**InCl₃** Observed in the Raman Spectra of Deuterated Acetonitrile Containing InCl₃

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Indium(III) halide complexes have shown a remarkably varied crystal chemistry; structures containing indium in 4+8 coordination are known, whereas only coordination numbers of 4 and 6 have been reported for the complexes in solution. Insertion of water molecule into the coordination sheath readily occurs, resulting in six coordinate complexes. Various mixed halogeno/aqua complexes In₃X₄(H₂O)₉−(X =F, Cl, Br, I) are observed in aqueous solution. More complex In₅X₆(H₂O)₉−(X=Cl, Br) species have also been identified in a recent ¹⁹F NMR study of indium fluoride complexes.⁵

Six coordinate In₅X₆L₄−⁵⁵ species can also be formed in nonaqueous media for L = dimethylformamide, dimethylnitroform, or tributyl phosphate and X = Cl or Br,⁶ whereas only four coordinate tetrahedral In₄⁺ anion is observed in the indium iodide aqueous solution with additional HL, mainly due to the large size of the iodine atom.⁵ It is also reported in ¹¹¹In NMR studies that four coordinate indium halide anions (InX⁺) are obtained in extraction with solvents such as acetone, methyl isobutyl ketone, ethyl ether, isopropyl ether, n-butyl acetate, cyclohexanone, and ethyl acetocetate from HCl, HIBr, and HI solutions.⁵⁷−⁶⁰ Tuck et al. substantiated in an ¹¹¹In NMR study formation of InCl₃⁺ in various organic solvents.⁴ Dissolution of RInX₃ (R = organic cations) salts in dichloromethane, acetone, acetonitrile, tetrahydrofuran, chloroform does not lead to indium-solvent bonding or dissociation of the anion.⁶

It is therefore intriguing to determine reliably the coordination number in a typical organic solvent containing indium halide. InCl₃ in fact provides a test case: GaX₃ forms four coordinate anions (GaX₄−) in solutions regardless of the solvent,⁵ whereas TiX₃ normally gives six coordinate anions (e.g. TiX₆⁴⁻).⁵ We report here a Raman study for CD₃CN solution of InCl₃. CD₃CN is used instead of CH₃CN for this study, to avoid the interference originating from the strong Fermi resonance between the ν₃ and the ν₃ + ν₄ vibration modes observed from CH₃CN,⁶ whose magnitude varies dramatically upon coordination.

CD₃CN (99.95%, Aldrich) in ampule was used without further treatment. Anhydrous InCl₃, pack-
aged under argon in ampoule, was also used as purchased from Aldrich. The concentration (molality) of InCl₃ in CD₄CN in this study ranges from 0 to 4.5 mol, close to the saturation point. Spectra were collected using a Raman module incorporated into an FT-IR spectrometer (Bio-Rad FTS 1750) with a resolution of 4.0 cm⁻¹, which was accompanied with a YAG laser, a Ge detector, and a holographic notch transmission filter as the light source, detector, and Rayleigh filter, respectively. Bulb-type Raman cell (Bio-Rad 925-0101) with reflective coating on one side was used for higher signal intensity.

Complementary density functional theory (DFT) calculations were carried out using the Gaussian 03 package, B3LYP density functional, 6-311++G (3df, 3pd) basis sets for Cl and SDD pseudopotential and basis set 12 for In (+6 electron core) to provide a consistent set of vibrational frequencies for the anticipated species in solution. Zero point energies were included in the calculation of product energies. The solvent effects are not counted in calculations.

Shown in Fig. 1 is the Raman spectrum of CD₄CN solution containing InCl₃ (4.0 mol) in the 106-400 cm⁻¹ region. Beside the v₁ CCN deformation band of free CD₄CN at 348 cm⁻¹, four more strong absorptions are observed at 371, 321, 112, and 89 cm⁻¹. Fig. 2 shows the variation of the v₁ CCN deformation band region with concentration. Evidently the two absorptions at 371 and 321 cm⁻¹ increase proportionally with InCl₃ concentration while the intensity of the v₁ band of free CD₄CN at 348 cm⁻¹ stays essentially the same. The band at 371 cm⁻¹ is attributed to the v₁ CCN deformation mode of CD₄CN coordinated to the cationic species (In(CD₄CN)₃)⁺. 13

The frequencies of other three bands (321, 112, and 89 cm⁻¹) are consistent with the previous values reported for InCl₃ by Woodward and Taylor in Raman studies for InCl₃ extracts from aqueous solutions of indium chloride containing hydrochloric acid. 9 They are, therefore, attributed to A₁ symmetric stretching, F₂ asymmetric deformation, and E symmetric deformation bands of InCl₃⁺, respectively. Much weaker F₂ antisymmetric stretching band at 337 cm⁻¹ is covered by the stronger v₁ band of free CD₄CN and the A₁ symmetric stretching band of InCl₃⁺ at 348 and 321 cm⁻¹, respectively, as shown in Fig. 1.

