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Reduced Ternary Halides of Scandium: $RbScX_3$ (X = Cl, Br) and $CsScX_3$ (X = Cl, Br, I)

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Reactions of $A_3Sc_2X_9$ (A = Cs, Rb, X = Cl, Br) and of CsI_3 with scandium in tantalum containers at 750 °C give the corresponding $AScX_3$ phases with the $CsNiCl_3$-type structure. A similar phase is obtained for $CsScCl_yBr_{3-y}$, $y = 1, 2$, but attempts to produce $KScX_3$ (X = Cl, Br, I) and $RbScI_3$ and to reduce $Cs_3Y_2Cl_9$ failed. The existence of a homogeneity range in ASc_xCl_3, $0.67 < x < 1.0$, between the end members $A_3Sc_2Cl_9$ ($=ASc_{0.67}Cl_3$, $Cs_3Tl_2Cl_9$-type structure) and $AScCl_3$ with their closely related structures was confirmed for $CsSc_xCl_3$ and established for $RbSc_xCl_3$. A similar range of composition does not occur for $CsSc_xBr_3$ and would not be expected for $CsSc_xI_3$ and $RbSc_xBr_3$ since all three corresponding $A_3Sc_2X_9$ phases have the less favorable $Cs_3Cr_2Cl_9$-type structure. Guinier-based lattice constants are reported for all phases as well as Raman spectra for $CsSc_xCl_3$ samples and XPS core spectra for $CsScX_3$ and $CsSc_xCl_3$ compositions. $CsScCl_3$ shows no phase transitions between −130 and 580 °C. The nonstoichiometry region ASc_xCl_3 (A = Cs, Rb) is thought to arise through filling of vacant metal positions in chains of confacial halide octahedra, with a subtle change in structure near the midpoint ($x \approx 0.87$, for A = Cs).

Introduction

Traditional chemistry of the rare earth element halides has focused on the trivalent state except for a few well-known examples with oxidation states of +2 (e.g., $EuCl_2$, $YbCl_2$, $SmCl_2$, in order of decreasing stability) and +4 (e.g., CeF_4[3]). Modern techniques using fluorine under high pressures have established a series of new ternary fluorides with Pr, Nd, Dy, and Tb in the +4 state.[4] The preparation of reduced rare earth metal halides was for a long time limited by the reducing power of hydrogen at elevated temperatures. It was the use of high-purity rare earth metals as reductants together with the inert container material tantalum that opened a new chemistry for halides of rare earth metals (including scandium).[5,6] The reduced binary systems are, however, not limited to the oxidation state +2, for a still widening series of more reduced chlorides, bromides, and iodides with average oxidation states between the +1 and +2 state also occurs.[7-11] The common structural feature of these compounds is an octahedral metal cluster which is surrounded by halide ions to form M_6X_8 or M_6X_{12} units, respectively. These may be isolated or, more commonly, connected via common metal edges to form chains or layers.

On the other hand, no such cluster units have yet been found in reduced ternary halide chemistry of these elements. Table I gives an overview of these systems. Their chemistry as known seems to involve normal solid-state structure types, most obviously documented by the example of Sm^{2+}, which shows a crystallographic behavior closely related to that of Sr^{2+} and Pb^{2+},[13-15] all of nearly equal ionic radius. So far $CsScCl_3$[12] is the only example in this series for which the related binary halide ($ScCl_2$) is not known. Furthermore, its crystal structure is closely related to that of the oxidized ternary halide $Cs_3Sc_2Cl_9$ ($=CsSc_{0.67}Cl_3$), which differs only in that one-third of the so-called octahedral interstices are now vacant between $CsCl_3$ layers stacked in an ABABAB... sequence. The wide homogeneity range reported for $CsSc_xCl_3$, $0.67 \leq x \leq 1.00$, underlines the close relationship between the two compounds.

$CsScCl_3$ is obtained by reduction of $CsCl/ScCl_3$ mixtures (3:2 molar ratio) or $Cs_3Sc_2Cl_9$[12] with scandium metal in sealed tantalum tubes. Attempts to establish further ternary halides with divalent scandium are reported here.

Experimental Section

$A_3Sc_2X_9$ (A = Rb, Cs; X = Cl, Br). $Rb_3Sc_2Cl_9$, $Cs_3Sc_2Cl_9$, $Rb_3Sc_2Br_9$, and $Cs_3Sc_2Br_9$ used as starting materials for reduction with scandium metal were prepared with the use of a general method described in more detail elsewhere.[16,17] Stoichiometric amounts (A:Sc = 3:2) of AX and Sc_2O_3 (Kristallhandel Kelpin, Leimen/Heidelberg, West Germany) were dissolved in hydrochloric (hydrobromic) acid with heating, the clear solution was evaporated to dryness, and the residue was heated in a dry-HCl (HBr) gas stream for 2 days at 500 °C. Colorless, slightly sintered powders were obtained.

