

## 단 신

### InCl<sub>3</sub>를 함유한 중수소 치환된 아세토나이트릴 용액의 라만 스펙트럼에서 관찰된 InCl<sub>4</sub><sup>-</sup> 이온

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### InCl<sub>4</sub><sup>-</sup> Observed in the Raman Spectra of Deuterated Acetonitrile Containing InCl<sub>3</sub>

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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.<sup>1</sup> Insertion of water molecule into the coordination sheath readily occurs, resulting in six coordinate complexes. Various mixed halogeno/aqua complexes InX<sub>n</sub>(H<sub>2</sub>O)<sub>6-n</sub><sup>3-n</sup> (X = F, Cl, Br, I) are observed in aqueous solution.<sup>2</sup> More complicate InF<sub>n</sub>X<sub>m</sub>(H<sub>2</sub>O)<sub>6-n-m</sub><sup>3-n-m</sup> (X=Cl, Br) species have also been identified in a recent <sup>19</sup>F NMR study of indium fluoride complexes.<sup>3</sup>

Six coordinate InX<sub>n</sub>L<sub>6-n</sub><sup>3-n</sup> species can also be formed in nonaqueous media for L = dimethylformamide, dimethylsulfoxide, or tributyl phosphate and X = Cl or Br,<sup>4</sup> whereas only four coordinate tetrahedral InI<sub>4</sub><sup>-</sup> anion is observed in the indium iodide aqueous solution with additional HI, mainly due to the large size of the iodine atom.<sup>2</sup> It is also reported in <sup>115</sup>In NMR studies that four coordinate indium halide anions (InX<sub>4</sub><sup>-</sup>) are obtained in extraction with solvents such as acetone, methyl isobutyl ketone,

ethyl ether, isopropyl ether, n-butyl acetate, cyclohexanone, and ethyl acetoacetate from HCl, HBr, and HI solutions.<sup>2,5,6</sup> Tuck et al. substantiated in an <sup>115</sup>In NMR study formation of In<sub>2</sub>Cl<sub>6</sub><sup>2-</sup> in various organic solvent.<sup>7</sup> Dissolution of RInX<sub>4</sub> (R = organic cations) salts in dichloromethane, acetone, acetonitrile, tetrahydrofuran, chloroform does not lead to indium-solvent bonding or dissociation of the anion.<sup>7</sup>

It is therefore intriguing to determine reliably the coordination number in a typical organic solvent containing indium halide. InX<sub>3</sub> in fact provides a test case; GaX<sub>3</sub> forms four coordinate anions (GaX<sub>4</sub><sup>-</sup>) in solutions regardless of the solvent,<sup>8</sup> whereas TiX<sub>3</sub> normally gives six coordinate anions (e.g. TiX<sub>6</sub><sup>3-</sup>).<sup>9</sup> We report here a Raman study for CD<sub>3</sub>CN solution of InCl<sub>3</sub>. CD<sub>3</sub>CN is used instead of CH<sub>3</sub>CN for this study, to avoid the interference originating from the strong Fermi resonance between the ν<sub>2</sub> and the ν<sub>3</sub> + ν<sub>4</sub> combination modes observed from CH<sub>3</sub>CN,<sup>10</sup> whose magnitude varies dramatically upon coordination.

CD<sub>3</sub>CN (99.95%, Aldrich) in ampule was used without further treatment. Anhydrous InCl<sub>3</sub>, pack-

aged under argon in ampule, was also used as purchased from Aldrich. The concentration (molality) of  $\text{InCl}_3$  in  $\text{CD}_3\text{CN}$  in this study ranges from 0 to 4.5 m, close to the saturation point. Spectra were collected using a Raman module incorporated into an FT-IR spectrometer (Bio-Rad FTS 175C) with a resolution of  $4.0\text{ cm}^{-1}$ , 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,<sup>11</sup> B3LYP density functional,<sup>12</sup> 6-311++G (3df, 3pd) basis sets for Cl and SDD pseudopotential and basis set<sup>13</sup> for In (46 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  $\text{CD}_3\text{CN}$  solution containing  $\text{InCl}_3$  (4.0 m) in the  $100\text{--}600\text{ cm}^{-1}$  region. Beside the  $\nu_8$  CCN deformation band of free  $\text{CD}_3\text{CN}$  at  $348\text{ cm}^{-1}$ , four more strong absorptions are observed at  $371$ ,  $321$ ,  $112$ , and  $89\text{ cm}^{-1}$ . Fig. 2 shows the variation of the  $\nu_8$  CCN deformation band region with concentration. Evidently the two absorptions at  $371$  and  $321\text{ cm}^{-1}$  increase proportionally with  $\text{InCl}_3$  concentration while the intensity of the  $\nu_8$  band of free  $\text{CD}_3\text{CN}$  at  $348\text{ cm}^{-1}$  stays essentially the same. The band at  $371\text{ cm}^{-1}$  is attributed to the  $\nu_8$  CCN deformation mode of  $\text{CD}_3\text{CN}$  coordinated to the cationic species  $(\text{In}(\text{CD}_3\text{CN})_x)^{3+}$ .<sup>14</sup>

