equatorial coupling (angle $H_BC_6C_5H_X$ in the solid, $-34 \pm 3°$). J_{BP} (5.7 Hz) is small (angle H_BC_6OP in the solid, $88 \pm 2°$). Predictably, $\delta_{H_B} > \delta_{H_A}$.[14,15] That **6** should populate a *single* twist form in solution is not surprising, since the 1,3,2-oxazaphosphorinane ring lacks the symmetry of the 2,5-disubstituted-2-oxo-1,3,-2-dioxaphosphorinanes in which two rapidly interconvertible mirror image 2,5-twist forms are populated.[15b,17]

The 1,3,2-oxazaphosphorinane **6** is *primarily* in the twist form (**8**) in solution with no more than minor amounts of chair conformer **9** or *other* twist form populated.[18] This twist preference appears even greater than that of the analogous 1,3,2-dioxaphosphorinane (**6**, PhN = O), 60% of which populates *dl*-pair twist conformers.[15b,19] The relative case of accessibility of twist forms to the 2-oxo-1,3,2-oxazaphosphorinane system is further illustrated by the fact that the trans counterpart of **6** is in a twist conformation in the solid though not in solution.[20]

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(18) Small temperature effects on the ^{1}H NMR spectra of **6** over the range -50 to $+105$ °C confirm the greater enthalpic stability of **8** over **9**.

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Outer-Sphere Chemical Activation for Electron Transfer in the Mixed-Valence Solid $Cs_2(Sb^{III}{}_xSb^V{}_xSn_{1-2x})Cl_6$

Sir:

Resonance Raman studies provide a direct probe of the structural changes required in going from a ground to an excited electronic state.[1] In the case of mixed-valence materials, resonance Raman data obtained when the excitation frequency is tuned to the intervalence transfer (IT) absorption band can clarify the Franck–Condon restrictions for electron transfer.[2-5] Further, those vibrational modes which show resonance enhancement through vibronic coupling to the IT transition are, in principle, the same modes involved in the chemical activation step for thermal electron transfer.[2-4] This is particularly true of outer-sphere mixed-valence solids wherein the coordination spheres of the metal ions involved do not share a common ligand, thereby creating a weak-overlap or localized-valence situation. We report a resonance Raman study of the outer-sphere mixed-valence solid $Cs_2(Sb^{III}{}_xSb^V{}_xSn_{1-2x})Cl_6$ where $(SbCl_6)^{-1}$-$(SbCl_6)^{-3}$ pairs have been doped into a host Cs_2SnCl_6 lattice. The results demonstrate resonance enhancement of the *host* Cs_2SnCl_6 vibrational modes due to Raman excitation within the dopant IT band.

In a recent resonance Raman study of the mixed-valence solid $Cs_2(Sb^{III}{}_{0.5}Sb^V{}_{0.5})Cl_6$, Clark and Trumble demonstrated the IT resonance enhancement of a combination band involving a lattice mode and the symmetric stretch of the $SbCl_6{}^{-1}$ ion.[6] This observation of IT enhancement of lattice modes suggests that lattice structural changes accompany the Sb^{III}-Sb^V electron transfer in addition to the expected structural changes of the $(SbCl_6)^{-3}$ and $(SbCl_6)^{-1}$ complex ions. In order to elucidate further the involvement of the lattice structure in solid-state electron transfer, a resonance Raman study of $Cs_2(Sb^{III}{}_xSb^V{}_xSn_{1-2x})Cl_6$ has been carried out. The host Cs_2SnCl_6 lattice has no electronic transition in the region of the Sb^{III}-Sb^V IT absorption.

The $Cs_2(Sb^{III}{}_xSb^V{}_xSn_{1-2x})Cl_6$ was synthesized using Day's previously reported rapid precipitation method.[7] The Raman spectra were gathered on a Cary-82 spectrometer using Ar^+ and Kr^+ ion lasers. Laser power was typically set at <100 mW to prevent sample decomposition. The excitation profile was obtained by using all available lines of the Ar^+ and Kr^+ lasers. Spectral response of the Cary-82 was calibrated for each point by comparison to a $CaSO_4$ standard. The excitation profile was obtained by plotting the intensity of the sample divided by the intensity of the standard vs. the laser exciting line. The sample was analyzed by X-ray fluorescence and found to contain 36% antimony.

