shoulder (MLCT) overlapping the 270-nm band of the unreacted oligomer.

There is some motivation for pursuing the photochemistry of these systems in view of the propensity for metal-free polysilanes to cross-link. This behavior offers the possibility of supplementary immobilization of preformed metal aggregates in the polymer matrix. Initial broad-band photolysis studies of oligosilastyrene-bound Ti showed that incorporation of the transition metal as the sandwich complex, however, suppresses photochemistry.

These experiments using transition-metal vapors to form metal-containing complexes in silastyrene derivatives can be viewed as successful first steps toward the synthesis of metal-doped polysilane polymers.

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Pressure Effects in Scalar Coupling in $Co(H_2O)_6^{2+}$ and High-Spin–Low-Spin Equilibria in (1,4,8,11-Tetraazaundecane)nickel(II) Studied by Oxygen-17 Nuclear Magnetic Resonance

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In a previous publication[1], we described the use of oxygen-17 NMR for studying high-spin–low-spin equilibria in nickel(II) tetraamines. To use our chemical shift approach at elevated pressures it is necessary to investigate the scalar coupling (A/h) between the paramagnetic metal ion and $^{17}OH_2$ as a function of pressure. The $Co(H_2O)_6^{2+}$ ion is a good species to use for this purpose as a relatively simple "fast-exchange" region is easily accessible. Merbach and co-workers[2] indicate that shifts in this region are "not strongly pressure dependent". We have undertaken a precise study of this point.

Work has appeared on some nickel(II) tetraamine systems including a ^1H NMR study by Merbach et al.[3] and an absorption spectral study by Kitamura[4] with ΔV° values ranging from +10 to ca. +1 cm³/mol for the process $Ni(H_2O)_2L \leftrightarrow NiL + 2H_2O$. Since the ΔV° values found are smaller than might have been anticipated, the systems are of considerable interest in understanding the basic factors that may contribute to volume changes.

Experimental Section

Oxygen-17 NMR was observed at ca. 12 MHz on instrumentation developed in our laboratories.[5] Purified[1] $^{17}OH_2$ was used at ca. 4–40% enrichment. Baker Analyzed $Co(NO_3)_2{\cdot}6H_2O$ (100.5%), Fisher "Purified" $NaClO_4$ and analyzed nickel(II) 1,4,8,11-tetraazaundecane perchlorate prepared by Pell[1] were used. The Co(II) solution was 0.0514 m in 4% $^{17}OH_2$. The Ni complex solutions were (1) 0.0496 m in Ni and 0.0992 m in $NaClO_4$ and (2) 0.0675 m in Ni and 4.013 m in $NaClO_4$. Both 28% and 40% $^{17}OH_2$ were used in the Ni studies. Reference solutions were made by using appropriate amounts of $Zn(NO_3)_2$ and ligand where applicable.

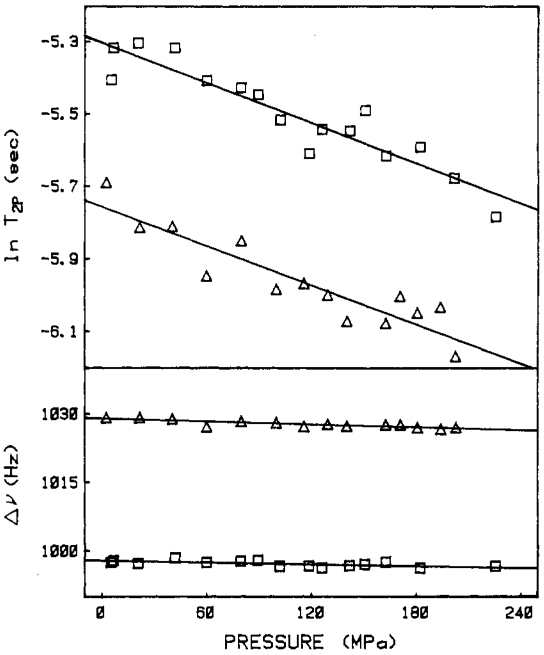

Figure 1. ln T^*_{2p} and shifts of the $^{17}OH_2$ NMR line, due to $Co(H_2O)_6^{2+}$, vs. pressure.