The frequencies of other three bands ( $321$ ,  $112$ , and  $89\text{ cm}^{-1}$ ) are consistent with the previous values reported for  $\text{InCl}_4^-$  by Woodward and Taylor in Raman studies for  $\text{InCl}_3$  extracts from aqueous solutions of indium chloride containing hydrochloric acid.<sup>5</sup> They are, therefore, attributed to  $A_1$  symmetric stretching,  $F_2$  antisymmetric deformation, and  $E$  symmetric deformation bands of  $\text{InCl}_4^-$ , respectively. Much weaker  $F_2$  antisymmetric stretching band at  $337\text{ cm}^{-1}$  is covered by the stronger  $\nu_8$  band

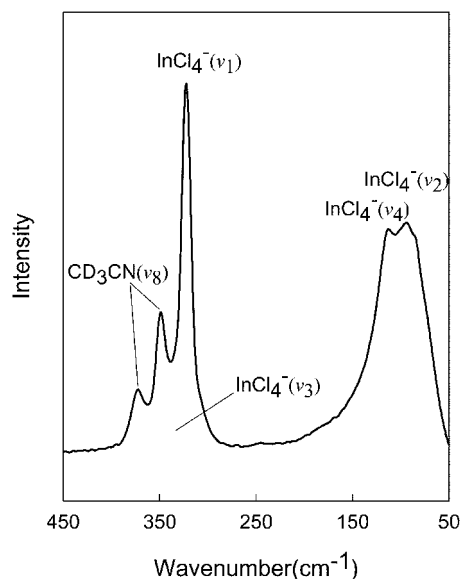


Fig. 1. Raman spectrum in the range of  $450\text{--}50\text{ cm}^{-1}$  of  $\text{InCl}_3$  solution in  $\text{CD}_3\text{CN}$  at 4.0 m. The CCN deformation bands of  $\text{CD}_3\text{CN}$  free and coordinated are observed at  $347$  and  $371\text{ cm}^{-1}$ , respectively. The  $A_1$  symmetric stretching ( $\nu_1$ ),  $E$  symmetric deformation ( $\nu_2$ ), and  $F_2$  antisymmetric deformation ( $\nu_4$ ) bands of  $\text{InCl}_4^-$  are located at  $321$ ,  $94$ , and  $113\text{ cm}^{-1}$ , respectively. The  $F_2$  antisymmetric stretching band ( $\nu_3$ ), expected at about  $337\text{ cm}^{-1}$ , is apparently overlapped by the  $\nu_7$  CCN deformation band of free  $\text{CD}_3\text{CN}$  and the  $\nu_1$   $A_1$  symmetric stretching band of  $\text{InCl}_4^-$ . No other considerable bands are observed in the spectrum, suggesting that  $\text{InCl}_4^-$  is the primary anion present in the solution.

of free  $\text{CD}_3\text{CN}$  and the  $A_1$  symmetric stretching band of  $\text{InCl}_4^-$  at  $348$  and  $321\text{ cm}^{-1}$ , respectively, as shown in Fig. 1.

$\text{InCl}_4^-$  with  $T_d$  symmetry has four vibrational modes,  $A_1$  symmetric stretch ( $\nu_1$ ),  $E$  symmetric deformation ( $\nu_2$ ),  $F_2$  asymmetric stretch ( $\nu_3$ ), and  $F_2$  asymmetric deformation ( $\nu_4$ ). Among them, only the latter two are IR active, whereas all of them are Raman active. The  $A_1$  symmetric stretch,  $E$  symmetric deformation, and  $F_2$  asymmetric deformation bands are expected to be reasonably strong and sharp, whereas, the  $F_2$  asymmetric deformation band weak and diffused.<sup>5</sup> 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

