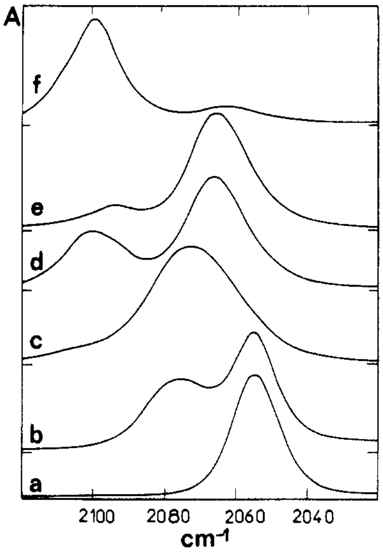

**Figure 1.** Infrared spectra of $SCN^-$ and CuSCN aggregates in soft donor solvents: $NBu_4SCN$ 1.16 M in DMTF (a); CuSCN 0.17 M in DMTF (b), 0.2 M in 80% THT + 20% DMTF (c), 0.034 M in THT (d), 0.0034 M in THT (e), and 0.0034 M in 90% $CS_2$ + 10% THT (f). Absorbances (*A*) are in arbitrary units.

Such an increase in integrated intensity of $\nu$(CN) is characteristic of isothiocyanate complexes.[3]

The proportion of CuNCS ion pair was found to increase when the less polar THT was added to DMTF solutions. For instances, the spectrum of a 0.2 M solution of CuSCN in a mixed solvent containing 80% THT showed the peak of CuNCS only (Figure 1c). The band of $SCN^-$ appeared again by dilution in the same solvent. A shift of the $SCN^-$ band, due to a dielectric effect,[4] from 2055 $cm^{-1}$ in pure DMTF to 2051 $cm^{-1}$ in pure THT, was observed. The shift of the CuNCS band was more important (from 2076 to 2066 $cm^{-1}$). Such a behavior has never been observed in LiNCS aggregates.

The IR spectrum of a saturated solution of CuSCN (0.037 M) in THT exhibited two weak bands at 2101 and 2093 $cm^{-1}$ in addition to the main band of CuNCS at 2066 $cm^{-1}$ (Figure 1d). The first of them disappeared on dilution (Figure 1e) and was therefore assigned to an aggregate $(CuNCS)_p$. The ratio of the height of the CuNCS band to that of the 2093-$cm^{-1}$ band ($\sim$6) was not dependent on dilution down to $10^{-4}$ M, and consequently this absorption was assigned to the isomer species CuSCN. Such a type of isomerism has been found between AuNCS and AuSCN.[5] For these two species the ratio of the frequency shifts relative to $SCN^-$ is equal to 26/70, or 0.37, which is very close to the same ratio 15/42, or 0.36, for CuNCS and CuSCN. In THT the AgSCN band was observed at the same frequency as for CuSCN. The polarizing powers of $Cu^+$ and $Ag^+$ ions toward the sulfur end of $SCN^-$ appear to be the same, but the interaction of the smaller and harder $Cu^+$ must be less covalent than that of $Ag^+$.

In solid CuSCN the SCN groups are in bridging positions[6] between one nitrogen and three sulfur atoms. The $\nu$(CN) absorption at 2173 $cm^{-1}$ is located 122 $cm^{-1}$ higher than for $SCN^-$.[7] This difference can be compared to the value calculated by applying an additivity rule to the shifts observed in both ion pairs: $15 + (3 \times 42) = 141$ $cm^{-1}$. It seems that such a rule gives an upper limit of the observed shifts and generally a rough estimation of them. When $CS_2$ was added to CuSCN–THT solutions, we observed an increase of the relative intensity of the $(CuNCS)_p$ band at 2101 $cm^{-1}$ (Figure 1f). In solutions containing 90% $CS_2$ the ion-pair absorption at 2065 $cm^{-1}$ disappeared almost completely. The frequency shift of the 2101 $cm^{-1}$ band relative to that of $SCN^-$ is 50 $cm^{-1}$ which can be compared to 42 $cm^{-1}$ for CuSCN and 14 $cm^{-1}$ for CuNCS in the same solvent. If the approximate additivity rule is followed, this band must be assigned to a bridging NCS group. The same assignment has been made for $AgNCSAg^+$.[8] Therefore, the aggregate $(CuNCS)_p$ is probably a centrosymmetric dimer.

