Conclusions

The neutral complexes [TcO(emaR)] show some very interesting features of the chemistry of technetium(V) that may be useful for the rational design of radiopharmaceutical tracers. In nuclear medicine one of the more important factors in the selection of a radiotracer is the efficiency with which it is "trapped" in a specific region of the body. The complexes prepared in this study display two mechanisms by which this might be realized, namely, reduction and dealkylation.

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Supplementary Material Available: Tables of anisotropic thermal parameters, bond distances, and bond angles (3 pages); a table of structure factors (13 pages). Ordering information is given on any current masthead page.

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Low-Temperature Synthesis of the Fluorite Modification of Lanthanoid(II) Chlorides

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Fluorite-type MCl_2 phases for M = Sm and Eu, previously reported to be stable only at elevated temperatures, have been prepared at room temperature by solvolytic decomposition reactions on mixed-valence lanthanoid chloride phases. The metastable character of these phases, which is evidenced by the transformation they undergo upon heating, and the synthesis and characterization of the mixed-valence phases $Sm_{14}Cl_{33}$, $Sm_9Gd_5Cl_{33}$, and $Sm_9Nd_5Cl_{33}$ are reported. Previously reported Sm_3Cl_7 is found to be $Sm_{14}Cl_{33}$. Lattice parameters and a probable space group for $YbCl_2{\cdot}THF$ are reported.

Introduction

It has long been known that by solvolytic decomposition (leaching) high oxidation state oxides can be synthesized from mixed-valence oxides.[1-5] For example, insoluble PrO_2 was prepared by selectively dissolving the Pr^{3+} ions from "Pr_6O_{11}" according to (1).[1,2] We wondered if lower valent compounds could

$$Pr_{12}O_{22}(s) + 12H^+(aq) = 4Pr^{3+}(aq) + 6H_2O + 8PrO_2(s) \quad (1)$$

be prepared by a comparable reaction in which the higher valent species was solvated preferentially. Crystal lattice energy considerations suggest that, for a given cation, salts with large, monovalent anions should dissociate more easily than salts in which the anion has a higher charge.[6] Hence heavy-metal mixed-valence chlorides, bromides, and iodides appeared to be a profitable area in which to initiate research. In the last decade numerous mixed-valence lanthanoid halide phases have been characterized. Examples include the vernier-type structures of the general formula M_nX_{2n+1} (M = lanthanoid; X = Cl, Br; n = 4-6)[7-10] and the $M_{14}X_{33}$ cluster-type compound.[9,10] Lanthanoid(III) chlorides are known to be soluble in tetrahydrofuran (THF); solubilities range from 0.5 to 1.9 g/100 mL of THF.[11] The dichlorides of samarium and europium are reported to be sparingly soluble in THF. They can be produced in THF by lithium metal/naphthalene reduction of the trichlorides. For Ln = Sm and Eu, the $LnCl_2$ phases are solvent-free, whereas for Ln = Yb, a solvate, $YbCl_2{\cdot}THF$ results.[12] We therefore investigated solvolytic decomposition reactions of lanthanoid chloride systems. Our primary goal was synthesis of $LnCl_2$ according to (2). An unexpected but interesting result

$$Ln^{II}{}_xLn^{III}{}_yCl_{2x+3y}(s) + ym\mathrm{THF} = xLnCl_2(s) + yLnCl_3{\cdot}m(\mathrm{THF}) \quad (2)$$

was the preparation at room temperature of the fluorite-type modification of $SmCl_2$ and $EuCl_2$. This modification had been reported previously to exist only at elevated temperatures. The low-temperature synthesis of this fluorite-type modification is presented and discussed.

Experimental Section

Chemical Reagents. Eu_2O_3 and Yb_2O_3: 99.99%, Research Chemicals, Phoenix, AZ. Sm_2O_3: 99.9%, Alfa Inorganics, Inc., Beverly, MA. Gd_2O_3: 99.9%, Michigan Chemical Corp., principal impurity of 500 ppm Ca. THF: "Baker Analyzed" reagent, J. T. Baker Chemical Co., Phillipsburg, NJ, was refluxed over sodium metal chips (benzophenone as indicator), distilled, and deoxygenated repeatedly prior to use by first

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freezing with liquid nitrogen, pumping to 10^{-5} Torr, and then warming to room temperature.