Scandium metal was used as sintered powder. This was obtained by hydrogenation of metal strips (Ames Laboratory, 99.8 atomic % purity) at 800 °C, grinding the ScH_2 in a drybox, and dehydrogenating in a vacuum ($\sim 10^{-5}$ torr) at 800 °C. This and all of the following products were handled only under drybox conditions.

$AScX_3$ (A = Rb, Cs; X = Cl, Br). The enneahalodiscandates(III) $A_3Sc_2X_9$ were reduced with a stoichiometric amount of scandium metal powder in sealed tantalum containers which had in turn been jacketed in silica tubes and sealed under vacuum. A standard temperature of 750 °C was used, far enough above the melting points of $Cs_3Sc_2Cl_9$ (694 °C[18]), $Rb_3Sc_2Cl_9$ (605 °C[19]), $Rb_3Sc_2Br_9$ (640 °C[19]), and $Cs_3Sc_2Br_9$ (728 °C[19]) to ensure fast and complete reduction (2–3 days). The samples were then cooled slowly by turning off the power to the furnace. Attempts to prepare the analogous potassium compounds $KScCl_3$ and $KScBr_3$ under the same conditions failed. When incongruent melting occurs (in the case of the chlorides), equilibration below the peritectic temperature is appropriate.[12] The chlorides and bromides obtained are, respectively, bluish black and a shiny greenish black in bulk and blue and green when ground to powders. The products are free of any ScOX impurity at the visual level (≤1%)

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Table I. Ternary Halides of Scandium and the Lanthanides in the Divalent State

	lattice constants	structure type	d(M-M)/Å	ref
$CsScCl_3$	$a = 7.350, c = 6.045$ Å; $\gamma = 120°$	$CsNiCl_3$	$3.023 = c/2$	12
$CsYbCl_3$	$a = 5.437$ Å	perovskite	$5.437 = a$	13
$CsTmCl_3$	$a = 5.455$ Å		a	13
$CsEuCl_3$	$a = 5.587, c = 5.625$ Å		a	13
$CsSmCl_3$	$a = 5.601, c = 5.640$ Å	$BaTiO_3$-II	a	13
$CsEuBr_3$	$a = 5.844, c = 5.888$ Å		a	14
Cs_2YbCl_4	$a = 5.420, c = 17.257$ Å	K_2NiF_4		14
KSm_2Cl_5	$a = 8.889, b = 7.846, c = 12.63$ Å; $\beta = 90.0°$			15
$RbSm_2Cl_5$	$a = 9.022, b = 7.911, c = 12.68$ Å; $\beta = 90.0°$			15
KSm_2Br_5	$a = 9.298, b = 8.282, c = 13.27$ Å; $\beta = 89.9°$	$TlPb_2Cl_5$		15
$RbSm_2Br_5$	$a = 9.448, b = 8.350, c = 13.27$ Å; $\beta = 90.2°$			15
KSm_2I_5	$a = 9.966, b = 8.913, c = 14.27$ Å; $\beta = 90.2°$			15

as well as to X-rays (≤2%), attesting to the effectiveness of the $A_3Sc_2X_9$ synthetic route. When exposed to air, the powders change colors to white within less than 1 min; water evolves hydrogen. Further reduction of $CsScCl_3$ by excess metal was not obtained. No significant reduction of $Cs_3Y_2Cl_9$ melt with Y metal was observed at 720 °C.

$RbSc_xCl_3$, $CsSc_xCl_3$, and $CsScCl_yBr_{3-y}$. The mixed crystals were obtained as powders in the same manner as described above for $AScX_3$ compounds by reduction of $Rb_3Sc_2Cl_9$ ($=RbSc_{0.67}Cl_3$), $Cs_3Sc_2Cl_9$ ($=CsSc_{0.67}Cl_3$), and mixtures of $Cs_3Sc_2Cl_9$ and $Cs_3Sc_2Br_9$ (1:2 and 2:1 molar ratios, respectively) with the appropriate amounts of scandium metal powder.