InCl₃ with T₃ symmetry has four vibrational modes, A₁ symmetric stretch (v₁), E symmetric deformation (v₂), F₂ asymmetric stretch (v₃), and F₃ asymmetric deformation (v₄). Among them, only the latter two are IR active, whereas all of them are Raman active. The A₁ symmetric stretch, E symmetric deformation, and F₃ asymmetric deformation bands are expected to be reasonably strong and sharp, whereas, the F₂ asymmetric deformation band weak and diffuse. The observed frequencies are compared with the predicted frequencies in Table 1, where they match within 5%.

No other considerable bands are observed in the
low frequency region even at high concentration as shown in Fig. 4, indicating that InCl$_7^-$ is the dominating anionic species in the acetonitrile solution of InCl$_3$. The present result, therefore, reconfirms that the four coordinate species is indeed the primary anion in typical organic solvents, and higher number of coordination is normally achieved by addition of water or in organic media with strong lightening group, such as carbonyl group.$^{15}$

InCl$_7^-$ is formed via disproportionation reaction of InCl$_3$ as shown in reaction (1).

$$4\text{InCl}_3 + \text{xCd}_2\text{CN} \rightarrow \text{(Cd}_2\text{CN)}_3\text{In}^{-} + 2\text{InCl}_3 \quad (1)$$

The stability of InCl$_7^-$ in solution originates from the low energy, which is 285.8 kcal/mol lower than the reactants (In$^3$P$_{6}^{+}$+2Cl$_{2}$) at the level of B3LYP 6-311++G(3d,$\phi$, 3pd) while InCl$_3$ is 64.2 kcal/mol more stable than the reactants. InCl$_7^-$ and InCl$_5^-$ are 238.6 and 219.4 kcal/mol lower than the reactants, respectively. The predicted In-Cl bond length is also the shortest (2.360 Å) for InCl$_7^-$, compared with those of 2.543 Å for InCl$_5^-$, 2.375 and 2.714 Å for InCl$_3$, and 2.464 and 2.494 Å for InCl$_5^-$.

It is also notable that the measured frequencies are essentially the same as the previous values, indicating that the vibrational characteristics of InCl$_7^-$ remain virtually unchanged regardless of the media. The effect of concentration is also negligible as shown in Fig. 2 while the chances to form counter-

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**Table 1. Observed frequencies in the low frequency region of CD$_2$CN solution containing InCl$_3$.**

<table>
<thead>
<tr>
<th>Obs</th>
<th>Calc</th>
<th>Obs/Calc</th>
<th>Int</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>340.9+0.6$^a$</td>
<td>306</td>
<td>1.05</td>
<td>25</td>
<td>CD-CN $v_5$ CCN deform</td>
</tr>
<tr>
<td>370.7(23.2)$^b$</td>
<td>322</td>
<td>1.03</td>
<td>10</td>
<td>InCl$_3$ $A$, sym. str.</td>
</tr>
<tr>
<td>89</td>
<td>85</td>
<td>1.05</td>
<td>2</td>
<td>InCl$_3$ $E$, sym. deform</td>
</tr>
<tr>
<td>337$^c$</td>
<td>328</td>
<td>1.03</td>
<td>10</td>
<td>InCl$_3$ $F$, antisym. str.</td>
</tr>
<tr>
<td>112</td>
<td>115</td>
<td>0.97</td>
<td>3</td>
<td>InCl$_3$ $F$, antisym. deform</td>
</tr>
</tbody>
</table>

$^a$All frequencies are in cm$^{-1}$.

$^b$Numbers in parentheses are the frequency shifts relative to the frequencies of free CD$_2$CN in the pure CD$_2$CN.

$^c$Predicted frequencies with B3LYP/6-311++G(3d,$\phi$, 3pd)/SDD

$^d$Predicted Raman scattering activity in $\AA^{2}$amu

$^e$Brief description of the vibrational mode.

$^f$Value taken from Ref.[5]. Frequencies could not be determined in this study because of severe overlap by the CCN deformation bands of free CD$_2$CN and those coordinated to the solute.

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2007, Vol. 51, No. 8
ion pairs rise with concentrations at 4.0 m, the molecular ratio between the solvent and solute is about 4.5:1. The invariance of the vibrational characteristics of the tetrachloroindate anion is compared to the dramatic variation in vibrational characteristics of acetonitrile upon coordination to the cation (In^3+).14,16

In conclusion, relatively strong bands are observed in the low frequency region of the Raman spectrum of acetonitrile containing InCl₄. The frequencies match with the previously observed tetrachloroindate anion (InCl₄⁻) in extracts from indium chloride solution containing hydrochloric acid.5 No other considerable bands are observed in the region, indicating that InCl₄⁻ is the primary anion, which is formed in disproportionation reaction of indium chloride. Stability of the four coordinate anionic species is also reproduced by DFT calculations. The present results reconfirm that InX₄⁻ is normally the major species in organic solvents, whereas the higher coordination number (e.g. 6) requires strong ligands, such as water and organic solvents with strong ligating group.14,15

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REFERENCES