The rearrangement products (3d, 3h, and 3i) were isolated as described above for the CoH₂ isomers.

Titanium-47 and Titanium-49 Nuclear Magnetic Resonance in Titanium(IV)-Halogen Compounds

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Abstract: Chemical shift data for the ^{47}Ti and ^{49}Ti nmr of TiCl₄, TiBr₄, and TiF₆$^{2-}$, and binary mixtures of TiCl₄–TiBr₄, TiCl₄–TiI₄, have been determined. The order of increasing shielding of the titanium nucleus by the halogen ligands is I, Br < Cl. The resonance absorptions for TiCl₄ and TiBr₄ are unshifted on dilution of these compounds in inert solvents. This provides evidence for the existence of monomeric molecules in the neat liquids. The mixture of TiCl₄ and TiBr₄ showed just one resonance signal, the chemical shift of which varied linearly with the mole fraction of the components, indicating rapid exchange between the parent compounds and the mixed species TiCl₃Br, TiCl₂Br₂, and TiClBr₃.

Extensive chemical shift data for the nmr of various atoms in tetrahedral or pseudo-tetrahedral halogen-containing environments have been reported in recent years. Apparently without exception, the order of increasing shielding of the nucleus under investigations is Cl < Br < I. In particular, the nuclei for which this trend has been found are ^{11}B,[1,2] ^{13}C,[3–7] ^{27}Al,[8] ^{29}Si,[9,10] ^{31}P,[11,12] ^{71}Ga,[13] ^{115}In,[14] and ^{119}Sn.[15] While investigating the feasibility of using ^{47,49}Ti nmr to derive information on structure and bonding in titanium compounds, we have obtained surprising chemical shift data for the titanium(IV) tetrahalides. Our results show that the order of increasing nuclear magnetic shielding is anomalous, *viz.*, I, Br < Cl.

The natural abundances and sensitivities[16] (relative to ^{1}H at constant field) of the two stable isotopes of titanium with nonzero spins are: ^{47}Ti ($I = {}^5/_2$), 7.3%,

2.09 × 10^{-3}; ^{49}Ti ($I = {}^7/_2$), 5.5%, 3.76 × 10^{-3}. These properties restrict detection of nmr signals in liquids to neat liquids or very soluble compounds. The values of the nuclear quadrupole moments for these nuclei do not appear to have been determined. Previous workers have observed ^{47,49}Ti nmr signals in liquid TiCl₄,[17,18] aqueous H₂TiF₆,[17] and in the solids SrTiO₃, TiCo, TiFe, and TiH₂.[19] The gyromagnetic ratios of ^{47}Ti and ^{49}Ti are remarkably close. The ratio $\nu(^{49}$Ti$)/\nu(^{47}$Ti$)$ at constant field has been determined in TiCl₄ as 1.00026 ± 0.00002.[17,18]

Recently, there has been some discussion in the literature concerning the state of aggregation of liquid titanium(IV) tetrachloride. Griffiths[20] has interpreted the results of Raman studies to imply that TiCl₄ is dimeric in the liquid state and monomeric in solution in carbon tetrachloride. A subsequent detailed study[21] of the intensity pattern of the a₁ vibrational mode of TiCl₄ has provided evidence that TiCl₄ is monomeric both as a pure liquid and in cyclohexane solution. We have investigated this problem using ^{47,49}Ti nmr and obtained results consistent with the existence of monomeric units in liquid TiCl₄. Similar observations were made for the analogous titanium(IV) tetrabromide system.

The utility of the nmr method in determining the nature of the products of redistribution reactions has been amply demonstrated for a variety of systems (*e.g.*, SnCl₄–SnBr₄–SnI₄,[15] POCl₃–POBr₃,[10] and AlCl₄$^-$–AlBr₄$^-$–AlI₄$^-$). Mixtures of TiCl₄ and TiBr₄ are known to contain an essentially random distribution of all possible species: TiCl₄, TiCl₃Br, TiCl₂Br₂, TiClBr₃ and TiBr₄.[21] We were unable to obtain ^{47,49}Ti chemi-

