is partly a change in the elastic energy of the crystal, while in step B the energy involved is partly U_{eff}, while a change in Coulomb energy occurs in each step. To clarify the various energy changes involved, we use the one-dimensional potential energy surfaces of the Sb(III, V) system drawn in Figure 1. Starting from the bottom of the potential well of the surface (III, V), in step A (eq 1) we end up on the crossing point of the surfaces (III, V) and (V, III) at $q = 0$. The second step B (eq 1) involves relaxing down to the (IV, IV) potential energy surface. q is some important vibrational coordinate along which electron transfer takes place.

Within the formalism of the rigid-ion lattice dynamical model the total potential energy change in these steps can be separated into Coulomb and short-range contributions. To calculate the Coulomb contributions to the total potential energy Φ for $\mathrm{Cs_2Sb^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6}$ and $\mathrm{Cs_2Sb^{IV}{}_{0.5}Sb^{IV}{}_{0.5}Cl_6}$, we note that from the definition of the Coulomb energy, if only the interaction of point charges is taken into account, the first derivative of the Coulomb energy $\Phi_C'(R) = -\Phi^C(R)/R$, where R is the distance between sites K and K′ in the lattice. This leads to the result[10] that the total Coulomb energy is given by $\Phi^C = -\sum_\alpha f_{\alpha\alpha}$ ($\alpha = x, y, z$), where $f_{\alpha\alpha}$ is the Coulomb contribution to the macroscopic stress of the crystal. The stress matrix has been explicitly calculated as part of the lattice dynamical calculations to ensure the stability of the crystal against external strain. For the hypothetical $\mathrm{Cs_2Sb^{IV}Cl_6}$ compound, the $\mathrm{Sb^{IV}}$–Cl bond length is taken as the average of the $\mathrm{Sb^{III}}$–Cl and $\mathrm{Sb^{V}}$–Cl bond distances;[5] similarly, the charge of the $\mathrm{Sb^{IV}}$ ion and the $\mathrm{Sb^{IV}}$–Cl, Cs–Cl, and Cl–Cl force constants are taken as averages of the corresponding parameters[8] of the $\mathrm{Cs_2Sb^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6}$ compound. From our calculation, we find

$$\Delta\Phi^C = \Phi^C(\mathrm{Cs_2Sb^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6}) - \Phi^C(\mathrm{Cs_2Sb^{IV}Cl_6}) = 3.8\ \mathrm{eV}$$

Considering only axially symmetric forces between neighboring atoms within the O'Leary and Wheeler[6] lattice dynamical model and making use of the force constants of $\mathrm{Cs_2SbCl_6}$, we can calculate the short-range energy needed to excite $\mathrm{Cs_2Sb^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6}$ to the equal bond length $[\mathrm{Cs_2Sb^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6}]^*$ state as $\Delta\Phi^{SR} = 2.1$ eV. Since the reaction (1) is endothermic, we have

$$-U_{\mathrm{eff}} + \Delta\Phi^{SR} + \Delta\Phi^{C} > 0 \qquad U_{\mathrm{eff}} < 5.9\ \mathrm{eV}$$

An approximate value of the endothermicity of the reaction can be obtained from the available optical data of $\mathrm{Cs_2SbCl_6}$. The intervalence band maximum occurs at ca. 2 eV, and it has been shown[11] that its position varies only slightly by doping it into the $\mathrm{Cs_2SnCl_6}$ lattice. The energy of step C corresponds to the onset of the intervalence band, i.e. to the zero phonon line. A reasonable value for this energy can be taken as 1.5 eV.[11,12] Then, $U_{\mathrm{eff}} <$ 4.4 eV. The value of U_{eff} obtained can be compared with the free-atom values above that indeed show a marked decrease with decreasing effective charge as expected. However, U_{eff} has been reduced from 11.9 eV in the gas phase to 4.4 eV in the solid; this value is smaller than even the gas-phase U_{eff} for the disproportionation $2\mathrm{Cd^+} \rightarrow \mathrm{Cd^0} + \mathrm{Cd^{2+}}$. Some idea of the reduction in U_{eff} due to screening by outer 5p electrons can be obtained by estimating the energy of the disproportionation $2(5s^1) \rightarrow 5s^0 + 5s^2$ in the presence of 5p electrons in the gas phase. For antimony we can estimate[4] the following energies

$$2(5s^1) \rightarrow 5s^0 + 5s^2 \qquad U_{\mathrm{eff}} = 11.9\ \mathrm{eV}$$

$$2(5s^1p^1) \rightarrow 5s^05p^1 + 5s^25p^1 \qquad U_{\mathrm{eff}} = 10.8\ \mathrm{eV}$$

$$2[5s^1(5p^2\,{}^3P)] \rightarrow 5s^0(5p^2\,{}^3P) + 5s^2(5p^2\,{}^3P) \qquad U_{\mathrm{eff}} = 10.4\ \mathrm{eV}$$

Again, only small changes in U_{eff} occur in the gas phase. This is because we have added only one or two electrons to $\mathrm{Sb^{3+}}$, compared with 12 added from six chloride ions.

