Volume 26
Number 2
January 28, 1987

Inorganic Chemistry

Communications

Action of Alkali Metals on Lanthanide(III) Halides: New Possibilities

Sir:

Low-temperature synthesis is one of the prevailing challenges of inorganic solid-state chemistry.[1] Mild reaction conditions are important to secure, e.g. compounds of marginal stability or in otherwise inaccessible forms, for example single crystals of low-temperature modifications. We wish to draw attention to the synthetic potential of so-called *metallothermic reductions*, i.e. the action of highly electropositive metals on metal halides.

Traditionally, the reduction of lanthanide(III) halides, MX_3, to lower oxidation states is carried out either with hydrogen (for M = Eu, Yb, Sm) or by synproportionation reactions with the same metal, both at elevated temperatures.[2] Other metals have been used only rarely as reductants for preparative means although, for example, alkali-metal reduction may be used as an industrial process for metal preparation.[3] Indeed, as early as 1828, Wöhler[4] reduced yttrium trichloride with excess potassium to produce (impure) yttrium metal for the first time. Klemm[5] and Zintl[6] used this route to produce all lanthanide metals for the investigation of their magnetic and crystallographic properties, among others. Especially Klemm found that the action of the reductant sodium on samarium trichloride led to incomplete reduction with $SmCl_2$ as an "impurity", also dependent upon the temperature.

These observations led us to a more systematic investigation of reactions between binary or ternary lanthanide halides, MX_3 (X = Cl, Br) or $A_xM_yX_z$ (for example KGd_2Cl_7), respectively, and alkali metals A (=Li–Cs). Tantalum or other refractory metal containers and strictly dry and anaerobic conditions are mandatory. The containers were sealed by He-arc welding,[7] jacketed under vacuum in silica tubes, and heated to 500–900 °C for several days to weeks. A selection of reactions with the conditions used and the products obtained is given in Table I.

Binary or ternary halides of the divalent lanthanides such as $NdCl_2$ or $RbYbBr_3$ are the products when the starting materials are lanthanide(III) halides that have low-lying reduction potentials for the reactions, $E°(M^{3+} \rightarrow M^{2+})$,[17] M = Eu, Yb, Sm, Tm, Dy, Nd, in order of increasing $|E°|$. Oxidic impurities like YbOCl that may occur easily when $YbCl_3$ is prepared via the ammonium chloride route[18] lead to the formation of M_4OX_6-type oxyhalides with O^{2-}-centered M_4 tetrahedra.[11] Such oxyhalides were obtained as single crystals for M = Eu (X = Cl, Br) and M = Yb and Sm (X = Cl). Bronze-colored Sm_4OCl_6 is the first example for a compound containing Sm^{2+}–O^{2-} bonds. The distances were found to be 236.0 and 237.6 (3×) pm, in contrast to that found in SmO (d = 247.0 pm), where mainly Sm^{3+} is present.[19] For M = Tm or Nd, no M_4OCl_6-type chlorides could be obtained. In these cases, oxidic impurities are trapped in MOCl-type oxychlorides that, at the reaction temperatures used, appear in the product as sometimes brownish or violet to black single crystals.[12]

All possible reactions to secure perovskite-type chlorides like $CsDyCl_3$ or $CsNdCl_3$, for example via Cs + $NdCl_3$ or 3CsCl + Nd + 2$NdCl_3$, have failed. It was therefore thought that reactions of the products previously obtained from metallothermic reductions, for example, LiCl + $NdCl_2$ from Li + $NdCl_3$, could be used as starting materials for low-temperature reactions with, for example, CsCl. However, even at a temperature as low as 550 °C, divalent neodymium disproportionates in the presence of alkali chlorides, in the present case with LiCl and CsCl to yield the very stable elpasolite $Cs_2LiNdCl_6$ and metallic neodymium. It was found that only in the cases of M = Eu, Yb, (partially) Sm, and (very little) Tm did such reactions lead to the formation of the perovskite-type chlorides $CsMCl_3$. This is surprising because $CsTmCl_3$ does exist[20] and, moreover, may be obtained by reduction of $TmCl_3$ with cesium.