Anhydrous lanthanoid trichlorides were synthesized from the oxides by the HCl–NH_4Cl procedure.[13,14] Typical yield: >90%. Reduction to the mixed-valence chloride was effected with Matheson prepurified hydrogen (>99.999%), which flowed first over a Pd catalyst and then through a liquid-nitrogen-chilled trap before being passed over the sample.

Products were characterized by Guinier X-ray powder diffraction with monochromatized Cu Kα_1 (λ_{α_1} = 1.540 50 Å) radiation. NBS certified Si [a_0 = 5.430 82 (3) Å] served as the internal standard. Samples placed on Scotch Tape backed planchets were coated with paraffin oil maintained over elemental Na to protect them from hydrolysis during transfer to the evacuated Guinier camera. The program ITO9[15] was used for indexing the observed diffraction lines, APPLEMAN[16] for refining lattice parameters, and POWD12[17] for calculating X-ray powder diffraction intensities. Sample manipulations were carried out in a glovebox whose recirculated Ar atmosphere was continuously purged of H_2O (molecular sieves) and oxygen (heated BASF catalyst). (Typical glovebox moisture content was 30 ppm.) To determine the thermal stability of the fluorite form of $LnCl_2$ (Ln = Sm, Eu), specimens were heated in a high vacuum (10^{-5}–10^{-6} Torr) at progressively increasing temperatures and then examined by X-ray diffraction.

Chemical analysis of $SmCl_2$ was effected by dissolving weighed specimens in distilled water. The mass of the insoluble residue, subsequently identified as SmOCl, was determined gravimetrically. Chloride ion content was determined by titration with $AgNO_3$.

Mixed-Valence Lanthanoid Chloride Preparation by Hydrogen Reduction. $EuCl_x$ (2.0 < x < 3.0). Hydrogen reduction of ~1-g specimens of $EuCl_3$ confined in a tube furnace at ~465 °C typically produced the pale blue intermediate chloride in 3–4 h. Because at this temperature $EuCl_3$ will subsequently reduce to the dichloride, the time required for the reduction to the intermediate halides is sample-size dependent. Reduction was stopped when visual inspection indicated a pale blue color across the surface of the specimen. This powder product consisted of a mixture of the three intermediate chlorides,[9] Eu_4Cl_9, Eu_5Cl_{11}, and $Eu_{14}Cl_{33}$, with a trace of unreacted $EuCl_3$. No $EuCl_2$ was detectable by X-ray diffraction.

$Sm_{14}Cl_{33}$ ($Sm^{II}_9Sm^{III}_5Cl_{33}$). Controlled reduction of $SmCl_3$ at 650 °C for 3 h followed by in situ heating to 750 °C in flowing H_2 produced a melt, which with subsequent slow cooling in the oven yielded a back rocklike material. The pulverized material appeared dark brown. X-ray powder diffraction revealed in addition to unreacted $SmCl_3$ only the intermediate phase, $Sm_{14}Cl_{33}$. This intermediate is the same as that originally formulated as Sm_3Cl_7,[18] but by analogy with $Eu_{14}Cl_{33}$[9] (also originally formulated as Eu_3Cl_7) is correctly formulated as $Sm_{14}Cl_{33}$. The intermediate can also be prepared by melting $SmCl_2$ with excess $SmCl_3$ at 700 °C for 30 min. Hexagonal lattice parameters for $Sm_{14}Cl_{33}$ are a = 12.864 (2) Å and c = 12.36 (4) Å.

$Sm_9Gd_5Cl_{33}$. Reduction of a 1:1 molar ratio mixture of $SmCl_3$ and $GdCl_3$ at ~660 °C for 4 h, above the melting point of $GdCl_3$ (602 °C), produced a black product that is also dark brown after being pulverized. The product was a mixture of $GdCl_3$ and a phase of intermediate composition, which could be identified as the title compound by analogy with $Sm_{14}Cl_{33}$. There is no direct evidence for the title formula, i.e., that Gd^{3+} is the only trivalent ion. However, the given formulation is the best approximation of the weight loss upon reduction data. Hexagonal lattice parameters are a = 12.845 (2) Å and c = 12.347 (4) Å.

$Sm_9Nd_5Cl_{33}$. A mixture of $SmCl_3$ and $NdCl_3$ in a 9:5 molar ratio was reduced in hydrogen at 660 °C for 7 h and finally heated to 850 °C to produce a melt. Weight loss data suggested complete reduction of the Sm^{3+} ion. The diffraction pattern of the product is similar to that of $Sm_{14}Cl_{33}$ and is given the title formula. Hexagonal lattice parameters are a = 12.894 (2) Å and c = 12.425 (3) Å.