However, the reductions in the value of U_{eff} are always large on going from the gas phase to the solid. Cox[13] has shown that as a result of polarization effects, both electronic correlation and lattice relaxation, the value of the intraatomic electron repulsion U_{eff} is reduced from about 15 eV in the gas phase to around 5 eV for the process $2(3d^n) \rightarrow 3d^{n-1} + 3d^{n+1}$ in oxides. Similarly, a study of the band structures of rare-earth metals by X-ray photoelectron spectroscopy and Bremsstrahlung isochromat spectroscopy[14] afforded an estimate of the intraatomic electron repulsion energies U_{eff} that are consistently lower by 11–12 eV than the corresponding free-atom values for the lanthanide series.

So far as we are aware, there are no other data on the reduction of U_{eff} in s shells of these elements and we are continuing our work for the estimation of U_{eff} in further mixed-valency systems involving post-4d and -5d elements.

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Registry No. $\mathrm{Cs_2Sb^{IV}Cl_6}$, 17805-64-0.

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Simplified Method for the Synthesis of Ceric Alkoxides from Ceric Ammonium Nitrate

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Cerium(IV) alkoxides can now be readily prepared in a one-step synthesis using ceric ammonium nitrite (CAN) as a starting material. CAN is a commercially available, stable, and soluble salt of cerium(IV). Previously reported syntheses have either been unsatisfactory or have required difficultly prepared starting material. A number of cerium(IV) alkoxides have been prepared from a tediously made dipyridinium cerium hexachloride.[4] Reaction of cerium metal with isopropyl alcohol in the presence of $\mathrm{HgCl_2}$ catalyst has been reported,[5] as well as the preparation of tricyclopentadienylcerium(IV) alkoxide.[6] There are relatively few reported studies and uses of cerium alkoxides, as compared to alkoxides of other metals. This may be partially a result of the difficulty of synthesis.

When CAN dissolved in a low molecular weight alcohol such as methanol, ethanol, or isopropyl alcohol is reacted with an appropriate base, the ceric alkoxide is formed readily and quantitatively. It is necessary for CAN to be in solution prior to the addition of the base. Since higher alcohols are less solubilizing for CAN, they can be used in admixture with methanol. In this case, methoxide is probably formed first and solubilized in the form of a complex with the higher alcohol. The alcohol exchange takes place very easily at relatively low temperatures. In some

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cases, a solvent such as benzene, hexane, or toluene may be added to the reaction mixture to keep the alkoxide in solution and facilitate separation from sodium or ammonium nitrate. When anhydrous ammonia is used as a base, 4 mol is sufficient as required by anhydrous reaction stoichiometry.

$$(NO_3)_4Ce{\cdot}2NH_4NO_3 + 4ROH + 4NH_3 \rightarrow Ce(OR)_4 + 6NH_4NO_3$$

When an alkali alkoxide is used instead of ammonia, it is preferable to provide some excess (up to 2 equiv) over the required 4 equivalents.

$$(NO_3)_4Ce{\cdot}2NH_4NO_3 + 4ROH + 6NaOCH_3 \rightarrow Ce(OR)_4 + 6NaNO_3 + 2NH_3 + 6CH_3OH$$

The excess of alkali alkoxide converts the NH_4NO_3 into alkali nitrate and ammonia, which makes the choice of workup less ambiguous and the material balance easier to establish.

Experimental Section

General Procedures. Ceric ammonium nitrate was dried at 115 °C overnight and stored under argon. Methanol was dried with sodium and distilled prior to use. Octyl alcohol was stored over Linde 3-Å molecular sieves. Ammonia gas was passed through a calcium oxide column before entering the reaction vessel. Fresh reagent grade 25% sodium methoxide in methanol was used. Weighing, filtering, and the preparation of cerium(IV) methoxide were done in an argon-filled glovebag. Distillations and the preparations of $Ce(OC_8H_{17})_4$ were done on the bench.

Cerium(IV) Methoxide. At room temperature under argon, 0.03 mol of ceric ammonium nitrate (16.45 g) (Rhone-Poulec Inc.) was dissolved in 304 g of methanol, resulting in a deep red solution. The argon flow was stopped, and ammonia gas was passed over the reaction solution. The absorption of the ammonia was so rapid that it was necessary to restore positive pressure by resuming the flow of argon. The ammonia uptake (24.7 g) was completed in 0.5 h, giving a bright yellow slurry. This reaction mixture was allowed to stir overnight.

In a glovebag, the product was filtered into a tared fritted glass funnel. The bright yellow product (10.1 g) was washed with methanol three times and dried in a desiccator over magnesium perchlorate under vacuum. Anal. Calcd for $Ce(OCH_3)_4{\cdot}CH_3OH$: C, 20.27; H, 5.44; Ce, 47.29; N, 0.00. Found: C, 18.70; H, 5.37; Ce, 46.58; N, <0.3%. To establish stoichiometry the colorless filtrate was distilled to dryness, giving 14.28 g of ammonium nitrate (calculated 14.41 g).