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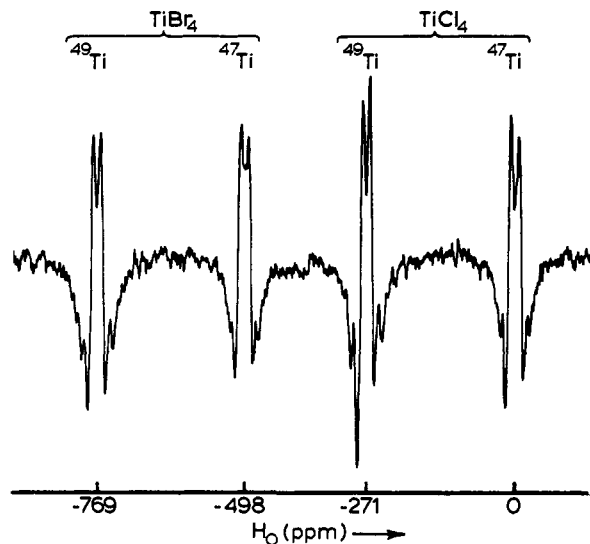(21) R. J. H. Clark and C. J. Willis, *Inorg. Chem.*, **10**, 1118 (1971).

Figure 1. The ^{47}Ti and ^{49}Ti nmr spectra of $TiCl_4$ and $TiBr_4$ recorded as the derivative of the dispersion mode. The splitting of each resonance is due to overmodulation at 40 Hz.

Figure 2. Plot of chemical shift vs. mole fraction of $TiBr_4$ for $TiCl_4$-$TiBr_4$ mixtures.

cal shift data for the individual mixed species due to rapid exchange between the species.

Experimental Section

Apparatus. The spectra were obtained with a Varian 4200B wide-line nmr spectrometer combined with a Varian 3400 9-in. magnet and Varian Fieldial Mark II sweep unit. The pole caps were modified to give a homogeneity of about 60 mG over the 15-mm o.d. sample tubes used in this study. At the operating frequency of 3.38 MHz, the ^{47}Ti and ^{49}Ti resonances were found at about 14.1 kG. The sweep frequency used to generate side bands, vide infra, was determined by comparison with that of a Hewlett Packard 241A oscillator using oscilloscope presentation of Lissajous' figures. The oscillator frequency was determined on a Hewlett Packard electronic counter 522B. The spectra were presented as the derivative of absorption or dispersion modes using a Varian G-10 recorder.

^{19}F nmr spectra were measured on a Varian HA-100 instrument operating at 94.1 MHz.

Measurement of Shifts. Initially, the shift between the ^{47}Ti and ^{49}Ti resonances was determined by operating in the absorption mode and using a sweep frequency of about 200 Hz to generate side bands while phasing out the center band. Thereafter, all spectra were calibrated using the ^{47}Ti–^{49}Ti resonance shift expressed as parts per million. Chemical shifts were measured by the sample replacement method and represent the average values obtained by sweeping the magnetic field at least five times in both increasing and decreasing directions. The quoted precision of the chemical shifts takes account of the calibration uncertainty.

Resonance Conditions. All chemical shift measurements were taken from spectra recorded as slow passage dispersion signals. The half-height line width for each isotope under the resonance conditions normally employed was about 50 Hz for both $TiCl_4$ and $TiBr_4$. Further examination of each of these four resonance lines revealed splitting by a 40-Hz sweep frequency and no splitting by a 20-Hz sweep frequency. This indicates that the natural line width approaches the limits of magnetic field homogeneity (about 25 Hz). Also, with the use of sweep frequencies less than 40 Hz, the signals were barely detectable. Thus useful line width measurements were precluded.

Sample Preparation. The titanium(IV) tetrahalides were obtained from Alfa Inorganics and, except for TiI_4, were normally used without further purification. A sample of $TiCl_4$ purified by distillation in a tapless vacuum line showed no detectable change in signal position or width compared to an unpurified sample. Since titanium(IV) tetraiodide is particularly susceptible to hydrolysis, it was purified by repeated vacuum distillation in a tapless apparatus. Spectroscopic grade cyclohexane and carbon tetrachloride were dried by standing over molecular sieves.