$CsScI_3$, $Cs_3Sc_2I_9$. The iodides were prepared by reduction of CsI_3[20] (obtained from CsI, (Merck suprapur) and elemental iodine at ~235 °C) with stoichiometric amounts of scandium metal powder in sealed tantalum containers at 750 °C (2 days, followed by slow cooling in the furnace). Use of CsI_3 avoided drybox contamination with elemental iodine because its decomposition pressure (to CsI + I_2) is very small.[21] $CsScI_3$ is purplish black in bulk and dark red-purple when ground to a powder and is appropriately oxygen and moisture sensitive. $Cs_3Sc_2I_9$ is colorless and hygroscopic. The reduction of KI_3 or RbI_3 with Sc under the same conditions used for the cesium salt does not yield $KScI_3$ or $RbScI_3$.

X-ray Data. Powder diffraction data were obtained with a Simon-Guinier camera[22] (model FR 553, Enraf-Nonius) equipped with a Johannson-type monochromator (quartz crystal cylindrically ground and polished, reflecting plane 10.1) to provide clean Cu $K\alpha_1$ radiation ($\lambda = 1.54051$ Å). The equipment also allows recording of powder patterns at low (≥−130 °C) or high temperatures (≤1000 °C) either at selected temperatures or with temperature and film speed programming. Sealed glass or quartz capillaries (o.d. 0.2 mm) were used as sample containers, filled under dry argon. Low quartz (hexagonal, $a = 4.91323$, $c = 5.40485$ Å[23]) was used as an internal standard for the calculation of all lattice constants. Films were measured with a coincidence measuring device, and the 4θ values calculated by using the program SOS1[24] (a version of the program GUIN, written in Fortran IV by H. Imoto at Ames Laboratory, which fits a quadratic equation in distance to the angles of the standard reflections). After indexing, lattice constants and standard deviations were calculated with use of the program SOS2[24] (an extended Fortran IV version of the program LATT, written in PL/I by F. Tagusakawa at Ames Laboratory). Relative powder intensities were calculated with the program LAZY-PULVERIX.[25]

Spectra. Raman data were recorded with a commercial Coderg 800 spectrometer at ambient temperature with use of an Ar laser (488 nm, 200 mW) as a light source. Photoelectron spectra were obtained with an Al $K\alpha$ radiation and an AEI Model ES200B spectrometer coupled with a Nicolet 1180 minicomputer. Samples were referenced to carbon 1s of the cellophane tape used for mounting, this having been previously calibrated with deposited gold.

Results

Several new ternary halides of divalent scandium with rubidium and cesium cations were obtained by reduction of ternary halides $A_3Sc_2X_9$ (A = Rb, Cs; X = Cl, Br) and CsI_3 with elemental scandium, namely, $CsScBr_3$, $CsScI_3$, $RbScCl_3$, and $RbScBr_3$. These and their X-ray data are listed in Table II. As with $CsScCl_3$,[12] they all belong to the $CsNiCl_3$-type structure[26] which may be described as hexagonal close-packed $CsCl_3$ layers (stacking sequence AB...or h) in which all nominally octahedral interstices defined by chloride are occupied by M^{2+} cations to form chains of confacial $^1_\infty[MCl_{6/2}]$ octahedra. These exhibit a much shorter M–M distance through the common face ($c/2$) than obtained with corner-sharing $^3_\infty[MCl_{6/2}]$ octahedra found in the polymorphic cubic perovskite with stacking sequence ABC... which is adopted by the larger divalent lanthanide ions of Sm, Eu, Tm, and Yb. Thus magnetic ordering may take place parallel to the octahedral chains (crystallographic c axis) in the hexagonal form.

Table II. Lattice Constants and Molar Volumes of Reduced Ternary Halides of Scandium

	a/Å	c/Å	c/a	V_M/cm³ mol⁻¹
$CsScCl_3$[a]	7.350 (2)[b]	6.045 (3)	0.822	85.17
$CsScCl_3$	7.3421 (6)	6.0395 (9)	0.823	84.91
$CsScCl_2Br$	7.4689 (5)	6.1728 (8)	0.827	89.81
$CsScClBr_2$	7.584 (1)	6.271 (2)	0.827	94.07
$CsScBr_3$	7.6868 (8)	6.364 (1)	0.828	98.07
$CsScI_3$	8.278 (1)	6.803 (2)	0.822	121.56
$RbScCl_3$	7.1631 (3)	5.9657 (4)	0.833	79.83
$RbScBr_3$	7.5653 (9)	6.322 (2)	0.836	94.36

[a] Reference 12. [b] Numbers in parentheses are estimated standard deviations in the last digit.

