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Synthesis and Properties of Two Novel Line Phases That Contain Linear Scandium Chains, $LiScI_3$ and $Na_{0.5}ScI_3$

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The title compounds are produced through reactions of Sc, ScI_3, and LiI or NaI at 750–850 °C in sealed niobium tubing. The slightly paramagnetic lithium phase has a fixed composition near $LiScI_3$ judging from Guinier powder data and direct analyses. The structure refined from single-crystal X-ray data ($P\bar{6}c2$, $Z = 2$, $a = 7.2861$ (9) Å, $c = 6.768$ (2) Å, $R/R_w = 0.96/3.2\%$) contains equally spaced scandium atoms (d(Sc–Sc) = 3.384 (1) Å) in chains of confacial $ScI_{6/3}$ octahedra that lie normal to hcp iodine layers. Lithium in iodine octahedra is ordered so as to define confacial trigonal prisms about each chain. The sodium phase has a fixed composition close to $Na_{0.5}ScI_3$ according to the same criteria as well as the structural refinement ($Na_{0.53(2)}ScI_3$: $P31c$, $Z = 4$, $a = 7.492$ (2), $c = 13.699$ (3) Å, $R/R_w = 2.2/3.2\%$ for data to $2\theta = 60°$). The scandium atoms are paired within slightly distorted chains of confacial octahedra normal to hcp iodine layers (d(Sc–Sc) = 3.278 (5), 3.572 (5) Å). Sodium at ~50% occupancy within iodine octahedra presents a novel arrangement, trigonal prisms centered around each dimer that are alternately rotated by ~60° along the chain. The phase exhibits a small, temperature-independent paramagnetism. The results are compared with those for other nominal d^1 trihalides.

Introduction

The solid-state chemistry of transition metal trihalides with nominal d^1 configurations affords some remarkable and diverse responses to what might be presumed to be a strong tendency for the formation of metal–metal bonds. In some instances, the actual structures remain somewhat uncertain because their descriptions have been based largely on Debye–Scherrer powder diffraction studies, and these could have missed weak reflections that signal distortions, pairing, etc. Only two of the trihalides, α-$TiCl_3$ and α-$TiBr_3$, apparently adopt the hcp BiI_3-type structure in which the metal atoms occupy two-thirds of the octahedral interstices between alternate pairs of halogen layers. Otherwise, d^1 trihalides, and many others as well, evidently occur in what has variously been called the β-$TiCl_3$, $ZrCl_3$, or ZrI_3 structure[1-3] in which the metal atoms instead occupy every third string of octahedral sites that run normal to the same hcp halogen lattice so as to generate quasi-infinite chains of confacial octahedra, viz., $^1_\infty[MX_{6/2}]$. This arrangement is geometrically more favorable for metal–metal bonding, and the magnetic susceptibilities are generally observed to be low.[4,5]

There is now compelling evidence that the foregoing structural description is only an approximation and that metal pairing is present in most if not all cases, the structure having a subtly different orthorhombic cell. We have recently shown this to be the case for ZrI_3, where the alternate Zr–Zr distances in the chains are 3.17 and 3.51 Å,[6] and similar unpublished refinements are available for β-$TiBr_3$, TiI_3, and $ZrBr_3$ as well as NbI_3 (d^2),[7] MoI_3, $MoBr_3$ (d^3), and $RuBr_3$ (d^5).[8] This structural feature has been known qualitatively for the last two for a longer time.[9,10]

Another way to form d^1 systems with similar structures and potentially comparable bonding schemes is illustrated by the AMX_3 phases in which A is an alkali metal, M is a group III element like scandium, and X = Cl, Br, or I. The crystal and metallic radii of scandium are both very similar to the respective zirconium quantities,[11,12] so some bonding similarity might be expected. The first examples of such phases were $CsScX_3$, $RbScCl_3$, and $RbScBr_3$ with the hexagonal $CsNiCl_3$ structure type.[13,14] This arrangement also contains hcp layers but of the AX_3 composition common to perovskites, and there are again equally spaced metal atoms centering strings of confacial octahedra, $^1_\infty[MX_{6/2}]$. The Sc–Sc distances are relatively short in the cesium and rubidium chlorides, 3.02 and 2.98 Å, increasing with halide size to 3.18 and 3.40 Å in the cesium bromide and iodide examples, respectively. Both chlorides also show more or less continuous nonstoichiometry regions down to $ASc_{2/3}X_3$ ($A_3Sc_2X_9$), this limit being a $Cs_3Tl_2Cl_9$-type structure with ordered pairs of metal atoms. Alternate structures showing either an ordering of the metal vacancies in intermediate regions or distortions appropriate to Sc–Sc pairing are not known.[15] However, the metal atoms did refine with elongated ellipsoids along the chains for the composition $CsSc_{0.79}Cl_3$ (3.7:1).[13]

A much closer analogy to ZrI_3, etc. has now been found for $AScI_3$ systems with small A, viz., Li and Na. These structures retain the basic arrangement of β-$TiCl_3$, ZrI_3, etc., an hcp iodine array with scandium in one-third of the channels normal to the layers, but alkali-metal cations now occupy half of the remaining octahedral interstices. However, the presence or absence of Sc–Sc pairing and stoichiometric differences are surprisingly variable judging from these first results for the LiI–ScI_3 and NaI–ScI_3 systems.