All sample handling operations involving $TiCl_4$, $TiBr_4$, and TiI_4 were carried out under a dry nitrogen atmosphere.
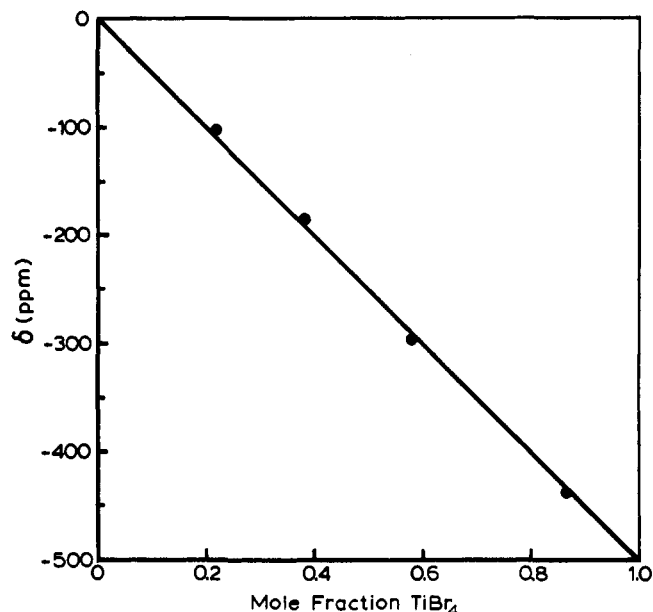
The ^{47,49}Ti nmr spectrum of titanium(IV) tetrabromide was obtained from a sample warmed to a little above its melting point (39°). All other samples were studied at room temperature.

Results

The ^{47,49}Ti nmr spectra of $TiCl_4$ and $TiBr_4$ are shown in Figure 1. The separation between the ^{47}Ti and ^{49}Ti resonances in each compound was found to be 271 (± 3) ppm, in good agreement with earlier studies.[17,18] Signals for $TiBr_4$ were found at 498 (± 5) ppm downfield from $TiCl_4$. Solutions of $TiCl_4$ and $TiBr_4$ in both cyclohexane and carbon tetrachloride (20 mol %) gave signals which were unshifted from those of the neat liquids. We were unable to detect a signal for TiI_4 either as a solid or in solution (see Experimental Section).

Two mixtures of neat titanium(IV) tetrahalides were studied: $TiCl_4$-$TiBr_4$ and $TiCl_4$-TiI_4. Although TiB_4 is a solid at room temperature, addition of even small amounts of the tetrachloride produced a homogeneous liquid. The ^{47,49}Ti nmr spectra of these mixtures showed just one resonance (for each isotope), the chemical shift of which varied linearly with the mole fraction of the tetrabromide (Figure 2). The line width was noticeably broader than those for $TiCl_4$ and $TiBr_4$ run under the same instrumental conditions. Titanium(IV) tetraiodide was only sparingly soluble in liquid $TiCl_4$. A mixture nominally 0.8 mol fraction in $TiCl_4$ consisted of a red-brown liquid and undissolved TiI_4. A resonance signal was observed for this mixture at 58 (± 7) ppm downfield from $TiCl_4$. Failure to observe any shift in the signal for $TiBr_4$ on adding TiI_4 to a solution of the bromide in carbon tetrachloride was probably due to the low solubility of TiI_4 in this solvent.

A solution of titanium(IV) fluoride in 48% aqueous HF gave a signal 1177 (± 7) ppm upfield from $TiCl_4$. The shift was independent of TiF_4 concentration in the range 0.8 M (the lower limit of detection) to 3.4 M. The resonance line widths were larger than those for $TiCl_4$ and $TiBr_4$. Similar unshifted signals were observed for aqueous solutions of TiF_4 and ammonium

fluoride in 1:1 and 1:2 mole ratios, but no resonance was detected for an aqueous solution of TiF_4.

Discussion

The observation that the [47,49]Ti nmr signals of $TiCl_4$ and $TiBr_4$ are unshifted by dilution in inert solvents supports the existence of monomeric units in the neat liquids. The assignment of the vibrational spectra of $TiCl_4$ and $TiBr_4$ in inert solvents in terms of the selection rules for tetrahedral symmetry appears to be generally accepted.[20,21] Molecular association in the pure liquids would necessitate a lowering of the symmetry from T_d and an increase in the coordination number ot titanium to five or six. It is anticipated that such changes would be reflected in the [47,49]Ti nmr spectra. The range of chemical shifts of titanium(IV) compounds measured in this study is about 2000 ppm. Shift ranges of comparable magnitude have been observed in the nmr spectra of many of the other heavier nuclei[22] and in these systems, changes in coordination number and symmetry are found to produce large changes in resonance position. It is therefore unlikely that the titanium nucleus in two different structural environments would give rise to a resonance absorption in precisely the same position. Thus we conclude that the same species (i.e., monomeric, tetrahedral $TiCl_4$ or $TiBr_4$) is responsible for the signals in the neat liquids and in solution. Qualitative observations of line widths and intensities for the spectra are consistent with this conclusion.