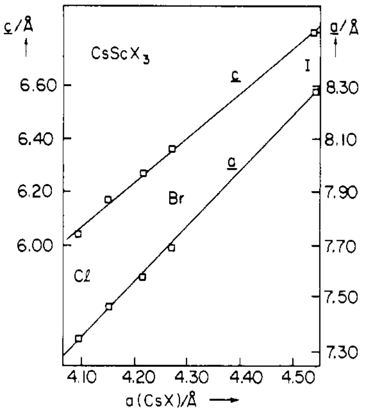

Figure 1. Hexagonal lattice constants for $CsScX_3$, X = Cl, Br, I, as well as $CsScCl_yBr_{3-y}$, $y = 1, 2$, as a function of the molar volume of the corresponding cesium halide.

Lattice constants as well as molar volumes of the ternary cesium scandium halides are linearily related to those of the corresponding binary cesium halide, as shown in Figure 1.

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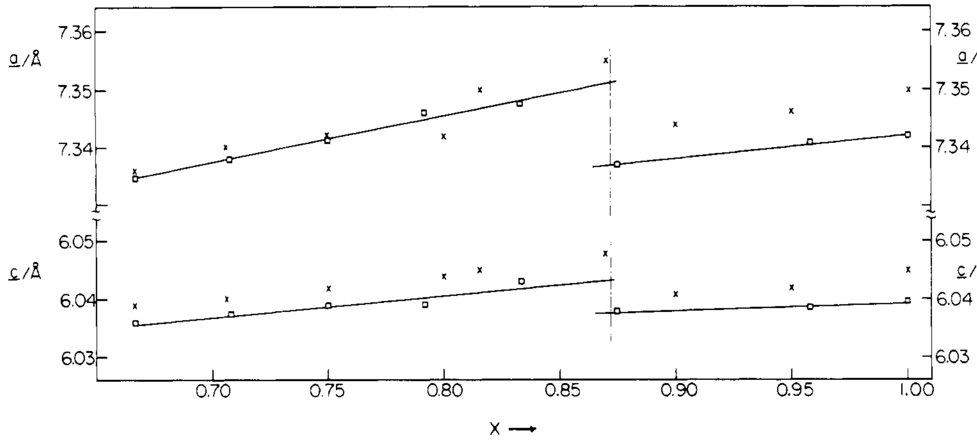

Figure 2. Hexagonal lattice constants in the homogeneity range of $CsSc_xCl_3$ as a function of x: □, present work; ×, ref 12.

Table III. Lattice Constants and Molar Volumes for the $CsSc_xCl_3$, $RbSc_xCl_3$, and $CsSc_xBr_3$ Systems

system	x	a/Å	c/Å	c/a	V_M/cm^3 mol^{-1}
$CsSc_xCl_3$	0.667[a]	7.335 (1)[b]	6.036 (1)	0.823	84.70
	0.708[a]	7.3380 (5)	6.0366 (7)	0.823	84.77
	0.750	7.3416 (5)	6.0393 (5)	0.823	84.89
	0.792	7.3461 (5)	6.0392 (7)	0.822	85.00
	0.833	7.3476 (6)	6.0425 (7)	0.822	85.08
	0.875	7.3371 (9)	6.038 (1)	0.823	84.77
	0.958	7.3407 (6)	6.0385 (9)	0.823	84.86
	1.000	7.3421 (6)	6.0395 (9)	0.823	84.91
$RbSc_xCl_3$	0.667[a]	7.1582 (3)	5.9643 (1)	0.833	79.70
	0.750[a]	7.1621 (4)	5.9638 (5)	0.833	79.78
	0.833[a]	7.1637 (2)	5.9660 (4)	0.833	79.85
	0.917	7.1633 (5)	5.9657 (7)	0.833	79.84
	1.000	7.1631 (3)	5.9657 (4)	0.833	79.83
$CsSc_xBr_3$[c]	0.667[d]	7.680	6.420	(0.836)	(98.76)
	0.708	7.692 (1)	6.366 (2)	0.828	98.23
	0.750	7.690 (1)	6.362 (1)	0.827	98.12
	0.833	7.692 (1)	6.363 (1)	0.827	98.19
	1.000	7.6868 (8)	6.364 (1)	0.828	98.07

[a] 1-3 additional weak lines are observed for the correct larger cell ($Cs_3Tl_2Cl_9$ type) which has $a' = 3^{1/2}a$ and $c' = 3c$.[12] [b] Numbers in parentheses are estimated standard deviations in the last digit. [c] Only the lattice constants computed for the $CsScBr_3$ component of the mixture are given for $x = 0.708$, 0.750, 0.833. [d] $Cs_3Sc_2Br_9$ crystallizes with the $Cs_3Cr_2Cl_9$-type structure with a as given here and with a tripled c axis (data from ref 17).