Experimental Section

The scandium employed was all vacuum sublimed, either Ames Lab 99.8% material[16] or a Johnson Matthey product. Both were stored and handled only in the glovebox. Scandium triiodide was prepared at 850–870 °C, as described before,[17] and was sublimed five times in a tantalum jacket under dynamic high vacuum. Sodium iodide (Baker) and lithium iodide (Aldrich) were vacuum sublimed twice at $<10^{-5}$ Torr and 650 and 750 °C, respectively. The two new phases as well as other products were identified by virtually quantitative agreements in intensities as well as positions obtained between the experimental Guinier films and the respective powder patterns calculated on the basis of the known structures. Least-squares analyses of line positions relative to Si as an internal standard were naturally a more rigorous test of the crystal class.

Syntheses. Both products are extremely sensitive to moist air, where they oxidize and hydrolyze in a few seconds. Therefore, all reactants and

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products were handled only in a glovebox. All reactions were carried out as before[16,18] in welded niobium tubing containers that were in turn sealed in evacuated fused silica jackets and heated at 750–850 °C for 2–4 weeks.

The phase subsequently established to be $LiScI_3$ is obtained in quantitative amounts from stoichiometric proportions of LiI, Sc, and ScI_3 after heating these at 750 °C for 3 weeks followed by slow cooling to room temperature. Macrocrystals in the form of black needles are readily grown in the presence of a 10–15 wt % excess of LiI. The compound slowly reacts with vacuum grease.

The phase that was established to be $Na_{0.5}ScI_3$ is regularly obtained from NaI, Sc, and ScI_3 reactions over a wide range of compositions and temperatures. The black compound appears slightly green colored when ground, especially when mixed with NaI, which presumably functions as a diluent. Three different crystals were studied by single-crystal diffraction means. A diffraction quality but relatively shapeless crystal (I) was first isolated from a reaction with an excess of both NaI and metal that had run at 650 °C for 12 weeks, and this enabled the structure and the composition to be well approximated. Better needle-shaped crystals (II) were then grown in a 850/800 °C gradient reaction for 2 weeks starting with an initial composition $Na_{0.75}ScI_3$, the crystals growing on the scandium metal at the hot end. Another batch of somewhat smaller acicular crystals (III) were isolated from a sample of composition Na_2ScI_3 that had been heated to 900 °C and then equilibrated more or less isothermally at 870 °C for 3 weeks.

Analyses. Samples of both phases were quantitatively analyzed for alkali metal by atomic absorption with the aid of a Perkin-Elmer spectrometer. Single crystals were selected in the glovebox with the aid of a microscope and brought out in a previously weighed vial. These were dissolved in ~1.5 M HNO_3 at ~60 °C and diluted. Comparable standard solutions were prepared from the nitrates.

Magnetic Susceptibilities. Samples on the order of 50 mg of each compound were weighed in the glovebox and sealed within standard fused silica susceptibility containers under He. The magnetization of each was first checked as a function of field and then measured at 3 T over the range $6 \le T < 300$ K on a Quantum Design SQUID magnetometer. Data for both were corrected for the susceptibility of the container and for the estimated core diamagnetism, 1.5×10^{-4} emu mol^{-1}. Two independent samples of each compound were studied and found to behave similarly.

Crystallography. $LiScI_3$. Oscillation and zero level (*hk*0) Weissenberg photographs showed $6/mmm$ Laue symmetry. The first crystal studied, which was held within the capillary by a small amount of vacuum grease, was found to decompose in this process in about 3 days, and so a zero-level precession photograph was secured on another crystal from the same sample. Neither of these showed any evidence of a superstructure along $\vec{c}$ like that found in Na_xScI_3 (below). A fresh crystal was mounted with a minimum amount of grease, and a three-dimensional data set was collected at room temperature on a Rigaku AFC6R diffractometer at a scan rate of 16° min^{-1}. Axial photographs agreed with the $6/mmm$ symmetry deduced from film studies, and no decay of the intensity standards was observed during the 14-h data collection period. An empirical absorption correction applied on the basis of three ψ scans resulted in $R_{av} = 0.046$ for all data and 0.023 for those with $I/\sigma(I) \ge 3.0$. The reduced data exhibited absences for hhl, $l \ne 2n$. Space groups consistent with this are $P6_3cm$ (No. 185), $P\bar{6}c2$ (No. 188), and $P6_3/mcm$ (No. 193). No solution could be found by direct methods in the last, and the thermal parameters for a model so derived in the first group persistently went negative. MITHRIL[19] gave a position for iodine in the remaining group $P\bar{6}c2$, and subsequent cycles of refinement and Fourier mapping located the scandium atom and then a prospective lithium position (3.4 e/Å^3) at reasonable distances from iodine. Isotropic refinement gave $R/R_w = 0.032/0.071$ with a rather small thermal parameter for lithium (0.69 Å^2), but this increased when all atoms were refined anisotropically. Refinement of the lithium occupancy gave a value of 0.90 (18), and subsequent retention of that atom at full occupancy gave a final refinement of all variables with $R/R_w = 0.0096/0.017$. Anisotropic refinement of Li was not meaningful, and its isotropic B value of 9 (3) Å^2, is marginal at the 3σ level. The final ΔF map was featureless, with the largest feature at 0.3 e/Å^3 being 0.57 Å from iodine.

Refinement on all measured intensities gave positional and thermal parameters within 1σ of the previous values and $R/R_w(I) = 0.018/0.042$. The space group $P6_3/mc$ (No. 186) was later tried as this allows the z coordinates of Li and Sc to vary; however, these remained within 0.25σ of their original values of zero. The space group contains a second, crystallographically inequivalent site for lithium (at $^2/_3$, $^1/_3$, 0) that conceivably might be partially occupied. However, refinement of models with such a disposition regularly ended up with lithium in only a single cation site.