The results for the mixtures of $TiCl_4$ and $TiBr_4$ indicate rapid chemical exchange of halogen atoms between the five species present[21] such that the titanium nuclei experience an average environment. Assuming that the chemical shifts of the mixed species increase in a roughly linear manner with progressive substitution of bromine for chlorine, the average lifetimes of the species can be estimated[23] as less than 10^{-4} sec.

A similar exchange process probably takes place between two or more species in the $TiCl_4$-TiI_4 mixture since only one signal was observed. The position of this resonance strongly suggests that the shift for TiI_4, if observable, would be downfield from $TiCl_4$.

The anomalous order of relative shielding at the titanium nucleus observed for titanium(IV) tetrahalides provides an interesting example of a departure from the usual relative magnitudes of the parameters which contribute to nuclear screening variation consequent on changing the ligands. The nuclear magnetic shielding can be expressed as the sum of diamagnetic and paramagnetic, σ_p, contributions.[24] For atoms other than hydrogen, the diamagnetic term is generally assumed to vary little from compound to compound,[25] although recent work[26,27] indicates that this assumption may not be entirely correct. Normally considered the dominant contribution to the shielding, σ_p, can be ex-

pressed in the form[25]

$$\sigma_p = -(2e^2\hbar^2/3\Delta m^2c^2)(\langle 1/r^3\rangle_p P_u + \langle 1/r^3\rangle_d D_u)$$

where Δ is the average excitation energy for the molecule, P_u and D_u are the respective "unbalance" of the valence electrons in the p and d orbitals, and $\langle 1/r^3\rangle_p$ and $\langle 1/r^3\rangle_d$ are the average values of the inverse cube radii of the p and d orbitals, respectively.

Both P_u and D_u depend on the hybridization of the bonding orbitals and on the ionicity of the bonds.[25] It is not apparent how these parameters will vary for the titanium(IV) tetrahalides although it is reasonable to assume that the term $\langle 1/r^3\rangle_p P_u$ is relatively unimportant because the hybridization is d^3s with a slight admixture of sp^3.[28]

Of the remaining terms, $\langle 1/r^3\rangle_d$ increases from TiI_4 to $TiBr_4$ to $TiCl_4$ consistent with the trend in electron delocalization expected from the nephelauxetic series.[29] Domination of σ_p by this term would imply an *increase* in shielding in the order Cl < Br < I. This is the order observed for tetrahedral halides of the main group elements. The variation of the magnitude of σ_p for the titanium(IV) tetrahalides, however, is quantitatively consistent with the decreasing values of Δ as approximated by the energies of the long wavelength electron-transfer transitions, viz., $TiCl_4$, 34,840 cm^{-1}; $TiBr_4$, 28,680 cm^{-1}; TiI_4, 19,400 cm^{-1}.[21] While tetrahedral compounds of main group elements exhibit a similar bathochromic shift as the ligands vary from Cl^- to Br^- to I^-, it is significant that the energies of the long-wavelength electron-transfer transitions are generally about 10,000 cm^{-1} or higher than for the corresponding titanium compounds. Thus, the titanium(IV) tetrahalides present a situation similar to that of symmetrical, octahedral complexes of cobalt(III) where a good correlation has been found between [59]Co chemical shifts and the energy of the relatively low-lying $^1A_{1g} \rightarrow {}^1T_{1g}$ transitions.[30,31]

The resonance observed for the solutions containing titanium(IV) tetrafluoride is due to the hexafluorotitanate(IV) ion. This was confirmed by obtaining ^{19}F nmr spectra of the same solutions. TiF_4 in 48% aqueous HF showed just two ^{19}F absorptions at -152.3 and $+92.2$ ppm (relative to trifluoroacetic acid). The position of the low-field absorption agrees well with that obtained previously for TiF_6^{2-} (-152.2 ppm),[32] while the high-field signal is attributed to F^- in 48% aqueous HF. The aqueous solutions of TiF_4 and NH_4F gave one signal at -152.6 ppm. We found no evidence for the instability of TiF_6^{2-} noted in previous work.[17] The broadening of the [47,49]Ti signals, relative to $TiCl_4$, is probably due to unresolved spin–spin coupling between titanium and fluorine nuclei. The [49]Ti–[19]F coupling constant has been determined[32] from the ^{19}F nmr of $(NH_4)_2TiF_6$ in aqueous solution as 33 Hz and the [47]Ti–[19]F coupling constant will have a value close to this. Thus, each of the [47]Ti and [49]Ti resonances should consist of seven lines covering a

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total of about 200 Hz. The observed line widths were about 220 Hz.