Ceric tetramethoxide can also be prepared from sodium methoxide instead of ammonia. The resulting sodium nitrate is separated from the product by extraction with methanol in a Soxhlet extractor.

Ceric Tetrakis(octyloxide). To a deep red solution of 0.01 mol of ceric ammonium nitrate (5.48 g) in 20.0 g of methanol was added 0.04 mol (5.2 g) of normal octyl alcohol followed by 13.1 g (0.06 mol) of 25% sodium methoxide solution (Aldrich Chemical Co., Milwaukee, WI). A bright yellow precipitate, probably the methoxide, formed immediately. The mixture was diluted with 25.3 g of toluene and stirred overnight. The methanol was completely removed by distillation, more toluene was added, and the sodium nitrate was removed by filtration and washed with five portions, 8 g each, of toluene. The mass of sodium nitrate recovered after drying was 5.0 g (calculated 5.1 g).

The toluene in the filtrate was removed under vacuum at room temperature (0.1 mm pressure), yielding 6.76 g of orange-red oil. Anal. Calcd for $Ce(OC_8H_{17})_4$: C, 58.50; H, 10.43; Ce, 21.3. Found: C, 58.44; H, 10.47; Ce, 21.8. ^1H NMR ($CDCl_3$): δ 0.90 (t, 3 H), 1.27 (s, 12 H), 3.56 (t, 2 H).

Discussion

In some cases the alkoxides can be used as intermediates for subsequent reactions directly in the reaction mixture in the presence of the nitrates. For instance, addition of acetylacetone instantly converts the alkoxide into ceric acetylacetonate. Thus, unnecessary workup can be avoided.

The methoxides, especially, are susceptible to rapid hydrolytic decomposition by the action of humidity. Only carefully handled samples show correct elemental analyses. The byproduct nitrates, however, can be separated from the product with relative ease; the amount recovered indicated quantitative reaction in most cases.

The octyloxides seem to be less susceptible to hydrolysis than the methoxides. Samples of $Ce(OC_8H_{17})_4$ were successfully prepared outside the glovebag in Boulder, CO, under the local, usually relatively low, humidity. However, $Ce(OC_8H_{17})_4$ is not as thermally stable as $Ce(OCH_3)_4$. It decomposes at 240–260 °C, while the methoxide is stable to at least 280 °C. A brownish yellow solid remained in the capillary tube used to obtain mass spectra of $Ce(OC_8H_{17})_4$. The largest peaks observed in the mass spectrum were at *m/e* 398 and 400, corresponding to $^{140}Ce(OC_8H_{17})_2^+$ and $^{142}Ce(OC_8H_{17})_2^+$ (70-eV electron impact ionization). The $Ce(OCH_3)_4$ showed no tendency to be volatilized in the mass spectrometer, possibly indicating that it forms a nonvolatile oligomer.

During all of these syntheses, we did not observe violent reactions between the ceric ammonium nitrate and the organic alcohols and solvents. One generally tries to avoid mixing organic materials with strong oxidizing agents such as Ce(IV). These reactions, however, are highly dependent on the acidity of the solution.[7] In strongly alkaline solutions the explosion hazards appear to be minimal.

Registry No. $(NO)_3)_4Ce{\cdot}2NH_4NO_3$, 22549-43-5; $Ce(OCH_3)_4$, 94957-38-7; $Ce(OC_8H_{17})_4$, 94957-39-8; CH_3OH, 67-56-1; sodium methoxide, 124-41-4; octyl alcohol, 111-87-5.

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^{95}Mo NMR Studies of Seven-Coordinate Molybdenum(VI) Monooxo, Nitrido, and Phenylimido Complexes and Their Derivatives

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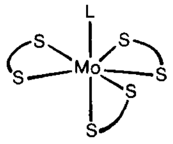
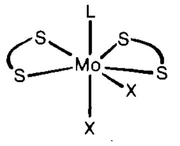
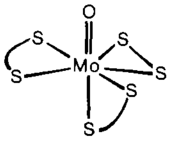
Molybdenum(VI) dioxo complexes have been extensively studied[1-7] by ^{95}Mo NMR, partly because the catalytic molybdenum center in enzymes such as sulfite oxidase and nitrate reductase is believed to have a $[MoO_2]^{2+}$ core in the oxidized state.[8,9] In contrast, no ^{95}Mo NMR data have been reported for Mo(VI) monooxo, nitrido, and phenylimido complexes. Here, we report the first ^{95}Mo NMR study of such complexes. The majority of the complexes studied possess one of the seven-coordinate structures shown (bidentate ligand = $S_2CNR_2^-$).



L = O, NPh (1+)
N, NO, NS.



L = O, NPh.
X = Cl, Br.



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