Table I. Crystal and Refinement Data for $LiScI_3$ and $Na_{0.5}ScI_3$

	$LiScI_3$	$Na_{0.53(2)}ScI_3$ (II)
space group (No.), Z	$P\bar{6}c2$ (No. 188), 2	$P31c$ (No. 159), 4
cryst dimens[a]		
a, Å	7.2861 (9)	7.479 (1)
c, Å	6.768 (2)	13.699 (3)
V, Å^3	311.2 (1)	663.6 (4)
μ(Mo Kα), cm^{-1}	241.0	152.0
no. of unique reflcns	102	977
no. of variables	11	29
transm factors: max–min	0.78–1.0	0.45–1.0
R[b]	0.0096	0.022
R_w[c]	0.017	0.032

[a] Guinier data with Si as an internal standard, $\lambda = 1.540\,56$ Å. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$; $w = [\sigma(F_o)]^{-2}$.

$Na_{0.5}ScI_3$. This structure was first solved with a full sphere of data collected to $2\theta = 50°$ with the aid of Mo Kα radiation, a SYNTEX P2$_1$ diffractometer, and crystal I (see Syntheses). Axial photographs suggested $\bar{3}1m$ Laue symmetry, and a reduced and absorption-corrected data set averaged much better in this class (3.1%) than for $6/m$ or $6/mmm$. Systematic absences (hhl, $l \ne 2n$) further limited the space group choice to either $P\bar{3}1c$ or $P31c$. The structure was solved by the Patterson method and refinement in the noncentrosymmetric $P31c$ (No. 159) after the centric choice resulted in an unreasonably large value of R_w (15%). The final refinement ($R/R_w = 0.022/0.027$) exhibited some troublesome coupling between thermal parameters and occupancies of the two independent and evidently fractional sodium atoms present in the structure. This and some resemblance of the result to the ZrI_3 structure with its manifold problems[6] led to a more detailed restudy using two better crystals and larger data sets collected on a Rigaku AFC6 diffractometer equipped with a rotating anode. Weissenberg studies and the collection of 500 reflections for the larger transformed ($\sqrt{3}$) orthorhombic cell established for ZrI_3[6] utilizing crystal I showed no evidence of extra reflections that would support a similar assignment.

A better needle crystal (II) grown under a temperature gradient was observed by oscillation together with zero- and first-level Weissenberg photographs to confirm to the original cell and space group choice. A full sphere of data up to $2\theta = 60°$ was collected at room temperature with a lower scan rate of 8.0° min^{-1}. These were corrected for absorption with three azimuthal (ψ) scans. High thermal parameters for the two sodium atoms at the point of isotropic convergence ($R/R_w = 0.045/0.072$) led to refinement of their occupancies with B's fixed. In the final stages, the occupancies (0.70 (2), 0.61 (2)) and isotropic B's for Na as well as all positional and anisotropic thermal parameters were varied to yield $R/R_w = 0.021/0.029$. The other enantiomorph gave significantly greater residuals. Both iodines showed effectively unit occupancies when refined relative to scandium. A final ΔF map was virtually featureless with deviations of ±0.8 e/Å^3 or less.

A somewhat more poorly diffracting needle crystal growth from excess NaI at 870° (III) was similarly studied by using two octants of data collected on the same instrument to $2\theta = 60°$ and corrected for absorption with four axial scans. The remainder of the procedure was very similar to that just described. The sodium occupancies were 0.56 (3) and 0.59 (4) at convergence with $R/R_w = 0.022/0.026$. Refinement on intensities using all measured data produced no significant changes and gave $R/R_w(I) = 0.043/0.055$.

The verity of the foregoing sodium occupancy refinements was suspect because of the relatively large B_{iso} values obtained for these atoms in the last two refinements, 3.8 (3), 3.6 (3), 3.1 (6), and 3.6 (6), respectively, which were up to twice the equivalent average for the heavier atoms. Fixing the B's at the latter value (1.90 Å^2) for crystal II gave smaller occupancies with lower errors (0.56 (1), 0.50 (1), corresponding to $Na_{0.53(2)}ScI_3$), together with 3σ changes in the z coordinates of Sc1 and NaI, $\le 1.5\sigma$ changes in all other parameters, and only slightly greater residuals, 2.2 and 3.2%. The same procedure with the poorer crystal III resulted in more dramatic decreases in the U values as well as in the errors for all positional parameters and the sodium occupancies (0.59 (2) and 0.35 (2), doubtlessly coupled), with convergence at $R/R_w = 2.9/4.4\%$. These refinements of the sodium levels are in both cases considered the more credible.

Crystal and refinement data on these two studies (II, III) are detailed in the supplementary material while information on the $LiScI_3$ and on the better crystal II for $Na_{0.5}ScI_3$ are included in Table I and utilized in the subsequent considerations.

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Table II. Positional and Equivalent Isotropic Thermal Parameters (Å²) for $LiScI_3$ and $Na_{0.5}ScI_3$

	occupancy	x	y	z	B_{eq}[a]
			$LiScI_3$ ($P\bar{6}c2$)		
I	1	0.0041 (2)	0.67725 (8)	$^1/_4$	1.77 (5)
Sc	1	0	0	$^1/_2$	1.47 (5)
Li	1	$^1/_3$	$^2/_3$	0	9 (3)
			$Na_{0.5}ScI_3$ ($P31c$, II)		
I1	1	0.3023 (1)	−0.02241 (9)	0.25[a]	2.09 (3)
I2	1	0.6855 (2)	−0.00139 (7)	−0.00029 (6)	2.34 (3)
Sc1	1	0	0	0.3734 (4)	1.77 (4)
Sc2	1	0	0	0.1341 (3)	1.41 (5)
Na1	0.56 (1)	$^2/_3$	$^1/_3$	0.1287 (7)	1.9[b]
Na2	0.50 (1)	$^2/_3$	$^1/_3$	0.3731 (8)	1.9[b]

[a] $B_{eq} = (8\pi 2/3)\sum_i\sum_j U_{ij}\mathbf{a}_i{}^*\mathbf{a}_j{}^*\vec{\mathbf{a}}_i\vec{\mathbf{a}}_j$. [b] Fixed parameters.