The mixed anion compositions $CsScCl_2Br$ and $CsScClBr_2$ are also seen to fit this relationship. The c/a ratio has a slight maximum at $CsScBr_3$, and all of the values are somewhat above that for an ideal hexagonal-close-packing, 0.8165; that is, the trigonal antiprism (D_{3d}) about scandium is always elongated.

The homogeneity range for $CsSc_xCl_3$ between $Cs_3Sc_2Cl_9$ and $CsScCl_3$ that was established by Poeppelmeier et al.[12] was confirmed for $CsSc_xCl_3$ and established for $RbSc_xCl_3$ (see Table III), but no such region was found in the case of the $Cs_3Sc_2Br_9/CsScBr_3$ system where the scandium(III) salt has a different structure (see Table IV) and a two-phase mixture is formed. A similar result would be expected for the $CsSc_xI_3$ and $RbSc_xBr_3$ systems, for the same reason. The lattice constants observed in the $CsSc_xCl_3$ system show a smooth increase on reduction with a sharp break between $x = 0.83$ and 0.88. These are compared with the similar results found earlier in Figure 2. The close correspondence in results for samples prepared by different routes and studied on different Guinier cameras with different internal standards is encouraging.

All attempts to prepare $RbScI_3$ as well as potassium compounds $KScX_3$ (X = Cl, Br, I) failed. Furthermore, it proved impossible to obtain a significant reduction of $Cs_3Y_2Cl_9$.

Table IV. Lattice Constants, Molar Volumes, and Crystal Structures of Halides $A_3Sc_2X_9$ (A = Rb, Cs; X = Cl, Br, I)

	structure type	a/Å	c/Å	V_M/cm^3 mol^{-1}	ref
$Rb_3Sc_2Cl_9$	$CsTl_2Cl_9$[a]	12.3984 (6)[c]	17.893 (2)	239.11	27
		12.707 (2)	18.117 (4)	254.31	12
$Cs_3Sc_2Cl_9$		12.704	18.109	254.08	17
$Rb_3Sc_2Br_9$	$Cs_3Cr_2Cl_9$[b]	7.548 (1)	19.149 (8)	284.53	27
$Cs_3Sc_2Br_9$		7.680	19.26	296.27	17
$Cs_3Sc_2I_9$		8.243	20.64	365.76	27

[a] Trigonal, $R\bar{3}c$, $Z = 6$.[30-32] [b] Hexagonal, $P6_3/mmc$, $Z = 2$.[34] [c] Numbers in parentheses are estimated standard deviations.

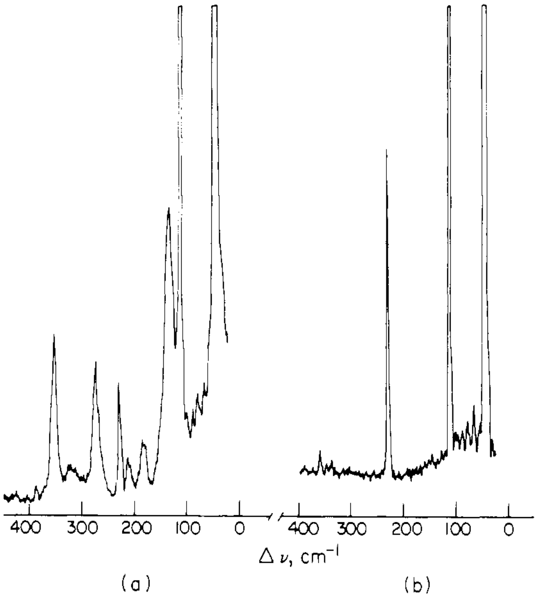

Figure 3. Laser Raman spectra for (a) $CsSc_{0.71}Cl_3$ and (b) $CsSc_{1.0}Cl_3$ samples (488-nm excitation).

Raman spectra of several samples of $CsSc_xCl_3$ within the homogeneity range show the same frequencies that are known for $Cs_3Sc_2Cl_9$[17] and which appear characteristic of the Sc_2Cl_9 bioctahedron. Additional lines are found in all samples for which $x \geq 0.79$. Figure 3 compares these results for $x = 0.71$ and 1.0.

Both low ($-130 \leq t/°C \leq 25$) and high temperature ($25 \leq t/°C \leq 725$) Simon–Guinier powder patterns were obtained by using cooling and heating rates of 10 and 20 K h^{-1}, respectively (film speeds 5 and 4 mm h^{-1}). Neither indicated any changes in the crystal structure of $CsScCl_3$. Under these conditions, decomposition (reaction with the capillary, presumably) takes place between 580 and 640 °C.

