H_2CHCH_2 (**3**) along with a trace of $[(CH_3)_3Ge]_2PCH_2CHCH_2$ (**4**); **4** condensed at 0 °C. Repeated fractionation yielded pure **3** and **4**.

Characterization of 3. ^{1}H NMR (40% in C_6D_6) δ 2.25 (d of t, J = 186.0 Hz, $^{3}J_{HH}$ = 7.0 Hz, area 1; PH) 0.3 [d, ^{3}J = 4.0 Hz, area 9; $(CH_3)_3Ge$], 2.0–2.6 (complex, area 2; CH_2), 4.7–6.1 (ABX, area 3; CH_2CH); ^{31}P NMR (40% in C_6D_6) δ −139.7 (d, J = 186 Hz); mass spectral, IR, and and elemental analyses not obtained, owing to rapid sample thermal decomposition.

Characterization of 4. Anal. Calcd for $C_9H_{15}PGe$: C, 35.16; H, 7.54. Found: C, 34.22; H, 7.37. ^{1}H NMR (10% in C_6D_6) δ 0.3 [d, J = 4.0 Hz, area 9; $(CH_3)_3Ge$], 2.45 (d, J = 9 Hz, area 1; CH), 4.7–6.1 (ABX, area 3; CH_2CH); ^{31}P NMR (20% in C_6D_6) δ −149.6 (s); mass spectrum, parent at *m/e* 308 $[C_9H_{23}{}^{76}Ge_2P^+]$; IR 3081 (s), 2978 (vs), 2913 (vs), 2801 (m), 1818 (m), 1637 (s), 1428 (m), 1410 (s), 1238 (vs), 1199 (m), 1059 (s), 990 (s), 909 (vs), 754 (s), 592 (vs), 512 (s), 406 (m) cm^{-1}.

Reaction of 1 and 3. Compounds **1** and **3** in C_6D_6 in NMR tubes in separate experiments were allowed to warm to 25 °C, while being monitored periodically by ^{31}P NMR spectral analysis. **1** reacts rapidly, yielding only resonances due to **2** (δ −168.1) and $CH_2CHCH_2PH_2$ (δ −132.6). **3** after 100 h at 25 °C underwent redistribution, exhibiting resonances attributed to **3**, **4**, and $CH_2CHCH_2PH_2$ in a ratio of 1.0:2.4:2.4.

Radical reactions of **3** were carried out in NMR tubes, typically by heating **3** (1.5 mmol) with ca. 8 mg of AIBN in C_6D_6 (5.0 mmol). After 3 h at 75 °C, the ^{31}P NMR spectrum showed a major doublet resonance at δ −228.1 [J = 182.0 Hz, singlet in $^{31}P\{^{1}H\}$ NMR spectrum] and a collection of very small peaks between δ −30 and δ −100. No **3** remained, and no **4** or $CH_2CHCH_2PH_2$ formed. Volatile material was removed in vacuo, separated by fractional condensation, and characterized as $[(CH_3)_3Ge]_2PH$ (**5**). Anal. Calcd for $C_6H_{19}Ge_2P$: C, 26.96; H, 7.16; P, 11.58. Found: C, 27.10; H, 7.21; P, 11.39. ^{31}P NMR δ −228.0; 1H NMR δ 0.4 [d, J = 4.5 Hz, area 18; $(CH_3)_3Ge$], 1.0 (d, J = 174 Hz, area 1; PH); mass spectrum, parent at *m/e* 268 $[^{12}C_6H_{19}{}^{76}Ge_2P^+]$; IR (neat film) 2977 (s), 2896 (vs), 2291 (vs), 406 cm−1.

Involatile reaction materials were partially soluble in C_6H_6. ^{31}P NMR spectra of this material exhibited complex resonances in the δ −30 and δ −100 regions; however, the material was not characterized further.

The rapid thermal decomposition of **1** in solution precluded studying its AIBN-promoted radical reactions.

Hydrolysis of **1** and **2** yields $CH_2CHCH_2PH_2$ and $[(CH_3)_3Si]_2O$ rapidly; **3** and **4** react slowly with H_2O to form $[(CH_3)_3Ge]_2O$ and $CH_2CHCH_2PH_2$.