Results and Discussion

Exploration of reduced M^I–Sc–I systems shows that two new and evidently unique phases are formed for M^I = Na, Li. The positional parameters for $LiScI_3$ and $Na_{0.5}ScI_3$ are given in Table II, and important distances and angles are listed in Table III. Anisotropic displacement parameters for the atoms and structure factor results are available as supplementary material. The structures of these are sufficiently novel and different that additional evidence regarding their compositions and phase characteristics was also sought.

$LiScI_3$. The behavior of $LiScI_3$ is the more straightforward. Black acicular crystals of the very air-sensitive phase up to 15 mm in length are easily obtained by reaction of the metal and ScI_3 in the presence of excess LiI at 750° followed by slow cooling of the niobium container in the furnace with the power off. Guinier patterns of the compositions Li_xScI_3, x = 0.8, 1.0, and 1.2, all yielded the same hexagonal lattice constants within ranges of 1.6σ and 0.6σ in the two dimensions, the average being a = 7.286 (1) Å and c = 6.7678 (7) Å. Semiquantitative SEM-EDX analyses gave I/Sc ~3.10 (5), while spectroscopic lithium analyses of solutions of single crystals selected from three different preparations of Li_xScI_3 yielded x values in the range 0.96 (5)–1.02 (8). These are nicely consistent with that from the somewhat less certain compositional refinement of the structure, $Li_{0.90(18)}ScI_3$.

The relatively small cell is defined by hexagonally close-packed iodine layers plus equally spaced scandium atoms in one (of three) strings of octahedral sites that run normal to the iodine layers. This generates confacial chains of octahedra (trigonal antiprisms) along $\vec{c}$. This part is very similar to the idealized structure originally assigned as the β-$TiCl_3$, $ZrCl_3$, or ZrI_3 type ($P6_3/mcm$), although such chains of equally spaced metal atoms are actually not present in many, if not all, examples.[6-8]

The $P\bar{6}c2$ space group of $LiScI_3$ differentiates between the remaining chains of octahedral sites along $^1/_3$, $^2/_3$, z and $^2/_3$, $^1/_3$, z, and one is fully occupied by lithium, the other remaining empty. A projection of the cell along c is shown at the top of Figure 1 while a side view of one chain of octahedra and the surrounding lithium atoms appears below. The single Sc–Sc distance, 3.384 (1) Å (=c/2) is only slightly different from the averages in $Na_{0.5}ScI_3$, 3.425 (1) Å, and ZrI_3, 3.340 (3) Å.[6] These intervals are largely determined by the iodine lattice.

The Sc–I distances in $LiScI_3$ are all equal, 2.9104 (5) Å, very comparable to the average in $Na_{0.5}ScI_3$. The $ScI_{6/2}$ octahedra are only slightly distorted, the I–Sc–I angles all lying within 1.1° of 90°. The I–I distances are plausible, 4.10 Å within and 4.16–4.24 Å between the chains. The Li–I distances, 2.970 (3) Å, compare well with 2.96 Å for the sum of six-coordinate crystal radii of the ions,[11] further evidence that the large B value refined for Li is an artifact (see Experimental Section). The empty cation sites along $^2/_3$, $^1/_3$, z are the same size.

$Na_{0.5}ScI_3$. The sodium example is especially unusual as the trigonal structure exhibits essentially 50% occupancy of two (of four possible) cation sites, yet it appears to be close to a line compound with a fixed composition. Powder patterns of Na_xScI_3 samples covering the range $0.24 \le x \le 2.0$ that had been allowed to equilibrate with excess metal at 750–850 °C for about 2 weeks exhibit, in addition to reflections for the new compound, reflections for $Sc_{0.93}I_2$[20] when $x \le 0.39$ and for NaI with $x \ge 0.75$. A more sensitive measure of phase breadth is the course of two lattice dimensions across the composition range, where these exhibit virtually no change (7.485 (2) Å $\le a \le$ 7.4983 (8) Å; 13.697 (2) Å $\le c \le$ 13.705 (2) Å). Samples that have been annealed at slowly decreasing temperatures are prerequisite for such precise results; crystals quenched from 800–850 °C exhibit broader diffraction lines that yield wider ranges of lattice dimensions and larger uncertainties, presumably reflecting greater crystal imperfections and possibly a greater phase breadth at higher temperatures. Direct sodium analyses of batches of single crystals picked from samples with overall compositions of x = 0.5, 1.0, and 1.4 that had been isothermally equilibrated at 750 °C for 2 weeks and then cooled slowly corresponded to x = 0.55 (6), 0.50 (5), and 0.60 (5), respectively. These data are in good agreement with compositions refined from X-ray data for two different crystals, x = 0.53 (2) and 0.47 (3) (see Experimental Section). We conclude