XPS measurements were made on core and valence levels of $CsSc_xCl_3$, $x = 0.71$, 0.83, 1.00, $CsScBr_3$, and $CsScI_3$. Core levels of Cs ($3d_{5/2}$, 725.1–725.4 eV) and Cl($2p_{3/2}$, 199.1–199.3 eV) showed negligible differences among these compounds, which is not unusual. More striking was the essential invariance of the Sc $2p_{3/2}$ levels to x in $CsSc_xCl_3$, 403.4–403.5 eV. This value is reasonable relative to the same quantity for $ScCl_3$ (404.0 eV) and the metallic chain in Sc_7Cl_{10} (399.2 eV).[28] A plausible shift relative to $CsScCl_3$ is also seen for Sc $2p_{3/2}$ in $CsScBr_3$ and $CsScI_3$ (402.5–402.6 eV). This transition exhibits essentially the same shape and width (1.9-eV fwhm) in all the compounds studied; in particular, there was no evidence for mixed oxidation states (or a chemical shift) in $CsSc_xCl_3$.

Useful information on the energy of the scandium valence electrons could not be obtained. The sensitivity problem is analogous to that recently discussed for $ZrCl_3$;[29] in addition, the low binding region was complicated by a weak component of Cs $5p_{3/2}$ from Al $K\alpha_3$ which falls at about 0.5 eV.

Discussion

Two series of enneahalodimetallates(III), $A^I_3M^{III}_2X_9$, of the rare earth metals were recently described: $Cs_3M_2Cl_9$ (M = Sc, Y, Lu–Ho) and $Cs_3M_2Br_9$ (M = Sc, Y, Lu–Sm).[17] The existence of $Rb_3Sc_2X_9$ (X = Cl, Br) and $Cs_3Sc_2I_9$ has also been established,[27] but no potassium compounds of this stoichiometry have yet been obtained. The scandium compounds belong to two different structure types, both containing confacial bioctahedra M_2X_9 but with different stacking sequences of the two dimensionally close-packed AX_3 layers.

In the $Cs_3Tl_2Cl_9$ structure type[30–32] that is observed for $Rb_3Sc_2Cl_9$[27] and $Cs_3Sc_2Cl_9$,[12] the stacking sequence of the ACl_3 layers is hcp. (ABABAB... or $(h)_6$). Sc^{3+} ions fill two-thirds of octahedral interstices between those layers so that confacial bioctahedra occur, but the arrangement between chains is more complicated than that for $Cs_3Fe_2F_9$.[33]

If the X^- ions have higher polarizabilities or are bound more covalently, the $Cs_3Cr_2Cl_9$-type structure[34] seems to be more favored and is adopted for $Cs_3Sc_2Br_9$, $Rb_3Sc_2Br_9$, and $Cs_3Sc_2I_9$. Here the Sc_2X_9 units are further separated from each other with a stacking sequence ABACBC... (alternative description $(chc)_2$). If all octahedral sites were filled, one would have the structure of hexagonal $BaTiO_3$[35] and $CsCdCl_3$,[36] which contain a kind of a "zigzag" chain made up of one-third face- and two-thirds corner-sharing MX_6 octahedra. Only those octahedral sites that lead to confacial bioctahedra are occupied in the $Cs_3Cr_2Cl_9$ type.

In the case of chlorides and bromides (and presumably also for iodides), compounds of stoichiometry $A_3Sc_2X_9$ prove to be good starting materials for the reductions with scandium metal which have to be carried out in tantalum containers to avoid highly exothermic reactions with, for example, silica containers. Some reasons may be outlined briefly.

(a) The $A_3Sc_2X_9$ (X = Cl, Br) phases may be obtained in high purity with respect to the very stable oxyhalides (e.g., ScOCl). The driving force in the preparation of $A_3Sc_2X_9$ from the hydrated halide and AX is apparently both the stability of the product lattice and the high concentration of gaseous HX (X = Cl, Br) in a flow system at moderate high temperatures (400–500 °C).

(b) Their use avoids the time-consuming preparation and purification of the scandium trihalides, purification of which requires vacuum sublimation at least twice in a tantalum apparatus.

(c) As ternary compounds they contain all the needed ions in an atomic dispersion which causes fewer kinetic problems during the reduction with metal.