Figure 1 shows the spectra of pure Cs_2SbCl_6, pure Cs_2SnCl_6,

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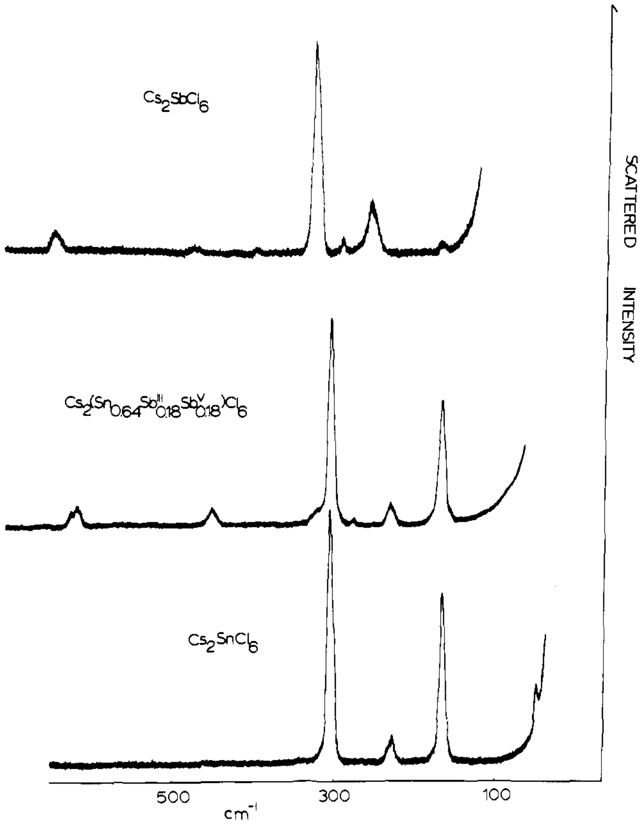

Figure 1. Raman spectra of Cs_2SnCl_6, $Cs_2(Sb^{III}_{0.5}Sb^{V}_{0.5})Cl_6$ and $Cs_2(Sb^{III}_{0.18}Sb^{V}_{0.18}Sn^{IV}_{0.64})Cl_6$ obtained using the 5208-Å line of the Kr ion laser.

and the doped material, $Cs_2(Sb^{III}_{0.18}Sb^{V}_{0.18}Sn_{0.64})Cl_6$. It should be noted that the doped compound exhibits many of the characteristics of the host Cs_2SnCl_6 nonresonance enhanced spectrum and a very weak contribution from the Cs_2SbCl_6. However, there are several new features as well. In particular, the appearance of higher frequency progressions indicates the presence of resonance enhancement. These bands, however, can only be assigned to progressions of the host Cs_2SnCl_6 modes and combination modes between $(SbCl_6)^{-1}$ and $(SnCl_6)^{-2}$ complex ion vibrations. An examination of the excitation profile (Figure 2) further demonstrates the resonance enhancement of the A_{1g} and T_{2g} modes of the host Cs_2SnCl_6 lattice. Thus, even though pure Cs_2SnCl_6 shows no resonance enhancement, doping the Sb^{III}–Sb^{V} electron-transfer pair into the Cs_2SnCl_6 lattice results in enhancement of the host vibrational modes. The frequencies and assignments[8] for the observed Raman modes of Cs_2SnCl_6, Cs_2SbCl_6, and $Cs_2(Sb^{III}_{0.18}Sb^{V}_{0.18}Sn_{0.64})Cl_6$ are given in Table I.

The resonance enhancement of the host Cs_2SnCl_6 phonons demonstrates that the host lattice is strongly involved in the electron-transfer process. We can exclude the possibility that an Sb^{III}–Sn^{IV} redox reaction during preparation resulted in the formation of Sn^{II}, thereby creating a Sn^{II}–Sn^{IV} chromophore in the doped compound. The absence of Sn^{II} vibrations in the Raman spectra and the unfavorable potentials for the reduction of Sn^{IV} by Sb^{III} make this unlikely. A second possibility, that Sb^{III}–Sn^{IV} electron transfer is the source of the absorption in the doped system rather than the Sb^{III}–Sb^{V} as in the pure compound, is similarly unlikely. If this were the case, one would expect resonance enhancement of the Sb^{III} modes and no involvement from the Sb^{V} vibrational modes. Instead, we observe enhancement of the $(Sb^{V}Cl_6)^{-1}$ modes and no discernible enhancement of the $(Sb^{III}Cl_6)^{-3}$ modes.