It is obvious from Table I that many of the desired products grow as single crystals from the reaction mixtures. In all indicated and many other cases, the crystals are of a quality that is perfectly suitable for X-ray structure determination. The metallothermic reduction as an alternative synthetic route to lower oxidation states is therefore often superior to synproportionation reactions because at the reaction temperatures all components are usually in the molten state so that crystal growth from the melt becomes possible at fairly low temperatures. So far, not too much attention has been given to optimization of the reaction temperatures. Those given in Table I are most likely unnecessarily high. Additionally, reaction times are rather arbitrary and certainly often unnecessarily long.

The advantage of crystal growth from the melt via this route was also used to grow single crystals of ternary alkali-metal/

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Table I. A Selection of Metallothermic Reductions of Lanthanide(III) Halides with Alkali Metals and a Few Subsequent Reactions

	conditions				
reactants	reactant ratio	T, °C	reacn time, days	products	ref[a]
$NdCl_3$, Li	1:1	850	7	$NdCl_2$(X),[b] LiCl	8
$DyCl_3$, Li	2:2	700	7	$LiDy_2Cl_5$(X), LiCl	9
$SmCl_3$, Na	1:1	900	3	$SmCl_2$, NaCl	8
		750	4		
$NdCl_3$, K	2:2	850	5	KNd_2Cl_5, KCl	10
$TmCl_3$, Cs	1:1	600	7	$CsTmCl_3$	
$YbBr_3$, Rb	1:1	750	7	$RbYbBr_3$(X)	
$YbCl_3$, Li (YbOCl)[c]	1:1:(0.1)	900	3	Yb_4OCl_6(X), $YbCl_2$, LiCl	11
		750	4		
$SmCl_3$, Sm_2O_3, Li	10:1:12	900	4	Sm_4OCl_6(X), LiCl	
		750	6		
$EuBr_3$, Eu_2O_3, Li	6:1:8	850	7	Eu_4OBr_6(X), LiBr, Li_2O	
$NdCl_3$, Na (NdOCl)[d]	1:1	850	7	NdOCl(X), ?[e]	12
($YbCl_2$, NaCl),[f] CsCl	(1:1):1	700	7	$CsYbCl_3$, NaCl	
($LiTm_2Cl_5$, LiCl), CsCl	(1:1):2	750	7	$Cs_2LiTmCl_6$, ($CsTmCl_3$), Tm	
($NdCl_2$, LiCl), CsCl	(1:1):1	550	3	$Cs_2LiNdCl_6$, Nd	
$PrBr_3$, Li	1:1	850	10	Pr_2Br_5(X), LiBr	
$GdCl_3$, Li	1:1	700	6	$LiGdCl_4$(X), Gd	13
$GdCl_3$, Na	1:1	700	3	Na_3GdCl_6(X),[g] Gd	14
$ErCl_3$, Na	1:1	700	9	Na_3ErCl_6(X),[h] Er	
$GdCl_3$, K	1:1	700	10	KGd_2Cl_7(X), K_2GdCl_5(X), Gd	
$LuCl_3$, Li	1:1	950	30	Li_3LuCl_6(X), Lu	
$CsLu_2Cl_7$, Li	1:1	500	19	$Cs_2LiLuCl_6$(X), Lu	15
KGd_2Cl_7, Li	1:1	500	20	Li_zGdClH_x(X),[i] K_2GdCl_5(X)	16
$LuCl_3$, Cs	2:1	700	7	$LuClH_x$(X),[i] $Cs_3Lu_2Cl_9$(X), $Cs_2Lu_7Cl_{18}C$(X)[i]	

[a] Unreferenced observations are previously unpublished. [b] X = single crystals. [c] An estimated 10% impurity because of the apparently incomplete conversion of Yb_2O_3 to $YbCl_3$ by NH_4Cl. [d] Traces of NdOCl. [e] The poorly crystalline main product could not be identified. [f] A 1:1 mixture from a previously reduction of, in this case, $YbCl_3$ with Na. [g] Low-temperature modification (Na_3GdCl_6-I). [h] Isotypic with Na_3GdCl_6-II (high-temperature modification). [i] The interstitials (hydrogen or carbon) arise from (ubiquitous) impurities in the starting materials or the reaction containers.