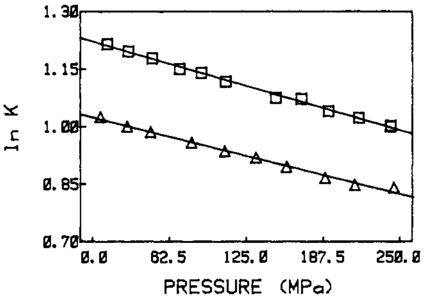

Figure 2. ln K for high-spin–low-spin equilibrium in Ni–2,3,2-tet vs. pressure: (□) data at 62 °C; (△) data at 45 °C.

Treatment of Data and Results

Figure 1 shows plots of ln T^*_{2p} and $\Delta\nu$ as a function of pressure for the Co(II) solution. We define $T^*_{2p} = [M]/[L]2\pi\Delta W$, where [M] is the metal concentration, [L] is the solvent water concentration, and ΔW is the line broadening (in Hz) relative to the Zn blank. The quantity $\Delta\nu$ is the paramagnetic shift (in Hz) in the bulk $^{17}OH_2$ line produced by Co(II), relative to the Zn blank. Both line broadenings and shifts are pressure-dependent although the shifts (which are known to better than 0.1%) are only slightly so and *decrease* with increasing pressure (ca. 0.01 Hz/MPa). The rate of exchange of H_2O can be obtained by the methods of Swift and Connick as shown by Hoggard.[6] From the relation $d \ln K/dp = -\Delta V^*/RT$ the pressure data yield $\Delta V^* = 5.5 \pm 0.6$ cm³/mol at 83.0 °C and $\Delta V^* = 5.2 \pm 0.7$ cm³/mol at 72.3 °C in good agreement with Merbach et al.[4] The observed decrease in shift with increasing pressure can be quantitatively accounted for by the fact that the water exchange rate is slowing with increasing pressure.

In the case of $Co(H_2O)_6^{2+}$, $1/T_{2M}$ is small and the Swift–Connick equations become

$$\Delta\nu = \Delta\nu_\infty/(1 + \tau_M^2\Delta\omega_M^2)$$

$$\Delta W = \tau_M\Delta\omega_M\Delta\nu$$

where $\Delta\nu$ is the shift of the resonance, $\Delta\nu_\infty$ is the shift when τ_M

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$\rightarrow 0$, τ_M is the mean lifetime of an H_2O in the Co(II) first coordination sphere, $\Delta\omega_M$ is the resonance frequency difference between a free H_2O and one in $Co(H_2O)_6^{2+}$, and ΔW is the width of the resonance. Near the fast exchange limit $\tau_M^2\ \Delta\omega_M^2 << 1$, so the shift equation can be written as

$$\Delta\nu = \Delta\nu_\infty(1 - \tau_M^2\Delta\omega_M^2) = \Delta\nu_\infty(1 - \Delta W^2/\Delta\nu^2)$$

The slope of a plot of $\Delta\nu$ vs. P can be obtained with sufficient accuracy by regarding $\Delta\nu$ in the right-hand side as constant so that

$$\left(\frac{\partial\Delta\nu}{\partial P}\right)_T = -\frac{2\Delta\nu_\infty\Delta W}{\Delta\nu^2}\left(\frac{\partial\Delta W}{\partial P}\right)_T$$

The shift data at 72.3 and 83.0 °C were fit with a linear least-squares program and gave slopes of −0.010 ± 0.002 and −0.006 ± 0.002 Hz/MPa, respectively, whereas the slopes calculated from the above equation and the W vs. P data were −0.0103 and −0.0059 Hz/MPa, respectively. This shows that the very slight decrease in shift observed with increasing pressure can be entirely accounted for by the decrease in rate of exchange with pressure and allows one to conclude that A/h must have been constant within about ±0.1% over the 200 MPa pressure range.