All of the ternary halides of divalent scandium of the type $A^ISc^{II}X_3$ (A^I = Rb, Cs; X = Cl, Br, I) obtained belong to the $CsNiCl_3$ structure type[26] which is closely related to the $Cs_3Tl_2Cl_9$ type. However, homogeneity ranges were found only for $RbSc_xCl_3$ and $CsSc_xCl_3$ ($0.67 \leq x \leq 1.00$) where the end members $AScCl_3$ and $A_3Sc_2Cl_9$ both have the same stacking sequences of ACl_3 layers. As the results of Poeppelmeier et al.[12] indicated, there is a pronounced break in the increase of the lattice constants a and c in the neighborhood of $x = 0.87$, and this is confirmed by the data presented here (Figure 2). This could arise from the transition from an ordered to a random distribution of the octahedral vacancies in the (001) direction; an earlier, limited refinement of a crystal of composition $CsSc_{0.78}Cl_3$ indicated fully occupied dimeric units of the parent $Cs_3Sc_2Cl_9$ persisted at that composition.

It is, however, not clear why the break in lattice constants arises and why at $x \approx 0.87$. In the $CsSc_xCl_3$ system, successive filling of empty confacial octahedra along the chains on reduction is evident. This may take place with statistical distribution over the entire homogeneity range or in a more or less ordered manner. An order–disorder transition in the scandium site occupancy was considered earlier. However, it is striking that the break in lattice constants on reduction arises after half of the empty octahedral holes are filled and that this has the greater effect on the a axis, perpendicular to the octahedral chains. Another interpretation, presently under investigation, should be considered—a first-order transition to another structure type in the $x \approx 0.87$ region, namely, to a partially occupied matrix of the $Cs_3Fe_2F_9$ type[33] which shows the same ABABAB... stacking sequence of AX_3 layers but has a smaller (by 3) hexagonal base through a simpler ordering of the empty octahedral holes. It also seems noteworthy that no shift of scandium core energies or evidence for mixed oxidation states could be discerned in the XPS spectra of $CsSc_xCl_3$.

A similar change in structure occurs in the case of $RbSc_xCl_3$ (Table III), with a slight decrease in both a and c constants in the interval $0.833 < x < 0.917$, although here fewer data were obtained. Within the limit of error, no such behavior seems to occur for the $Cs_3Sc_2Br_9/CsScBr_3$ system where the powder pattern instead indicated the existence of only a wide two-phase region. This is obviously because $Cs_3Sc_2Br_9$ and $CsScBr_3$ do not occur in related structures. The crystal structure of $Cs_3Sc_2Br_9$($Cs_3Cr_2Cl_9$ type) with the stacking sequence ABACBC... does not allow the ready formation of one-dimensional chains of face-sharing octahedra.

Raman spectra seem to support the above interpretation. For $CsSc_{0.708}Cl_3$ (less than one-sixth additional octahedral hole filled statistically), the characteristic spectrum for an "isolated" Sc_2Cl_9 bioctahedron occurs plus additional bands obviously characteristic of an infinite linear chain $^{1}_{\infty}[ScCl_{6/2}]^{2-}$. The latter bands are the only ones observed for $x \geq 0.79$ where more than one-third of the octahedral holes are occupied, and there is only a minor chance to preserve "isolated" confacial bioctahedra. That the spectrum in Figure 3b is of a definite phase and not of a mixture of $Cs_3Sc_2Cl_9$ and $CsScCl_3$ is also likely because of the increased lattice constants observed.

At least under the preparative conditions used in this work, ternary potassium halides $KScX_3$ (X = Cl, Br, I) as well as

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Table V. Ratios of Effective Ionic Radii[37] of A$^+$ (CN 12) and X$^-$ (CN 6) for AScX$_3$ Compounds

(KScCl$_3$)^a 0.906	(KScBr$_3$) 0.837	(KScI$_3$) 0.745
RbScCl$_3$ 0.950	RbScBr$_3$ 0.878	(RbScI$_3$) 0.782
CsScCl$_3$ 1.039	CsScBr$_3$ 0.959	CsScI$_3$ 0.855

[a] Compounds in parentheses are unknown.