Table II. Interatomic Distances in $Cs_2Lu_7Cl_{18}C$, $LuClH_x$, and $Cs_3Lu_2Cl_9$

compd	dist, pm
$Cs_2Lu_7Cl_{18}C$	Cs–Cl: 366.8–376.7 [12]; 370.5[a]
	Lu1–Cl: 258.3 [6][b]
	Lu2–Cl: 259.7–269.1 [5]; 262.9
	Lu2–Lu2: 357.7–361.5 [2 + 2];[c] 359.6
	Lu2–C: 254.3 [6]
	C–Cl: 369.4 [12]
$LuClH_x$	Lu–Cl: 268.5 [3]
	Lu–Lu: 336.4–363.8 [3 + 6]; 354.7
	Lu–H: 213.6–215.7 [1 + 3];[d] 215.2
	H–H: 266.8 [3]
$Cs_3Lu_2Cl_9$	Cs–Cl: 367.9–381.7 [12]; 374.2
	Lu–Cl: 249.6–269.0 [3 + 3]; 259.3
	Lu–Lu: 365.9 [1]

[a] Twelve distances ranging from 366.8 to 376.7 pm, averaging to 370.5 pm. [b] Six equal distances of 258.3 pm. [c] Two and two equal distances of 357.7 and 361.5 pm, respectively. [d] One distance of 213.6 pm and three additional distances of 215.7 pm each; hydrogen in tetrahedral interstices (z(H) = 0.197).

lanthanide(III) halides. The examples of $GdCl_3$ with lithium or sodium are especially noteworthy because crystals of ternary chlorides were obtained that either decompose in the solid state ($LiGdCl_4$, around 300 °C) or have a fairly low-lying phase transition (Na_3GdCl_6, at 205 °C). Furthermore, metallothermic reductions seem to have the capacity of an alternative route to metal-rich pseudobinary and -ternary lanthanide halides when the necessary impurities that serve as interstitials are present. Li_zGdClH_x from, principally, KGd_2Cl_7 or GdH_y, $GdCl_3$, and lithium[16] and $LuClH_x$ and red transparent $Cs_2Lu_7Cl_{18}C$[21] both from the reduction of, principally, $LuCl_3$ with cesium at 700 °C are prominent examples. The latter reaction was especially fruitful in that it also provided single crystals of $Cs_3Lu_2Cl_9$. This is important because with the confacial bioctahedron $[Lu_2Cl_9]^{3-}$ therein it contains probably the shortest possible Lu^{3+}–Lu^{3+} distance in such a chloride. Surprisingly, at 365.9 pm this is almost equal to that found in the Lu_6 octahedral cluster in $Cs_2Lu[Lu_6Cl_{12}]Cl_6C$ with d = 357.7 and 361.5 pm (Table II). Even with interstitial carbon,[21] the electron count per Lu in the cluster is only 1.5. This is especially noteworthy because isotypic zirconium (with which lutetium has a diagonal relationship within the periodic table) compounds like $K_2Zr_7Cl_{18}$ have been reported,[22] probably also containing an interstitial (hydrogen). In this compound the electron count for the cluster zirconium atoms yield a more comfortable 2.0 electrons/Zr (not counting the interstitial's electron(s)).

It is expected that the metallothermic reduction of lanthanide(III) halides with purposely added impurities that might form interstitials and stabilize metal clusters through their contribution of electrons will further add to the wealth of the more reduced halide chemistry of the lanthanides because reaction temperatures may be considerably lower. Except for the low number of valence electrons of the lanthanides, high reaction temperatures are apparently a real disadvantage for lanthanide cluster chemistry although they seemed to be mandatory in synproportionation reactions because of the high melting points and low vapor pressures of the trihalides and the high melting points of the metals.

Acknowledgment. Support by the Deutsche Forschungsgemeinschaft, Bonn, through a research grant, the Verband der Chemischen Industrie, Frankfurt, and W. C. Heraeus (tantalum tubing), Hanau, all West Germany, is gratefully acknowledged.

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(21) X-ray structure determination gives some evidence for carbon as interstitial, refining to an occupation factor of 98 (2)% with an isotropic U of 658 (390) pm^2 for R = 0.082 and R_w = 0.053. However, with 254.3 pm the Lu–C distance is possibly a little large, yielding an interstitial radius of 154 pm, which is in other cases found to be more like 146 pm (Smith, J. D.; Corbett, J. D. *J. Am. Chem. Soc.* **1986**, *108*, 1927).

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Received August 28, 1986