These facts lead us to conclude that the Sb^{III}–Sb^{V} intervalence-transfer excitation is responsible for the IT absorption

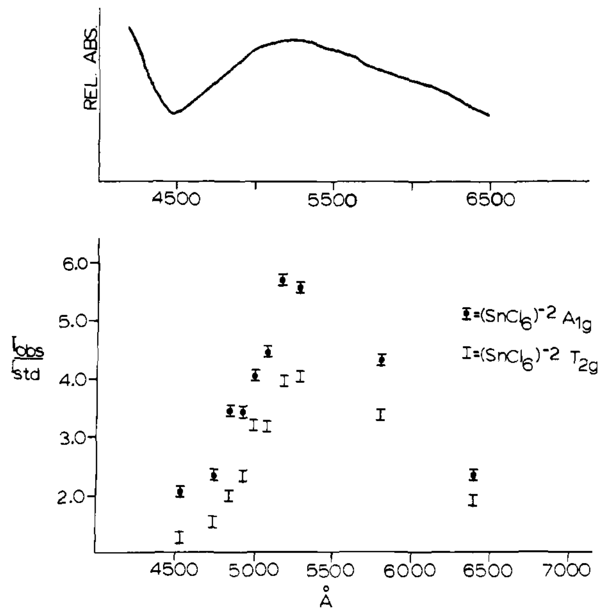

Figure 2. Top: the photoacoustic spectrum (PAS) of $Cs_2(Sb^{III}_{0.18}Sb^{V}_{0.18}Sn^{IV}_{0.64})Cl_6$. Bottom: Excitation profile of ν_1 (A_{1g}, Sn–Cl stretch) and ν_5 (T_{2g} Cl–Sn–Cl deformation) obtained for the doped compound $Cs_2(Sb^{III}_{0.18}Sb^{V}_{0.18}Sn^{IV}_{0.64})Cl_6$.

Table I. Observed Raman Frequencies[a]

assignments	Cs_2SnCl_6	$Cs_2(Sb^{III}_{0.18}Sb^{V}_{0.18}Sn_{0.64})Cl_6$	Cs_2SbCl_6
$2\nu_1$ (A_{1g}, Sb^{V}–Cl str)			650
ν_1 (A_{1g}, Sb^{V}–Cl str) + ν_1 (A_{1g}, Sn–Cl str)		627	
$2\nu_1$ (A_{1g}, Sn–Cl str)		619	
ν_5 (T_{2g}, Cl–Sb^{V}–Cl def) + ν_1 (A_{1g}, Sb^{V}–Cl str)			501
ν_5 (T_{2g}, Cl–Sn–Cl def) + ν_2 (E_g, Sb^{V}–Cl str)		454	
ν_1 (A_{1g}, Sb^{V}–Cl str) + ν_2 (Sb lattice)			384
ν_1 (A_{1g}, Sb^{V}–Cl str)		324	324
ν_1 (A_{1g}, Sn–Cl str)	310	308	
ν_2 (E_g, Sb^{V}–Cl str)			286
ν_1 (A_{1g}, Sb^{V}–Cl str) − ν_9 (T_{2g}, Cs trans)		279	
ν_1 (A_{1g}, Sb^{III}–Cl str)			257
ν_2 (E_g, Sn–Cl str)	230	229	
ν_5 (T_{2g}, Cl–Sb–Cl def)			175
ν_5 (T_{2g}, Cl–Sn–Cl def)	170	168	
ν_9 (T_{2g}, Cs trans)	48		

[a] Reciprocal centimeters.

and that the Cs_2SnCl_6 resonance enhancement reflects tremendous structural response of the host lattice to the inner-sphere ("intramolecular") reorganizations accompanying the Sb^{III}–Sb^{V} electron transfer. The appearance of combination modes of both $(SbCl_6)^{1-}$ and $(SnCl_6)^{2-}$ complex ion vibrations also indicate that the chromophore and host phonon modes are strongly coupled. To the extent that the response of a host lattice to the dynamic motion accompanying solid-state electron transfer resembles the outer-sphere structural rearrangement required for electron transfer in solution, the present work provides the first example of a direct probe of the reorganization associated with outer-sphere chemical activation in electron-transfer reactions. In the present case the lattice relaxation must involve distortions along the totally symmetric $(SnCl_6)^{-2}$ stretch (str) and the T_{2g} symmetry Cl–Sn–Cl deformation (def) as well as the expected changes in the geometries of the $(SbCl_6)^{-1}$ and $(SbCl_6)^{-3}$ complex ions. Generally, only totally symmetric vibrations are resonance enhanced. The observed resonance enhancement of the T_{2g} Cl-Sn-Cl deformation and the combination band involving T_{2g} and E_g symmetry modes (Table I) suggests that the F_{m3m} selection rules, which apply to the pure Cs_2SnCl_6 lattice, are removed in the doped compounds.

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Chemistry of Transition Metal-Phosphine and -Phosphite Complexes. 1. Photochemical Substitution Reactions of Tetrakis(triphenyl phosphite)cobalt(I) Hydride

Sir:

Trialkyl and triaryl phosphite stabilized cobalt hydrides have been shown to be relatively inert to phosphite substitution reactions.[1-3] The substitution of a phosphite ligand in general requires long reaction times (1-6 weeks), elevated temperatures (~100 °C), and/or elevated pressures (1-10 atm of CO) with resulting low yields.