$YbCl_x$ (2.0 < x < 3.0). Reduction of $YbCl_3$ at 600–650 °C for 1 h gave a mixture of melted black and unmelted yellow compounds. The complicated mixture could not be characterized completely by X-ray diffraction. The intermediate phase reported to be $YbCl_{2.26}$[19] or Yb_6Cl_{13}[20] is observable. Unfortunately, the specimen contained substantial amounts of the oxide chloride.

Table I. Lattice Parameters and Calculated Densities of $LnCl_2$ (Ln = Sm, Eu) Fluorite-Type Phases

compd	a, Å	d, g cm^{-3}	T, °C	ref
$SmCl_2$	7.1496 (2)	3.996 (2)	775–785	21
	6.9827 (5)	4.3167 (9)	23 (2)	a
$EuCl_2$	7.150 (1)	4.073 (2)	800	20
	6.961 (1)	4.387 (2)	23 (2)	a

[a] This work.

Solvolytic Decomposition of the Mixed-Valence Chlorides by THF. An all-glass system with a Soxhlet extractor fitted with Teflon stopcocks and joint sleeves was used for the decomposition reactions. Dehydrated and deoxygenated THF was transferred under high vacuum to the reflux flask. The extractor with the sample in a removable thimble and transferred under Ar from the glovebox to the extraction apparatus. Extraction was effected in a dry argon atmosphere a minimum of 48 h to ensure complete trichloride removal even when the reaction seemed to occur rapidly. The $SmCl_2$–$NdCl_3$ system extraction required more than 5 days because of the low solubility of $NdCl_3$ in hot THF. When extraction was complete the leached product was pumped to dryness, blanketed with argon, and transferred into the glovebox for further treatment and analysis.

Results

Solvolytic Decomposition Products. Ytterbium dichloride was obtained as a yellow solvate with the approximate composition $YbCl_2 \cdot THF$, as reported by Rossmanith.[12] The composition was determined from weight loss upon THF removal at 200 °C in a 10^{-6} Torr vacuum. The recovered product is SrI_2-type $YbCl_2$.

Fluorite-type $EuCl_2$ was obtained as a fine white powder. Fluorite-type $SmCl_2$, a blue powder, resulted from extraction of both $Sm_{14}Cl_{33}$ and $Sm_9Gd_5Cl_{33}$. Chemical analysis indicated the composition to be $SmCl_{1.99(1)}$. Extraction of $Sm_9Nd_5Cl_{33}$ also yielded the fluorite modification, but the product was impure and exhibited a reddish color, a result that may be due to the low solubility of the $NdCl_3$ in THF.

Confirmation and Stability of the Structure. Lattice parameters for both $EuCl_2$ and $SmCl_2$ and their calculated densities are listed in Table I together with previously observed high-temperature literature values.[21,22] Experimental d values and powder diffraction intensities agree well with results calculated for a fluorite-type structure.

The fluorite modifications of $SmCl_2$ and $EuCl_2$ are definitely stable toward phase transformation at ambient temperature. Thermal tests indicate stability to 300 °C in high vacuum. After 9 h at 300 °C only a very small fraction of the fluorite forms of both dichlorides had transformed to the normal $PbCl_2$-type structure. Even after 11 h at 360 °C or 4 h at 430 °C only a portion of the $EuCl_2$ specimen had transformed. At 440 °C the fluorite form of $SmCl_2$ (blue) changed quantitatively into the thermodynamically stable low-temperature (red) form within hours.

Discussion

Although formulation of the reactants as $Sm_9M_5Cl_{33}$, for M = Gd and Nd, is based only upon X-ray and mass balance data, it is almost certainly correct. $GdCl_3$ cannot be reduced to a discrete Gd^{2+} ion even when elemental Gd is the reducing agent. $NdCl_3$, on the other hand, can be reduced to $NdCl_2$ with strong reducing agents,[23,24] but not with hydrogen.[25] Given the high moisture sensitivity of $M_{14}Cl_{33}$ phases and the known oxide chloride phase, $Nd_{14}Cl_{32}O$,[10] whose structure is almost indistin-