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Registry No. **1**, 94570-42-0; **2**, 94570-46-4; **3**, 94570-43-1; **4**, 94570-44-2; **5**, 94570-45-3; $CH_2CHCH_2PH_2$, 81637-99-2; $(CH_3)_3SiI$, 16029-98-4; $(CH_3)_3GeBr$, 1066-37-1; $[(CH_3)_3Si]_2O$, 107-46-0; $[(CH_3)_3Ge]_2O$, 2237-93-6.

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Estimation of the Effective On-Site One-Center Coulomb Repulsion Energy *U* in Mixed-Valence Cs_2SbCl_6

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Mixed valency[1] is a widespread phenomenon in the periodic table. In the groups 11–17,[15] particularly for post-4d and -5d elements, the oxidation state $N-2$, where N is the group oxidation state, is frequently stabilized. Thus, the usual combination of oxidation states when mixed-valency compounds are formed by these elements is $(N-2, N)$. Other examples of mixed valency with a difference of 2 in oxidation state are provided by the later 4d and 5d transition elements, where compounds with electron configurations d^6, d^8 (e.g., $Pt(NH_3)_2Cl_3$) and d^8, d^{10} (e.g., $CsAuCl_3$) are found.

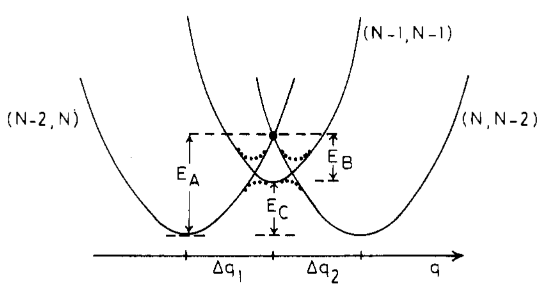

Figure 1. Potential energy surfaces for two-electron-difference mixed-valency systems. E_A, E_B, and E_C refer to (1).

In such crystals, a charge-ordered class II[1] ground state results from the localization of electron pairs on alternate metal ion sites and charge density alternation between neighboring sites. An alternative way of viewing $(N-2, N)$ mixed-valency compounds is to say that disproportionation of the type $e^1 + e^1 \rightarrow e^2 + e^0$ has taken place. These two-electron-difference mixed-valency systems are then examples of what solid-state physicists[2] have called the "negative *U*" effect;[2] i.e., in the Hubbard[3] model the Hamiltonian of the system includes a single-center Coulomb repulsion parameter U_{eff} that appears to be negative. Physically this means that the repulsion U of two electrons occupying the same orbital is outweighed by the gain in lattice Coulomb energy and the gain in elastic energy associated with strong electron–phonon coupling.

In the gas phase the energy U required to accomplish the disproportionation $5s^1 + 5s^1 \rightarrow 5s^2 + 5s^0$ for isolated ions is simply the difference between the Nth and the $(N-1)$th ionization potentials of the elements involved: Cd, $I_2 - I_1$ = 7.9 eV; In, $I_3 - I_2$ = 9.2 eV; Sn, $I_4 - I_3$ = 10.2 eV; Sb, $I_5 - I_4$ = 11.9 eV. In a solid, $U_{eff} < U$ as a result of increasing effects, reduced ionicity, and electron correlation.

Considering the Sb(III, V) salt Cs_2SbCl_6 as an example, recent experiments in this laboratory have accumulated enough information to place an upper limit on U_{eff} for the above disproportionation reaction. We have determined the crystal structure of Cs_2SbCl_6[5] and identified the superlattice ordering of Sb(III) and Sb(V), including the bond lengths and angles of the constituent $SbCl_6{}^{3-}$ and $SbCl_6{}^{-}$. Further, a set of force constants and ionic charges for this lattice is available from a rigid-ion[6,7] lattice dynamical calculation[8] fitted to published[9] infrared and Raman data, which also gives a good account of the complete phonon density-of-states up to 400 cm^{-1} measured by incoherent inelastic neutron scattering.[8] Consider the following thermodynamic cycle:

$$\begin{tikzcd}
Cs_2Sb^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6 \arrow[rr, "C"] \arrow[dr, "A"'] & & Cs_2Sb^{IV}{}_{0.5}Sb^{IV}{}_{0.5}Cl_6 \\
& {[Cs_2Sb^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6]^*} \arrow[ur, "B"'] &
\end{tikzcd} \quad (1)$$

$Cs_2Sb^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$ refers to the equilibrium state of the (III, V) mixed-valency salt. In step A, we produce an excited state $[Cs_2Sb^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6]^*$ by contracting the Sb^{III}–Cl and extending the Sb^{V}–Cl bond lengths to the Sb^{IV}–Cl equilibrium bond lengths. In step B, electron transfer between the Sb^{III} and Sb^{V} sites results in the relaxed $Cs_2Sb^{IV}{}_{0.5}Sb^{IV}{}_{0.5}Cl_6$ state.