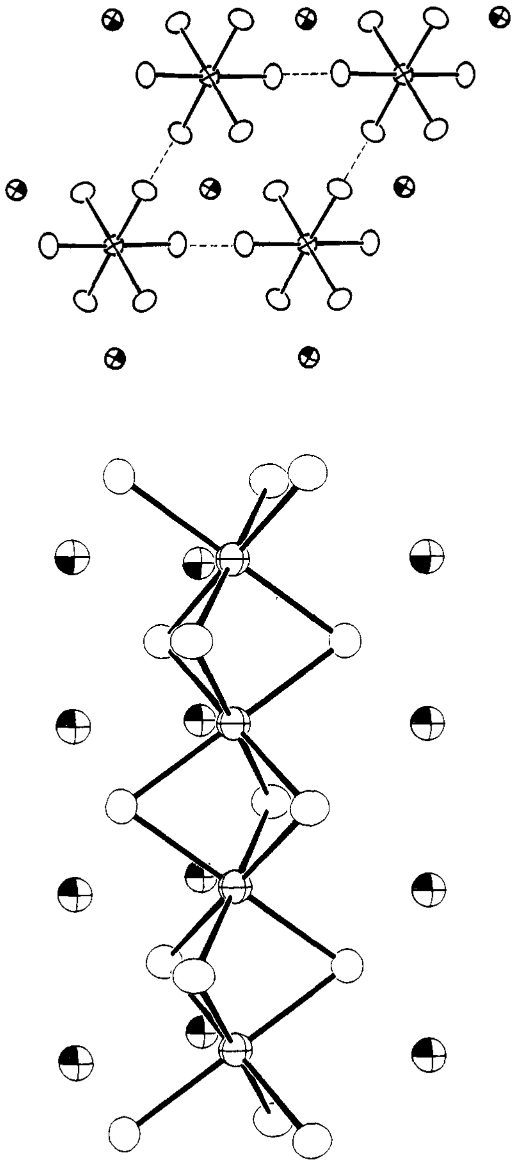

Figure 1. Top: [001] projection of the $LiScI_3$ structure with Sc as crossed, I as open, and Li as shaded ellipsoids (90% probability for Sc and I, arbitrary for Li). Bottom: Side view of one chain and the surrounding cations in $LiScI_3$ with the Sc–I interactions emphasized (two cells).

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[20] Dorhout, P. K.; Corbett, J. D. *Inorg. Chem.*, following paper in this issue.

Table III. Principal Bond Distances (Å) and Angles (deg) in $LiScI_3$ and $Na_{0.5}ScI_3$

			$LiScI_3$				
Sc–Sc	3.384 (1)	I–I	4.099 (1)	I–Sc–I	89.58 (1)	I–Li–I	87.48 (2)
			4.104 (1)		91.14 (4)		90.71 (2)
Sc–I	2.9092 (5)				89.71 (5)		91.15 (4)
		I–I	4.155 (2)[a]		179.01 (3)		177.42 (3)
Li–I	2.968 (1)		4.223 (3)[a]				
			4.239 (2)[a]				
Li–Li	3.384 (1)						
			$Na_{0.5}ScI_3$ (II)				
Sc1–Sc2	3.278 (5)	Na1–I2	3.124 (6)	I1–Sc1–I1	89.3 (1)	Sc1–I1–Sc2	69.78 (9)
Sc1–Sc2′	3.572 (5)	Na2–I2	3.094 (6)	I2–Sc1–I2	88.4 (1)	Sc1–I2–Sc2	74.52 (9)
				I1–Sc1–I2	89.29 (2)		
Sc1–I1	2.894 (3)	I1–I1	4.069 (2)	I1–Sc1–I2	93.05 (2)	Na1–I1–Na2	63.7 (2)
Sc1–I2	2.916 (3)	I1–I2	4.081 (1)	I1–Sc1–I2	177.23 (5)	Na1–I2–Na2	126.77 (7)
		I1–I2	4.083 (1)				
Sc2–I1	2.836 (2)	I2–I2	4.065 (2)	I1–Sc2–I1	91.70 (9)	I1–Na1–I2	89.32 (2)
Sc2–I2	2.983 (2)			I2–Sc2–I2	85.90 (9)	I1–Na1–I2	84.57 (2)
		I1–I2	4.216 (1)[a]	I1–Sc2–I2	89.04 (2)	I1–Na2–I2	89.49 (2)
Na1–I1	3.165 (5)	I1–I2	4.232 (1)[a]	I1–Sc2–I2	93.29 (2)	I1–Na2–I2	84.48 (2)
Na2–I1	3.178 (6)	I1–I1	4.243 (2)[a]	I1–Sc2–I2	174.9 (1)		
Na1–Na2	3.35 (1)						
Na1–Na2′	5.56 (1)						

[a] Interchain I–I distances < 4.25 Å.

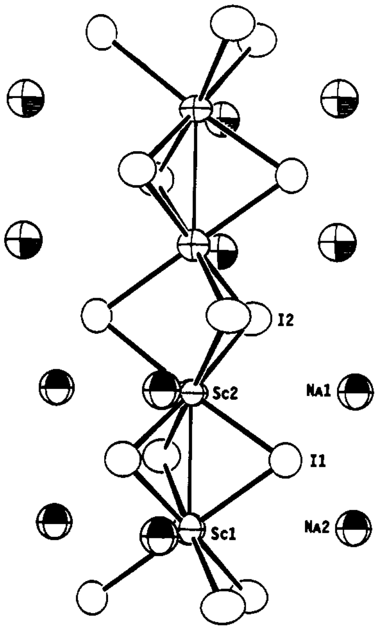

Figure 2. Side view of one $^1_\infty[Sc_2I_{6/2}]$ chain and the surrounding sodium atoms in $Na_{0.5}ScI_3$ (one cell) with Sc–I and short Sc–Sc bonds emphasized. Note that the 50% occupied sodium positions define trigonal prisms that alternate in their orientation about $\vec{c}$.

that the composition of the phase is not significantly different from $Na_{0.5}ScI_3$, and that any real nonstoichiometry in annealed samples is less than can be well determined by any of the means applied.