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guishable from that of the $M_{14}Cl_{33}$ phases, the presence of oxide chloride impurities in the reactants must be considered. Since lanthanoid oxide halides are insoluble in THF, any oxide chloride impurity would result after extraction as the MOCl phase, as was always observed for the oxide chloride contaminated $YbCl_2$. Typically, one very weak MOCl X-ray reflection was observed in the X-ray powder diffractograms of the fluorite-type dichlorides, and on occasion the same reflection was seen in the X-ray diffractograms of the $M_{14}Cl_{33}$ reactants. A lanthanoid oxide chloride impurity level of ~3% should normally be detected in the Guinier films because of the high symmetry of the cell and the large scattering power of the cation. Thus, it can be assumed from mass relationships that the specimens contained <~2% oxide chloride as $M'_8M_6Cl_{32}O$.

The hexagonal *c* lattice parameters observed for the various mixed $M_{14}Cl_{33}$ phases are half that reported for $Eu_{14}Cl_{33}$; the *a* parameters are similar. X-ray powder intensities calculated with the $Nd_{14}Cl_{33}$ atomic parameters[10] yielded intensities in general agreement with those observed and indicated that the "missing" reflections should be observable. The reason for this cell volume difference is not known but must reflect a subtle symmetry change.

Fluorite-type modifications of $SmCl_2$ and $EuCl_2$ have been observed at elevated temperatures with transformation temperatures of 768 ± 4 and 747 ± 5 °C, respectively.[26,27] This low-temperature solvolytic decomposition procedure provides a convenient mild condition synthesis route for the fluorite modification.

Efforts to extend this work to prepare $NdCl_2$ have been unsuccessful. The mixed-valent $NdCl_{2.29}$, prepared by reduction of $NdCl_3$ with elemental neodymium,[23] could not be decomposed to $NdCl_2$ by THF even in 9 days of extraction. The extraction product always contained some of the initial halide and, based upon weight loss on heating, an $NdCl_x$·THF complex. Since $NdCl_3$ could be recovered from the *solvent*, limited extraction did occur. The low-temperature $PbCl_2$ form of $NdCl_2$ is preparable by neodymium[23] or lithium[24] reduction of the trihalide. The unsuccessful preparation by the solvolytic decomposition method of either the fluorite or $PbCl_2$ form could be the result of instability of the assumed intermediate, the fluorite form of $NdCl_2$. This fluorite form would be the expected direct product of a leaching experiment based upon the similarity of structural properties of neodymium compounds and those of the samarium and europium analogues. On the other hand, the very low solubility of the $NdCl_3$·*x*THF solvate in THF could be the problem. However, the trihalide is completely removable, albeit under extended extraction conditions.

Even though at the microscopic level the formation mechanism of the fluorite form is uncertain, it is reasonable to speculate that formation of an apparently higher energy modification is kinetically controlled. While direct formation of the $PbCl_2$-type low-temperature form of the dichloride could occur via solvolytic decomposition by a one-step process, the presence of the fluorite-type high-temperature modification at low temperatures requires a valley in the reaction coordinate and, hence, a two-step process. The activation energies of the one-step process and the second step of the two-step process are presumed to be large because they involve structural changes from a fluorite or fluorite-related structure to the orthorhombic nine-coordinated $PbCl_2$-type structure common to $LnCl_2$ for Ln = Nd, Sm, and Eu.[28] The first step of the two-step process involves minimal structural change since the structures of the mixed-valence lanthanoid chlorides are closely related to that of fluorite[9] and hence are presumed to have a small activation energy. As the thermal tests indicate, the polymorphic transformation of fluorite form into the $PbCl_2$-type form indeed has a very high activation energy. However, on the basis of color change, formation of the fluorite modification begins almost instantly when the mixed-valence compound contacts the solvent. Therefore, under leaching conditions (~66 °C), the kinetically stabilized fluorite form is obtained.

The $YbCl_2$·THF solvate was a well-crystallized powder. We were unable to prepare single crystals suitable for structure determination because of the very low solubility in THF. This observation is inconsistent with a previous report,[12] which indicated the $YbCl_2$ solvate to be more soluble in THF than is $YbCl_3$. The $YbCl_2$·THF complex exhibits monoclinic symmetry with lattice parameters of $a = 12.591$ (7) Å, $b = 8.519$ (2) Å, $c = 7.290$ (3) Å, and $\beta = 102.30$ (3)° in space group $P2/c$ as determined by systematic extinctions of its powder diffraction pattern. The figure of merit for the indexing of the first 40 reflections is 21.9.[29]

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