostructural with the sulfide analogue $BaVS_3$,[25] a metallic conductor which has been the subject of recent interest.[18,26]

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Synthesis and Structure of a New Class of Metallophthalocyanines: Carbonyl(phthalocyanato)(pyridine or tetrahydrofuran)ruthenium(II) and Carbonyl(phthalocyanato)(pyridine or tetrahydrofuran)osmium(II)

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During our synthesis of (phthalocyanato)ruthenium(II) and (phthalocyanato)osmium(II) complexes reported by Berizin and Sennikova and by Krueger and Kenny, we observed a remarkable solubility of these complexes in common organic solvents. The solubility of these complexes enabled us to isolate several pure reported and new phthalocyanine complexes. Among the complexes we studied, carbonyl(phthalocyanato)(pyridine)ruthenium(II) [PcRu(CO)(py)], carbonyl-(phthalocyanato)(pyridine)osmium(II) [PcOs(CO)(py)], and carbonyl(phthalocyanato)(tetrahydrofuran)ruthenium(II) [PcRu(CO)(THF)] were isolated in pure form. They are among the first reported metallophthalocyanines with a carbonyl as one of their axial ligands. Furthermore, several new ways of synthesizing these complexes in quantitative yields have been established. The structure of PcOs(CO)(py) is elucidated by the X-ray diffraction analysis. The osmium ion is octahedrally coordinated with the carbonyl and pyridine groups axially coordinated. The pyridine ring is tilted slightly with respect to the perpendicular to the phthalocyanine ring. The interplanar angle is 98.6°. Interesting comparisons may be made between PcOs(CO)(py) and related porphyrin complexes.

Phthalocyanine and metallophthalocyanines demonstrate significant electrical and photo properties,[1,2] e.g., semiconductivity, photoconductivity, photochemical reactivity, luminescence, and fluorescence, which are relevant to the current world problem of conversion and production of energy. The number of publications per year on chemistry of phthalocyanines and metallophthalocyanines has tripled during the past decade. During 1977, nearly 700 papers and patents were published. In spite of the increasing interest in this area and the near completion of the synthesis of all metal ions having the normal classic configuration, basic phthalocyanine chemistry has lacked the advantage of any dynamic or extraordinary

progress. Many metalloporphyrins[3] have been made and studied extensively, and a large body of coordination chemistry of these complexes has been developed, while the coordination chemistry of metallophthalocyanines has been poorly developed. This contrast is mainly due to the significantly lower solubility of metallophthalocyanines and has led to the presumption that the development of coordination chemistry of phthalocyanines is difficult in general.

During our synthesis of (phthalocyanato)ruthenium(II) and (phthalocyanato)osmium(II) complexes reported by Berizin and Sennikova[4,5] and by Krueger and Kenny,[6a] we have found

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