The structure of this compound exhibits a further reduction of symmetry from that of $LiScI_3$ to $P31c$ and a nominal 50% occupancy of two (of four) independent cation sites. The mirror planes and 2-fold axes normal to $\vec{c}$ that contain the atoms in $LiScI_3$ are gone, and the c axis length is doubled. The latter changes produce only subtle changes in the iodine layers, which are still very close to an ideal packing, and nearly all the diffraction differences arise from the sodium distribution. Figure 2 shows a side view of one chain and the surrounding sodium atoms in $Na_{0.5}ScI_3$ along with the atom-numbering scheme. Pairing of the scandium atoms yields alternating Sc1–Sc2 distances of 3.278 (5) and 3.572 (5) Å. The triangles of I1 and I2 atoms that roughly bisect the short and long metal separations do not respond by expanding and contracting in size, respectively (in contrast to the behavior in ZrI_3); instead, the paired scandium atoms lie somewhat closer to the intervening layer of I1 atoms. The $ScI_{6/2}$ octahedra are not quite ideal; the adjoining iodine triangles about the 3-fold axis along 0, 0, z deviate in projection by ~2.5° from the ideal 60° rotation between them, and the smaller angles at scandium range between 85.9 and 93.3°.

The distribution of sodium in this phase is unusual but in complete concert with the effect the lower symmetry has on the calculated energy bands.[20] One-third of the interstitial sites between hcp iodine layers are filled by strings of scandium along $\vec{c}$, while the remaining antiprismatic sites between every pair of iodine layers are alternately (and fractionally) occupied by one sodium or the other in a regular way. As seen in the chain elevation in Figure 2, Na1 and Na2 generate a trigonal prism about each dimer $[Sc1(I1)_3Sc2]$, with the orientation of this figure alternating along $\vec{c}$ between $^1/_3, ^2/_3, z$ and $^2/_3, ^1/_3, z + ^1/_2$. The pairs of sodium atoms defining the edges of the prisms are in fact displaced from one another so that d(Na1–Na2) along $\vec{c}$, 3.35 (1) Å, is a little greater than the dimer separation d(Sc1–Sc2), 3.28 Å. (Of course, the fractional occupancies may be correlated on a short-range scale.)

Other dimensional details of this structure show that some distinct distortions are present. The Sc–I1 distances about the center of the dimer (2.865 (4) Å average) are clearly less than for those without, Sc–I2 (2.950 (4) Å). This may represent either crowding or participation of I1 in the metal–metal bonding. (Although the metal atom displacements in ZrI_3 are a little greater, this Sc–I difference is clearly smaller where there are no additional cations, 0.059 (2) Å.) Some real differences in charge transfer to the two types of iodine seem likely since the opposed Na–I2 separations (3.109 (8) Å average) are less than those for Na–I1 (3.172 (8) Å). Moreover, the scandium atoms are not symmetrically placed with respect to the iodine layers, I1 being 0.058 (4) Å closer to Sc2 while I2 is 0.067 (4) Å closer to Sc1. None of these differences appear to involve significant refinement artifacts from parameter coupling; instead, a real distortion appears to be present. The Na–I distances average 3.14 Å, somewhat less than the crystal radius sum, 3.22 Å, but the significance of this is difficult to judge for fractionally occupied atom sites since their effective sizes often vary in parallel. The radii of the empty cation sites are 0.10 Å less. The presence of the cations may be the cement that reduces distortions within the iodine layers, contrary to the behavior of ZrI_3 where the range of d(I–I) within the chains is quite a bit larger, 0.08 Å.

Properties. The molar magnetic susceptibilities of $LiScI_3$ and $Na_{0.5}ScI_3$ are shown as a function of temperature in Figure 3. For the lithium compound (B), the principal feature of the data is a small paramagnetism that slowly increases from about 8.6×10^{-5} to 11×10^{-5} emu mol^{-1} Oe^{-1} as the temperature increases from 30 to 300 K. (The small feature at ~275 K appears to be an

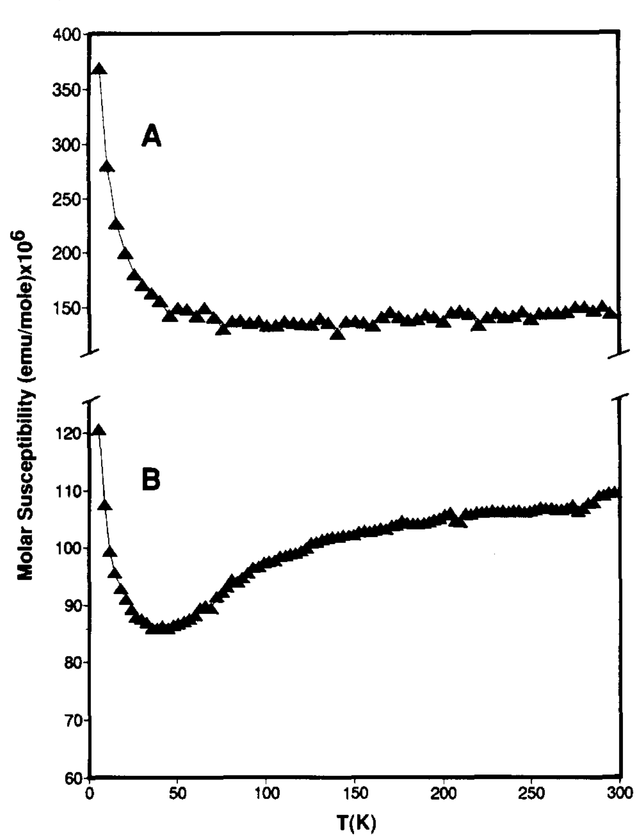

Figure 3. Molar magnetic susceptibilities of (A) $Na_{0.5}ScI_3$ and (B) $LiScI_3$ as a function of temperature (K). Both data sets have been corrected for core diamagnetism.