During the course of our studies on the chemistry of $HCo[P(OC_6H_5)_3]_4$ we have found that this complex undergoes facile ligand substitution reactions when irradiated with 340-nm light in the presence of another ligand according to

$$HCo[P(OC_6H_5)_3]_4 + L \xrightarrow{h\nu} HCo[P(OC_6H_5)_3]_3L + P(OC_6H_5)_3 \quad (1)$$

Good yields have been obtained in relatively short reaction times. The substitution of the first $P(OC_6H_5)_3$ was found to be essentially complete after only 20-min photolysis.[4] Typically, for L = CO, a solution of 9.7 g (7.35 mmol) of $HCo[P(OC_6H_5)_3]_4$ in 300 mL of tetrahydrofuran (THF) was purged with CO for 5 min. The solution was then irradiated with a 450-W Ace-Hanovia immersion lamp for 20 min while the CO bubbling was maintained. Vacuum removal of the THF and a benzene-*n*-propanol recrystallization afforded 6.0-6.5 g (83-90% theoretical) of pure $HCo[P(OC_6H_5)_3]_3CO$.[5] Yields of monosubstituted products where L = phosphite were in general slightly lower. Shorter photolysis times left unreacted $HCo[P(OC_6H_5)_3]_4$, while longer reaction times produced less of the desired $HCo[P(OC_6H_5)_3]_3L$ products.

Infrared analysis of the reaction mixture, where L = CO, photolyzed for several hours indicated the presence of significant amounts of $HCo[P(OC_6H_5)_3]_2(CO)_2$ and $[Co(CO)_3P(OC_6H_5)_3]_2$. Indeed, both of these complexes were isolated in significant yield from the reaction mixture any time the photolysis exceeded 1 h. The substitution of the second phosphite to form the $HCoL_2L'_2$ complexes was found to proceed far more slowly than the substitution of the first phosphite under identical conditions. These observations indicated to us that the photochemical substitution process, for L = CO, was proceeding stepwise according to Scheme I. The tricarbonyl hydride, $HCo(CO)_3P(OC_6H_5)_3$, has been reported[6] to decompose rapidly above 0 °C to form H_2 and $[Co(CO)_3L]_2$ analogous to the thermal decomposition[7] of $HCo(CO)_4$ to produce H_2 and $[Co(CO)_4]_2$.

Scheme I

$$HCoL_4 + CO \xrightarrow{h\nu} HCoL_3CO + L$$
$$\xrightarrow[h\nu]{+CO} HCoL_2(CO)_2 + L \xrightarrow[CO]{h\nu} HCoL(CO)_3 \longrightarrow [CoL(CO)_3]_2$$

Scheme II

$$HCoL_4 + S \overset{h\nu}{\rightleftarrows} \text{“}HCoL_3S\text{”} + L \underset{-L'}{\overset{+L'}{\rightleftarrows}} HCoL_3L' + S$$

The monocarbonyl was found to be photochemically inert to the substitution of the CO by phosphite, even in the presence of a 10-fold excess of phosphite. Thus, it appears that reaction 1, for L = CO, is photochemically as well as thermally[3] irreversible. Consequently, when $HCo[P(OC_6H_5)_3]_3CO$ was photolyzed as described above, but in the absence of added substrate, essentially quantitative recovery of $HCo[P(OC_6H_5)_3]_3CO$ occurred. Preliminary studies indicate that for L = phosphite, reaction 1 is photochemically reversible and the reaction rate is independent of the amount of added phosphite. This implies that ligand dissociation to form the coordinatively unsaturated "$HCoL_3$" intermediate is the rate-determining step as shown in Scheme II. It is quite likely that the coordinatively unsaturated intermediate "$HCoL_3$" exists as a THF solvate, "$HCoL_3$-THF", analogous to the known acetonitrile complex $HCo[P(OC_6H_5)_3]_3(CH_3CN)$.[8] Infrared analysis of the reaction mixture produced when $HCo[P(OC_6H_5)_3]_4$ is photolyzed in a 50:50 THF-CH_3CN mixture under nitrogen, followed by bubbling with CO, shows the presence of both the monocarbonyl and dicarbonyl substitution products. This can be taken to indicate the presence of a solvated intermediate "$HCoL_3$-solvate" in the ligand substitution process. However, it does not entirely rule out the possibility of an ortho-metalated intermediate.[1] The failure of our attempts to isolate the solvated complex is probably due to the presence of the liberated phosphite, which is known to rapidly displace acetonitrile from $HCoL_3(CH_3CN)$ complexes to form $HCoL_4$.[8]

The synthetic utility of this very interesting photochemical reaction warrants further study. Studies directed along these lines as well as at establishing the nature of the purported intermediate are currently in progress in our laboratories.

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