Crystal Structure and Molecular Stereochemistry of α,β,γ,δ-Tetraphenylporphinatodichlorotin(IV)[1]

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Abstract: Tetragonal crystals, space group $I4/m$, of α,β,γ,δ-tetraphenylporphinatodichlorotin(IV) (Cl₂SnTPP) are of extraordinarily high quality for X-ray analysis. The unit cell containing 2Cl₂SnTPP has $a = 13.673$ (1) Å and $c = 9.961$ (1) Å (λ 0.70926 Å) at 19°. Diffracted intensities were recorded with Mo Kα radiation on a computer-controlled diffractometer with a scanning rate of 1°/min and a background counting time of 80 sec. Of the 4450 independent reflections scanned for $(\sin\theta)/\lambda \lesssim 1.03$ Å⁻¹ ($2\theta \lesssim 94°$), the 3909 retained as observable corresponded to a conventional data/parameter ratio of 54.3 for anisotropic, full-matrix, least-squares refinement of the structure. All C–H bond densities in the molecule of required C_{4h} symmetry were clearly defined in a Fourier difference synthesis; the customary quasi-refinement of the hydrogen parameters, using two distinctive weighting schemes, led to C–H distances of 0.89–1.10 Å and thermal parameters for hydrogen atoms of 1.4–5.5 Å². The persistent interference of the hydrogen contributions with the quantitatively unambiguous positioning of those carbon atoms which carry hydrogen atoms was then eliminated by the exclusion from the final least-squares refinements of all low-angle data (573) for which $(\sin\theta)/\lambda < 0.517$ Å⁻¹. Positions of all other carbon and heavier atoms were practically invariant to the details of refinement. The octahedral coordination group of the Cl₂SnTPP molecule has Sn–Cl = 2.420 (1) Å and Sn–N = 2.098 (2) Å. C–C and N–C bond lengths in the radially expanded porphinato core carry esd values of 0.002–0.003 Å; dimensional variations from full D_{4h} symmetry are altogether trivial. Comparison of the expanded porphinato core of a tin(IV) porphyrin with the contracted core of a nickel-(II) porphyrin leads to some stereochemical generalizations of both practical and theoretical interest.

A definitive X-ray analysis of structure for truly excellent crystals of α,β,γ,δ-tetraphenylporphinatodichlorotin(IV) (written as Cl₂SnTPP; see Figures 1 and 2 for skeletal diagrams) is presented herein. Crystalline Cl₂SnTPP, as anticipated,[2] provides the first *ordered* example of the tetragonal structural type that, in a statistically disordered version, is utilized by the crystalline chloroiron(III),[3] aquozinc(II),[4] aquomagnesium(II),[5] and nitrosylcobalt(II)[6] derivatives of tetraphenylporphine. Precise intensity measurements for all independent reflections having $(\sin\theta)/\lambda \lesssim 1.03$ Å⁻¹ yield a data/parameter ratio of ∼54 for the comparatively simple structure, thus permitting the relative merits of various structural models and refinement procedures to be evaluated. The large, strongly complexing, tin(IV) atom is centered in a highly expanded porphinato core of required C_{4h} symmetry, with no dimensionally significant departure from the maximum possible symmetry of D_{4h}. Comprehensive analysis of the redistribution of strain in the porphinato skeleton[2] as a function of the "radius of the central hole"—the Ct···N radius shown in Figure 2 that, in the Cl₂SnTPP molecule, is identical with the complexing Sn–N bond length—is now feasible. Such analysis benefits also from stereochemical data recently obtained by other workers; see Discussion.

Experimental Section

Crystalline Cl₂SnTPP was prepared and purified following the procedures of Rothemund and Menotti.[7] Large well-formed crystals exhibiting tetragonal-bipyramidal morphology were then obtained by allowing methanol to diffuse slowly into a nearly saturated solution of Cl₂SnTPP in chloroform. Preliminary X-ray study of a single crystal by photographic techniques led to a body-centered tetragonal lattice and delimitation of the probable space groups to $I4$, $I\bar{4}$, and $I4/m$. Negative tests for piezoelectricity in the crystals, using a Geibe-Schiebe detector, and every detail of the subsequent analysis of structure supported the choice of the centrosymmetric $I4/m$-C_{4h}^{5} as the space group.[8] The experimentally measured density, 1.43 g/cc at 23°, led to a two-molecule unit cell; use of the precisely measured lattice constants, $a = 13.673$ (1) Å and $c = 9.961$ (1) Å (Mo Kα₁; λ = 0.70926 Å) gave a calculated density of 1.431 g/cc at 19°. These lattice constants came

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