artifact as it did not appear in other runs or with other samples.) The sodium phase, Figure 3A, exhibits a small and virtually temperature independent paramagnetism of ~1.5 × 10^{-4} emu mol^{-1} Oe^{-1} between ~40 and 300 K. Measurements as a function of field suggested that the increase at lower temperatures for both $LiScI_3$ and $Na_{0.5}ScI_3$ arose from very small amounts of paramagnetic impurities that varied in amount from sample to sample.

Band calculations on these products as well as on the related ZrI_3 and NbI_3 at the extended-Hückel level that are described in the companion paper[20] provide considerably more understanding of the structures, their bonding, and their magnetic characteristics. Of course, such calculations of electronic structure are not sufficient to account for all of our observations in a thermodynamic sense since they lack any real account for both elastic and Coulombic contributions to the stability of a given phase as well as any consideration of the stabilities of alternative products.

The unusual characteristics of $LiScI_3$ in both stoichiometry and the absence of pairing are manifest, this phase seeming to provide a novel undistorted example of a half-filled d_{z^2} band. The band calculations[20] support this assessment, yet the room-temperature structure shows no hint of the expected Peierls distortion and dimerization.[21] On the other hand, the decrease in its small paramagnetism between 300 and 30 K (Figure 3B) could reflect a decrease in Pauli paramagnetism with decreasing temperature. This property is often taken to be the signature of the alternative charge-density-wave (CDW) deformation, the transition to a commensurate semiconducting $LiScI_3$ in some superstructure being near 70 K on the basis of Johnston's analysis.[22] A paramagnetic impurity evidently obscures the magnetic behavior below ~50 K; the similar effect with $Na_{0.5}ScI_3$ may be related.

A most provocative feature of $Na_{0.5}ScI_3$ with ~50% occupancy of two independent sodium sites is that scandium is only halfway reduced to scandium(II). A localized picture of the bonding is clearly inappropriate. As far as we can tell, the compound exhibits a fixed composition as well, the lattice dimensions probably being the most sensitive measures of this. (We have recently reported another substoichiometric line phase, $Sc_{0.93}I_2$, that occurs in a simple cation-defect CdI_2 structure.[23]) The reasons for the lower symmetry and sodium disposition become more obvious following the band calculations. With a doubled cell content, the bands split such so that only the lowest nondegenerate level is filled. On the other hand, the observed Pauli-like paramagnetism (Figure 3A) is not the simple diamagnetism that one might expect on the basis of the calculations. Several effects could counteract that: a van Vleck or impurity paramagnetism, a band gap that is <50 K, or a compound that is not precisely the stated composition, but is slightly over- or underreduced. A deviation of ±0.05, or even ±0.10, in the sodium coefficient probably can not be excluded with the present data.

Four-probe resistivity measurements on both $LiScI_3$ and $Na_{0.5}ScI_3$ would obviously be helpful in assessing their electronic properties. However, such studies will not be easily forthcoming because the extreme sensitivity of these phases to moisture, to oxygen, and to all conducting paints we have tried. These problems were very evident earlier for $Y_6I_7C_2$.[25]

Some further comparisons among ZrI_3, $LiScI_3$, and $Na_{0.5}ScI_3$ are informative. Scandium is generally taken to be slightly larger than zirconium, by 0.050 Å in standard crystal diameters[11] but only by 0.012 Å in metallic diameters,[24] and the *average* *d*(M–M) in the isoelectronic pair ZrI_3 and $LiScI_3$ show a plausible difference, 3.34 and 3.39 Å. However, the first exhibits alternate zirconium displacements of ±0.17 Å to generate relatively strongly bound Zr–Zr pairs at 3.17 Å (bond order = 0.38), whereas the lithium analogue retains an equal spacing. The Li interactions may provide a sufficient increase in the elastic energy (stiffness) of the lattice to preclude a distortion. On the other hand, the presence of 0.5 Na in a more complex structure gives the opposite result; the averager Sc–Sc separation of 3.42 Å is altered by ±0.15 Å to give dimers at 3.27 Å. The larger average Sc–Sc separation presumably reflects in part a 50% reduction in the bonding electron population. The magnitude of the pairing displacements possible as well as the metal separations in the undistorted examples are, of course, somewhat determined by the matrix provided by the iodide lattice and the alkali-metal ions, if any. In the undistorted examples, *d*(Sc–Sc) = 3.22 Å in $LiScI_3$ compares with 3.02 Å in $CsScCl_3$ and 2.98 Å in $RbScCl_3$,[14] hexagonal perovskites in which the alkali-metal cations are part of smaller, close-packed ACl_3 layers. In the present examples, the smaller cations accompanying the reduction of scandium occupy interstitial positions between the iodine layers. The perovskite lattices are probably more resistant to pairing deformations. The factors involved in determining the pairing or not of nominal d^1 ions in all of these examples appear to be complex with present information. Further investigations are underway.