RbScI$_3$ were not obtained. This may be because of an inability to obtain good two-dimensional packing within the AX$_3$ layers when cations and anions are of very unequal size. Qualitative support for this consideration might be the radius ratios given in Table V for A$^+$ and X$^-$ ions. Here effective ionic radii[37] for A$^+$ and X$^-$ with CN 12 and 6, respectively, were chosen because their sums are close to the interatomic distances observed or estimated. In this point of view, the best packing should occur for a ratio of 1.00, which is approximately the case for CsScCl$_3$. If either the A$^+$ radius becomes smaller or the X$^-$ radius enlarges, the radius ratio decreases and AScX$_3$-type compounds become less stable or do not exist. However, the case of KScCl$_3$, which therefore should exist, makes it clear that the radius ratio can not be the only reason for stability or instability of these compounds. A significant contribution of van der Waals energy to the lattice stability for the heavier elements may be a factor. The inability to reduce yttrium in Cs$_3$Y$_2$Cl$_9$ is surprising in view of the stability of other reduced phases such as Y$_2$Cl$_3$ and YCl.[10] Although the Y^{2+} ion may be too large for the CsNiCl$_3$-type structure, this should not be true in a CsCdCl$_3$ analogue. Perhaps reduced yttrium is stable only when strongly metal–metal bonded and not as the dipositive ion.

On the other hand, it is striking that only those ternary trihalides were observed that form a corresponding enneahalide, independent of the structure type for the latter. Additionally, only AScX$_3$-type compounds with the CsNiCl$_3$ structure type were observed, with all scandium–scandium distances equal and as short as possible. Whether this implies some kind of metal–metal interaction cannot be decided from structural data alone. However, it should be noted that the shared octahedra(trigonal antiprisms) are always elongated along the threefold axis and that the Sc–Sc distance ($=c/2$) seems to be quite normal in comparison with other CsM^{II}Cl$_3$ compounds of the first transition series. With the exceptions of Cr^{2+} and Cu^{2+}, where Jahn–Teller type elongations occur, the observed M–M distances decrease slightly for heavier metals as far as the known experimental data allow such a comparison. Unfortunately no special efforts have yet been made to determine lattice constants of these compounds systematically and with high precision, which makes a detailed structural comparison much more difficult.

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Registry No. CsScCl$_3$, 65545-44-0; CsScCl$_2$Br, 77648-22-7; CsScClBr$_2$, 77648-23-8; CsScBr$_3$, 77648-24-9; CsScI$_3$, 77648-25-0; RbScCl$_3$, 77648-26-1; RbScBr$_3$, 77648-27-2; Rb$_3$Sc$_2$Cl$_9$, 12272-72-9; Rb$_3$Sc$_2$Br$_9$, 12431-62-8; Cs$_3$Sc$_2$I$_9$, 74472-54-1; Cs$_3$Sc$_2$Br$_9$, 12431-61-7; Cs$_3$Sc$_2$Cl$_9$, 12272-71-8; CsI$_3$, 12297-72-2.

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Preparation and Properties of Poorly Crystallized CoS$_2$ and RuS$_2$

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Amorphous or poorly crystallized samples of RuS$_2$ and CoS$_2$ were made by sulfurizing (NH$_4$)$_2$RuCl$_6$ and [Co(NH$_3$)$_6$]Cl$_2$ at low temperatures with H$_2$S. The amorphous products were annealed under various conditions, and the resulting degree of crystallinity was determined. For RuS$_2$, the average crystallite sizes ranged from 26 Å for the poorly crystallized material to greater than 2000 Å for the well-crystallized material. CoS$_2$ average crystallite sizes ranged from 130 Å to greater than 2000 Å. The stoichiometry, appearance of the crystalline pyrite phases, cell parameters, and magnetic properties were studied as a function of annealing temperature.

Introduction

There has recently been reported[1] a technique for the preparation of a number of poorly crystallized platinum metal dichalcogenides. These materials were prepared by the reaction of the ammonium hexachlorometalate complex with hydrogen sulfide. X-ray diffraction patterns of these compounds resemble those obtained for materials which might be classified as being almost amorphous.[2,3] The presence of only a small degree of short-range order, as evidence by the shape of the X-ray diffraction pattern obtained, forms the basis for the term "poorly crystallized". This work describes the synthesis of amorphous CoS$_2$ from hexaamminecobalt(II) chloride, as well as a study of the properties of poorly crystallized CoS$_2$ and RuS$_2$ as a function of annealing temperature. The characterization methods employed were X-ray powder diffraction analysis, thermogravimetric analysis, scanning electron microscopy, and magnetic susceptibility.

Experimental Section

Preparation of RuS$_2$. Poorly crystallized RuS$_2$ was prepared from the reaction between hydrogen sulfide and ammonium hexachlororuthenate(IV) as reported previously.[1]

Preparation of CoS$_2$. Anhydrous CoCl$_2$ was prepared[4] from CoCl$_2$·6H$_2$O (Baker). The anhydrous CoCl$_2$ was ground thoroughly under nitrogen with use of an agate mortar and pestle. The sample

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