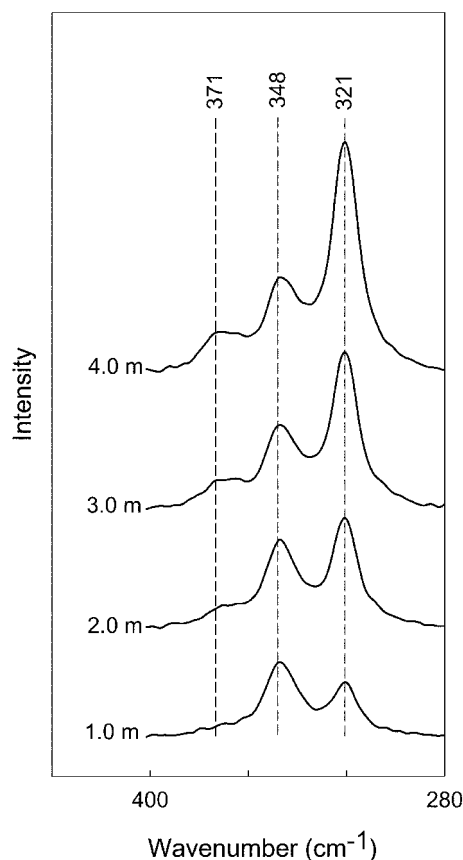


Fig. 2. The emerging bands on the both side of the  $\nu_8$  CCN deformation band of free  $\text{CD}_3\text{CN}$  with increasing  $\text{InCl}_3$  concentration. The emerging band at  $371\text{ cm}^{-1}$  is believed to arise from the coordinated  $\text{CD}_3\text{CN}$  to  $\text{In}^{3+}$  ( $\text{In}(\text{CD}_3\text{CN})_x^{3+}$ ). The strong  $A_1$  symmetric stretching band of  $\text{InCl}_4^-$  at  $321\text{ cm}^{-1}$  grows proportionally with  $\text{InCl}_3$  concentration.

low frequency region even at high concentration as shown in Fig. 1, indicating that  $\text{InCl}_4^-$  is the dominating anionic species in the acetonitrile solution of  $\text{InCl}_3$ . 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 ligating group, such as carbonyl group.<sup>15</sup>

$\text{InCl}_4^-$  is formed via disproportionation reaction of  $\text{InCl}_3$  as shown in reaction (1).



The stability of  $\text{InCl}_4^-$  in solution originates from the low energy, which is  $285.8\text{ kcal/mol}$  lower than the reactants ( $\text{In}(\text{P}_{1/2}) + 2\text{Cl}_2$ ) at the level of B3LYP/6-311++G(3df, 3pd) while  $\text{InCl}_3$  is  $64.2\text{ kcal/mol}$  more stable than the reactants.  $\text{InCl}_5^-$  and  $\text{InCl}_6^-$  are  $238.6$  and  $219.4\text{ kcal/mol}$  lower than the reactants, respectively. The predicted In-Cl bond length is also the shortest ( $2.360\text{ \AA}$ ) for  $\text{InCl}_4^-$ , compared with those of  $2.543\text{ \AA}$  for  $\text{InCl}_3$ ,  $2.375$  and  $2.714\text{ \AA}$  for  $\text{InCl}_5^-$ , and  $2.464$  and  $2.494\text{ \AA}$  for  $\text{InCl}_6^-$ .

It is also notable that the measured frequencies are essentially the same as the previous values, indicating that the vibrational characteristics of  $\text{InCl}_4^-$  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-

Table 1. Observed frequencies in the low frequency region of  $\text{CD}_3\text{CN}$  solution containing  $\text{InCl}_3$ <sup>a</sup>

Obs <sup>b</sup>	Calc <sup>c</sup>	Obs/Calc	Int <sup>d</sup>	Description <sup>e</sup>
346.9 (-0.6) <sup>e</sup>				$\text{CD}_3\text{CN}$ $\nu_8$ CCN deform
370.7 (23.2) <sup>d,e</sup>				$\text{CD}_3\text{CN}$ coordinated to $\text{In}^{3+}$ $\nu_8$
321	306	1.05	25	$\text{InCl}_4^-$ $A_1$ sym. str.
89	85	1.05	2	$\text{InCl}_4^-$ $E$ sym. deform
337 <sup>f</sup>	328	1.03	10	$\text{InCl}_4^-$ $F_2$ antisym. str.
112	115	0.97	3	$\text{InCl}_4^-$ $F_2$ antisym. deform

<sup>a</sup>All frequencies are in  $\text{cm}^{-1}$ .

<sup>b</sup>Numbers in parantheses are the frequency shifts relative to the frequencies of free  $\text{CD}_3\text{CN}$  in the pure  $\text{CD}_3\text{CN}$ .

<sup>c</sup>Predicted frequencies with B3LYP/6-311++G(3df, 3pd)/SDD

<sup>d</sup>Predicted Raman scattering activity in  $\text{\AA}^4/\text{amu}$ .

<sup>e</sup>Brief description of the vibrational mode.

<sup>f</sup>Value taken from Ref.[5]. Frequencies could not be determined in this study because of severe overlap by the CCN deformation bands of free  $\text{CD}_3\text{CN}$  and those coordinated to the solute.

ion pairs rise with concentration; 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 ( $\text{In}^{3+}$ ).<sup>14,16</sup>

In conclusion, relatively strong bands are observed in the low frequency region of the Raman spectrum of acetonitrile containing  $\text{InCl}_3$ . The frequencies match with the previously observed tetrachloroindate anion ( $\text{InCl}_4^-$ ) in extracts from indium chloride solution containing hydrochloric acid.<sup>5</sup> No other considerable bands are observed in the region, indicating that  $\text{InCl}_4^-$  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  $\text{InX}_4^-$  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.<sup>2,4,15</sup>

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