In Figure 2 values of ln K_{eq} vs. P are shown for two temperatures for the solution 0.0675 m in Ni complex and 4.0 m in $NaClO_4$. The K_{eq} values are calculated for the process $Ni(H_2O)_2\,L \leftrightarrow NiL + 2H_2O$ from the fast-exchange relation[1] $K_{eq} = (8.0 - Q)/Q$ where 8.0 is the Q value expected for a solution containing 100% $Ni(H_2O)_2L$ and Q is the observed shift function, $Q \equiv T\Delta\nu[L]/[M]\nu_0$, where T is in K, $\Delta\nu$ is the observed frequency shift of bulk $^{17}OH_2$ in the Ni solution relative to a blank, ν_0 is the ^{17}O resonance frequency in the blank and [M] and [L] are defined above. We calculate ΔV° from d ln $K_{eq}/dP = -\Delta V^\circ/RT$. The solution containing only the Ni complex at 0.0496 m yields $\Delta V^\circ = 3.1 \pm 0.3$ cm³/mol at 56.8 °C; for the 0.0675 m Ni and 4.0 m $NaClO_4$ solution at 62 °C, $\Delta V^\circ = 2.53 \pm 0.08$ cm³/mol, and at 45 °C, $\Delta V^\circ = 2.09 \pm 0.07$ cm³/mol. The latter value may well be somewhat low as the water exchange rate is slowing down at 45 °C. Line broadening data were also obtained on the Ni solutions, but they are imprecise and difficult to interpret in any case, so they are not reported here.

Discussion

Whereas one might expect some increase in A/h as pressure on an aqueous ion increases (due to a slight compressibility), there is no significant effect observed in the pressure range to ca. 2 kbar (200 MPa). Thus, one can use ^{17}O shift measurements to study complex equilibria as a function of pressure to obtain ΔV° values.

The small positive ΔV° found for the Ni–2,3,2-tet system is similar to those found by Kitamura[3] using a spectral method (note that his values are given for the reverse of our equation). These small values are in contrast to the +10 cm³/mol found by Merbach et al.[4] in the tetramethylcyclam case. Kitamura considers that the smaller size of the low-spin Ni complex accounts for the small ΔV° values (+36 cm³/mol is expected if the high- and low-spin forms are of equal molal volume); i.e., a contraction occurs that offsets H_2O loss. As we discussed in our earlier paper,[1] we feel that ClO_4^- plays a specific role in the conversion to low-spin Ni. The ClO_4^- ion has a molal volume of ca. +36 cm³/mol, and if ClO_4^- is removed from solution by some "complexing" in the low-spin form, the low ΔV° values can also be accounted for. Perhaps both factors are operative. Possibly steric effects prevent ClO_4^- from as close an approach in the tetramethylcyclam system, resulting in a larger ΔV°.

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Registry No. NiL^{2+}, 46365-93-9; $Ni(H_2O)_2L^{2+}$, 64616-26-8; ^{17}O, 13968-48-4; $Co(H_2O)_6^{2+}$, 15276-47-8; Co, 7440-48-4.

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Solid-State ^{13}C NMR Probe for Organotin(IV) Structural Polymorphism

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Two types of structural polymorphism are not uncommon in organotin(IV) chemistry: (A) where there is more than one structural modification present per unit cell[2–6] and (B) where two or more crystalline modifications of a single compound exist.[5–9] While single-crystal X-ray studies can readily reveal the former case, many instances of type B polymorphism may be presumed to go unnoticed in routine structural studies.

In contrast to X-ray diffraction studies carried out on single crystals, solid-state NMR spectra are acquired on bulk, polycrystalline samples of 0.1–0.4 g, which ensures more representative sampling of a material. In our structural investigations of methyltin(IV) compounds by solid-state ^{13}C NMR[8,10] we have found that ^{13}C chemical shifts of methyls bonded to tin are very sensitive to the local environment (which, unlike the case in solution, is generally static in the crystalline state). This sensitivity suggests that solid-state NMR can provide a convenient tool for revealing the presence of structural polymorphism in crystalline samples.[11] We describe below examples that confirm the general utility of the method for determining the occurrence and type of methyltin(IV) (and, by extension, other organometal) polymorphism.

Results and Discussion

Table I gathers solid-state ^{13}C NMR data obtained for three pure, polycrystalline methyltin(IV) compounds at 15.08 MHz with cross-polarization and magic-angle spinning (CPMAS) and high-power proton decoupling. Both hexacoordinated $Me_2Sn(S_2CNEt_2)_2$[6,8] and the tetracoordinated cyclic trimer $[Me_2SnS]_3$[9] are known from single-crystal X-ray diffraction studies to exist in two or more crystalline modifications. For each compound we have been able to isolate one of the characterized crystalline modifications in pure form and to obtain crops of crystals in which other forms are present in varying amounts. The presence of

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