Finally, it is worth noting that the general characteristics of the new ternary scandium halide phases reported here continue the novel behavior established earlier for other reduced scandium halides: the scandium compounds, in distinct contrast to the usual 3d metal halides, clearly contain delocalized if not itinerant valence electrons rather than localized magnetic states. The quasi-infinite, metallic chains of condensed octahedra in Sc_7Cl_{10}[26,27] and Sc_4Cl_6B[16] for example, as well as the layered metallic $Sc_{0.93}I_2$[23] and $Sc_7Cl_{12}N$ clusters,[16] all represent a novel chemistry that is not

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found with the later metals, being in general much more characteristic of 4d and 5d element chemistry.[28,29]

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Supplementary Material Available: Tables of data collection and refinement information and anisotropic atom displacement parameters for $LiScI_3$ and $Na_{0.5}ScI_3$ (two crystals) (2 pages); listings of F_o and F_c data for the two structures reported (5 pages). Ordering information is given on any current masthead page.

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Bonding Considerations in Metal Iodide Chain Compounds: A_xScI_3 and MI_3 (A = Li, Na; M = Zr, Nb)

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The bonding in four phases containing confacial trigonal-antiprismatic chains $^1_\infty[MI_{6/2}]$ has been examined by extended Hückel methods. The compounds, electron counts, metal periods, and the respective space groups are as follows: $LiScI_3$, d^1, equal, $P\bar{6}c2$; $Na_{0.5}ScI_3$, $d^{0.5}$, paired, $P31c$; ZrI_3, d^1, and NbI_3, d^2, both paired and *Pmmn*. In $LiScI_3$, a half-filled 1a′ band is generated by d_{z^2} interactions through the shared faces. A Peierls-like pairing distortion is evidently precluded by the stiffness of the lattice; instead, an alternate charge density wave deformation is consistent with the magnetic susceptibility data. The low symmetry and doubled chain period in the unusual $Na_{0.5}ScI_3$ structure combine to open up a gap in the bonding d_{z^2} band at E_F even though higher a′ states are still bonding. The unusual stoichiometry limit is postulated to be thermodynamic in nature. The remainder of this d_{z^2} band is filled in the more normal, metal-paired chains in ZrI_3, the predicted semiconduction being in agreement with reported data. Greater pairing displacements in NbI_3 increases the d_{z^2} band dispersion. A narrow neighboring a″ band also splits off, and its occupation gives relatively localized π bonding in the metal dimers. The compound is also predicted to be a semiconductor. The course of this bonding scheme for later MI_3 examples is also considered.

Introduction

Trihalides of the group III–V transition metals offer some remarkable examples of the various structures attained in response to metal–metal bonding possibilities. The more common β-TiX_3 (or ZrX_3) structure has been described as an hcp halogen lattice in which one-third of the octahedral sites are filled by metal atoms so as to generate chains of these atoms perpendicular to the hcp halogen layers.[1-4] This packing generates quasi-infinite chains of confacial octahedra, $^1_\infty[MX_{6/2}]$, an arrangement that would appear to favor pairing of d^1 metal atoms to give alternately long and short metal–metal interactions along the chain axis, although such distortions were not recognized for many years.

Recently, detailed studies of the structures of ZrI_3[5] and NbI_3 (among others)[6] as well as of the closely related A_xScI_3 (A = Li, x = 1; Na, x = 0.5)[7] have revealed that subtle chemical and geometrical changes occur in most of these chain compounds. In the ZrI_3 and NbI_3 cases, decreases in alternate M–M separations along the chains are accompanied by an orthorhombic distortion of the hcp iodine layers, presumably to better accommodate the intruding M–M bonding. The isostructural MoI_3, $MoBr_3$, and $RuBr_3$ have also been so quantified recently.[8] In the A_xScI_3 phases, Sc–Sc pairing accompanies the fractional inclusion of sodium into two types of octahedral sites in $Na_{0.5}ScI_3$, whereas full occupation of one type of lithium site in $LiScI_3$ gives a structure in which the confacial iodine octahedra containing d^1 atoms show *no* pairing distortions.

These results have prompted us to investigate the impetus and alternatives for bonding in these group III, IV, and V trihalide phases. Extended Hückel treatments of other, somewhat related one-dimensional transition-metal chalcogenides and chlorides have been presented by Whangbo et al.,[9] Bullett,[10] and Shima and Kamimura.[11] However, the chloride studies[10] pertained to A^IMCl_3 (hexagonal perovskite) compounds of 3d metals that exhibit only localized metal states, as manifested in their magnetic and insulating properties. On the other hand, properties of the scandium, zirconium, and niobium triiodide phases clearly reflect strong metal–metal interactions, giving rise to several questions that beg for serious consideration: (1) For the A_xScI_3 series, why and how does lithium in one set of octahedral sites yield an undistorted d^1 chain structure whereas sodium with a fractional occupation of two yields a $d^{0.5}$ system with long–short Sc–Sc interactions? (2) How does the bonding in these two compounds compare with that in the d^1 binary ZrI_3? (3) How does the bonding in the MI_3 host change to accommodate additional electron density on the metal as one goes from group III to group V? Table I lists dimensional data and bonding characteristics for those compounds that are relevant to our inquiry.

Experimental Section

The atomic positions and unit cell parameters for the title compounds have been described elsewhere.[5-7] Tight-binding, extended Hückel calculations were performed on one-dimensional Brillion zones containing 17 k points along the chain axes, defined in all cases as z. This is the

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