The chemical fact of the nonexistence of $Cs_2Sb^{IV}Cl_6$ indicates that the overall reaction in (1) is endothermic. In step A, there

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(1) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

(2) Anderson, P. W. *Phys. Rev. Lett.* **1975**, *34*, 953.

(3) Hubbard, J. *Proc. R. Soc. London, Ser. A* **1964**, *276*, 238.

(4) Moore, C. E. "Atomic Energy Levels"; National Bureau of Standards: Washington, DC, 1952.

(5) Prassides, K.; Day, P.; Cheetham, A. K. *J. Am. Chem. Soc.* **1983**, *105*, 3366.

(6) O'Leary, G. P.; Wheeler, R. G. *Phys. Rev. B: Solid State* **1970**, *1*, 4909.

(7) Sutton, M.; Armstrong, R. L.; Powell, B. M.; Buyers, W. J. L. *Phys. Rev. B* **1983**, *27*, 280.

(8) Prassides, K.; Day, P. *Inorg. Chem.*, in press.

(9) Clark, R. J. H.; Trumble, W. R. *J. Chem. Soc., Dalton Trans.* **1976**, 1145. Clark, H. W.; Swanson, B. I. *J. Am. Chem. Soc.* **1979**, *101*, 1604. Burrowcliffe, T.; Beattie, I. R.; Day, P.; Livingstone, K. *J. Chem. Soc. A* **1967**, 1810.

0020-1669/85/1324-1109$01.50/0

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 $Cs_2Sb^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$ and $Cs_2Sb^{IV}{}_{0.5}Sb^{IV}{}_{0.5}Cl_6$, 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 $Cs_2Sb^{IV}Cl_6$ compound, the Sb^{IV}–Cl bond length is taken as the average of the Sb^{III}–Cl and Sb^{V}–Cl bond distances;[5] similarly, the charge of the Sb^{IV} ion and the Sb^{IV}–Cl, Cs–Cl, and Cl–Cl force constants are taken as averages of the corresponding parameters[8] of the $Cs_2Sb^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$ compound. From our calculation, we find

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

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 Cs_2SbCl_6, we can calculate the short-range energy needed to excite $Cs_2Sb^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$ to the equal bond length $[Cs_2Sb^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6]^*$ state as $\Delta\Phi^{SR} = 2.1$ eV. Since the reaction (1) is endothermic, we have

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

An approximate value of the endothermicity of the reaction can be obtained from the available optical data of 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 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, $U_{eff} <$ 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 $2Cd^+ \rightarrow Cd^0 + Cd^{2+}$. 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

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

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

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

Again, only small changes in U_{eff} occur in the gas phase. This is because we have added only one or two electrons to 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. $Cs_2Sb^{IV}Cl_6$, 17805-64-0.

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(10) Boyer, L. L.; Hardy, J. R. *Phys. Rev. B: Solid State* **1973**, *7*, 2886.
(11) Atkinson, L.; Day, P. *J. Chem. Soc. A* **1968**, 2423.
(12) Prassides, K.; Day, P. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 85.
(13) Cox, P. A. "Proceedings of International Symposium on Properties of Transition Metal Oxides", in press.
(14) Lang, J. K.; Baer, Y.; Cox, P. A. *J. Phys. F* **1981**, *11*, 121.
(15) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

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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 $HgCl_2$ 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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(1) Rhone-Poulec Inc.
(2) University of Colorado, Denver.
(3) University of Colorado, Boulder.
(4) (a) Bradley, D. C.; Chatterjee, A. K.; Wardlaw, W. *J. Chem. Soc.* **1956**, 2260–2264. (b) *Ibid.* **1956**, 3469–3472; (c) *Ibid.* **1957**, 2600–2604.
(5) Brown, L. M.; Mazdiyasni, K. S. *Inorg. Chem.* **1970**, *9*, 2783–2786.
(6) Kapur, S.; Multani, R. K. *J. Organomet. Chem.* **1973**, *63*, 301–303.