The addition of a large excess (5/1) of triphenylphosphine ($Ph_3P$) to a saturated solution of CuSCN in THT caused the bands at 2093 and 2101 $cm^{-1}$ to disappear and the band at 2066 $cm^{-1}$ to shift slightly to 2064.5 $cm^{-1}$. At the same time the integrated intensity of this band increased from 20 700 to 27 600 $cm^{-1}$. These changes arise from a preferential solvation of $Cu^+$ by $Ph_3P$. We did not observe any difference between the $\nu$(CN) IR and Raman frequencies of these solutions. Therefore the formation of a centrosymmetric dimer is unlikely in this case even though some solid compounds of $Ph_3P$ with copper(I) salts are dimerized.[9] On the other hand the compound $(Bu_3P)_2$ CuNCS has been found to exhibit a $\nu$(CN) band at 2077 $cm^{-1}$.[10] Hence, the addition of $Ph_3P$ does not seem to induce an important change in aggregation of CuNCS, but the strong increase in intensity due to the addition of $Ph_3P$ has not been yet interpreted.

The IR spectra of saturated solutions ($\sim 10^{-2}$ M) of CuSCN in $Me_2SO$ and in HMPT were also investigated. The main band (at 2089 $cm^{-1}$ in $Me_2SO$ and 2085 $cm^{-1}$ in HMPT) gradually shifted to 2076 $cm^{-1}$ when DMTF was added to the solutions and no splitting was observed. Consequently, this band was assigned to CuNCS. There is little ionization of CuNCS in these solvents because their ability to solvate $Cu^+$ through the oxygen atom is poor. On the contrary, the relatively strong Cu–NCS interaction induces a large frequency shift on $\nu$(CN) (31 $cm^{-1}$ in $Me_2SO$ compared to 21 $cm^{-1}$ in DMTF).

The mixtures of CuSCN and $NBu_4SCN$ were studied by Job's method. A new band at 2075 $cm^{-1}$ was attributed to $Cu(NCS)_2^-$. The Raman frequency of this species was observed at 2086 $cm^{-1}$. $Cu(NCS)_2^-$ is probably centrosymmetric even though the Raman band at 2086 $cm^{-1}$ appeared as a shoulder in the IR spectrum and vice versa. This complex is of the isothiocyanate type because its $\nu$(CS) IR band was observed at 791 $cm^{-1}$ instead of 737 $cm^{-1}$ for $SCN^-$. The difference between Raman and IR $\nu$(CN) frequencies is nearly the same as for $Cu(CN)_2^-$ (2137 and 2125 $cm^{-1}$),[11] as expected for similar groups coupled through the same $Cu^+$ ion.

In conclusion, $Cu^+$ generally acts as a hard cation toward $SCN^-$, contrary to $Ag^+$ and $Au^+$, which are known to be softer.[12] Consequently, $Cu^+$ should be considered, like $Cd^{2+}$, as being in a borderline position between hard and soft cations.

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**Registry No.** $Cu(NCS)_2^-$, 60896-41-5; CuNCS, 1111-67-7; $SCN^-$, 302-04-5; $Cu^+$, 17493-86-6.

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## Raman Spectroscopic Evidence for the Existence of $TiO^{2+}$ in Acidic Aqueous Solutions

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The existence of solid vanadium(IV) oxo complexes containing a true vanadyl (V=O) moiety is well established.[1,2] The vibrational frequencies $\tilde{\nu}$(V=O) are observed in the region of 940–1000 cm$^{-1}$.[3] The water exchange of VO(H$_2$O)$_5^{2+}$ was investigated[4] and found to be consistent with four equatorial water ligands exchanging at a rate of 550 s$^{-1}$ and one weakly bound axial water exchanging too fast on the NMR time scale.

In contrast, solid titanium(IV) oxo complexes are rarely found to exhibit a true titanyl (Ti=O) moiety.[1,2,5] Some exceptions, however, exist: TiO(porphyrin),[6] TiO(phthalocyanine),[7] $(R_4N)_2TiCl_4O$,[8] TiO(edtaH$_2$)(H$_2$O),[9] and salts containing $[TiOF_5]^{3-}$.[10] These compounds exhibit a Ti=O bond length of 1.62 Å for the porphyrin or $\tilde{\nu}$(Ti=O) at 972, 975, 950, and 890–920 cm$^{-1}$, respectively, for the remaining four.

Acidic aqueous solutions of titanium(IV) were shown[11] to contain species with a charge of 2+, $TiO^{2+}$ or $Ti(OH)_2^{2+}$. On the basis of electron-transfer[11,12] and ligand substitution[13] reactions, Sykes and co-workers obtained evidence of the existence of $TiO^{2+}$. However, they[12] were not able to detect $\tilde{\nu}$(Ti=O) in 2 M HClO$_4$ by Raman solution spectroscopy. This study reports on the Raman solution spectra of titanium(IV) in aqueous HClO$_4$ and HCl and provides clear information about its structure.

### Experimental Section

**Preparation of the Solutions.** A solution of VO(ClO$_4$)$_2$ (0.12 M) in HClO$_4$ (0.36 M) was prepared as described in the literature.[14] Solutions of TiO(ClO$_4$)$_2$ and TiOCl$_2$ in HClO$_4$ (0.2, 2.0 M) and HCl (2 M) respectively were prepared by addition of respective solutions of Ba(ClO$_4$)$_2$ and BaCl$_2$ to acidic solutions of titanyl sulfate (Tioxide) that was analyzed to contain 46.4% $SO_4^{2-}$ and 19.7% Ti (gravimetry) or 19.2 ± 0.2% Ti (ICP and RFS).

**Physical Measurements.** The Raman spectra were measured on a Spex 1401 spectrophotometer using an argon ion laser ($\lambda$ = 514.5 nm, 0.8 W).

### Results and Discussion

An aqueous solution of $VO^{2+}$ (0.12 M) in perchloric acid (0.36 M) exhibits—in addition to the modes of $ClO_4^-$—a polarized Raman band at 997 cm$^{-1}$, which is undoubtedly due to $\tilde{\nu}$(V=O) as in the solids.[1,2]

Sykes et al.[12] reported the failure to detect $\tilde{\nu}$(Ti=O) in the Raman solution spectrum of TiO(ClO$_4$)$_2$ (0.05 M TiO(ClO$_4$)$_2$ in 2 M HClO$_4$). We found, however, that the Raman spectra of similar solutions (0.08 M TiO(ClO$_4$)$_2$ in 2 M HClO$_4$) exhibited a weak shoulder at $\tilde{\nu}$ = 975 cm$^{-1}$ close to the strong A$_1$ mode of $ClO_4^-$. In 0.2 M HClO$_4$ the shoulder appeared very distinctively, but colloidal TiO$_2$ particles were already formed and gave rise to strong Rayleigh scattering. In HCl (2 M), $\tilde{\nu}$(Ti=O) was easily detected as a broad band at 975 cm$^{-1}$. The $\tilde{\nu}$(Ti=O) vibration is polarized as well as the A$_1$ mode of $ClO_4^-$, and its frequency does not depend on the concentration and nature of the acid, although chloro complexes of $TiO^{2+}$ are likely to be formed to some extent. No other bands (except those of $ClO_4^-$) were detected in the region of 300–1200 cm$^{-1}$.

A hypothetical (cis or trans) $Ti(OH)_2^{2+}$ complex is expected to give rise to $\tilde{\nu}$(Ti—OH) at ca. 500 cm$^{-1}$, since $\tilde{\nu}$(M$^{IV}$—OH) of $Sn(OH)_6^{2-}$, $Pt(OH)_6^{2-}$, and $Pb(OH)_6^{2-}$ are reported[15] to occur around 500 cm$^{-1}$. Thus the vibration at 975 cm$^{-1}$ is certainly not due to $\tilde{\nu}$(Ti$^{IV}$—OH).

The IR spectra[10] of NaK$_2$[M$^{IV}$OF$_5$] salts (M = Ti, V) are very similar. The $\tilde{\nu}$(M=O) frequencies were found to be 943 and 920 cm$^{-1}$ for M = V and Ti, respectively. Substitution of V$^{IV}$ by Ti$^{IV}$ causes a shift (23 cm$^{-1}$) of $\tilde{\nu}$(M=O) to lower energies. Exactly the same shift is observed when V$^{IV}$ is substituted by Ti$^{IV}$ in aqueous $MO(H_2O)_5^{2+}$ complexes.

The solid (NH$_4$)$_2$[TiO(C$_2$O$_4$)$_2$]·H$_2$O is known[16] to form a tetrameric ring with cis-(–Ti–O–) units. Solutions of K$_2$[TiO(C$_2$O$_4$)$_2$]·H$_2$O (0.1 M) in H$_2$C$_2$O$_4$ (ca. 0.06 M) do not exhibit a polarized Raman band around 950 cm$^{-1}$. Obviously the (oxalato)titanates do not contain Ti=O moieties also in solution and, consistent with Clark's[2] statement, the Ti=O unit is observed rather exceptionally.

**Acknowledgment.** Titanyl sulfate (with analytical data) was donated by Dr. D. Urwin from British Tioxide UK Limited. The Raman spectra were recorded at the Department of Physics with Prof. Dr. P. Cornaz's advice. The ICP and RFS analyses were carried out by Prof. Dr. B. Magyar.

**Registry No.** TiO(ClO$_4$)$_2$, 13637-79-1; $TiO^{2+}$, 12192-25-5.

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## Structure of Polymeric Zinc Phenoxyisobutyrate

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In an investigation of the mode of interaction of the divalent metal ions with the phenoxyalkanoic acids, which include the commercial auxin herbicides 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), 4-chloro-2-methylphenoxyacetic acid (MCPA), and their 2-propionic acid analogues, the structural systematics of a number of the metal complexes have been determined by single-crystal X-ray diffraction.[1,2] So far, the zinc complexes[1,3] have been monomers unlike a number of zinc carboxylates that form polymer struc-

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