

단 신

InCl₃를 함유한 중수소 치환된 아세토나이트릴 용액의 라만
스펙트럼에서 관찰된 InCl₄⁻ 이온

조준성* · 조한국*
인천대학교 화학과
*계북포고등학교
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InCl₄⁻ Observed in the Raman Spectra of Deuterated Acetonitrile
Containing InCl₃

Jun-Sung Cho[†] and Han-Gook Cho^{*}

Department of Chemistry, University of Incheon, 177 Dohwa-dong, Nam-ku, Incheon, 402-749, Korea

[†]Jemulpo High School, 26 Jun-dong, Joong-ku, Incheon, 400-190, Korea

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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.¹ Insertion of water molecule into the coordination sheath readily occurs, resulting in six coordinate complexes. Various mixed halogeno/aqua complexes InX_n(H₂O)_{6-n}³⁻ⁿ (X = F, Cl, Br, I) are observed in aqueous solution.² More complicate InF_nX_m(H₂O)_{6-n-m}^{3-n-m} (X = Cl, Br) species have also been identified in a recent ¹⁹F NMR study of indium fluoride complexes.³

Six coordinate InX_nL_{6-n}³⁻ⁿ species can also be formed in nonaqueous media for L = dimethylformamide, dimethylsulfoxide, or tributyl phosphate and X = Cl or Br,⁴ whereas only four coordinate tetrahedral InL₄⁻ anion is observed in the indium iodide aqueous solution with additional HI, mainly due to the large size of the iodine atom.² It is also reported in ¹¹⁵In NMR studies that four coordinate indium halide anions (InX₄⁻) are obtained in extraction with solvents such as acetone, methyl isobutyl ketone,

ethyl ether, isopropyl ether, n-butyl acetate, cyclohexanone, and ethyl acetoacetate from HI, IBr, and III solutions.^{2,5,6} Tuck et al. substantiated in an ¹¹⁵In NMR study formation of In₂Cl₆²⁻ in various organic solvent.⁷ 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.⁷

It is therefore intriguing to determine reliably the coordination number in a typical organic solvent containing indium halide. InX₃ in fact provides a test case; GaX₃ forms four coordinate anions (GaX₄⁻) in solutions regardless of the solvent,⁸ whereas TlX₃ normally gives six coordinate anions (e.g. TlX₆³⁻).⁹ 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 ν₂ and the ν₃ + ν₄ combination modes observed from CH₃CN,¹⁰ whose magnitude varies dramatically upon coordination.

CD₃CN (99.95%, Aldrich) in ampule was used without further treatment. Anhydrous InCl₃, pack-

aged under argon in ampule, was also used as purchased from Aldrich. The concentration (molality) of InCl_3 in CD_3CN 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 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,¹¹ B3LYP density functional,¹² 6-311++G (3df, 3pd) basis sets for Cl and SDD pseudopotential and basis set¹³ 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 CD_3CN solution containing InCl_3 (4.0 m) in the $100\text{--}600\text{ cm}^{-1}$ region. Beside the ν_8 CCN deformation band of free CD_3CN 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 ν_8 CCN deformation band region with concentration. Evidently the two absorptions at 371 and 321 cm^{-1} increase proportionally with InCl_3 concentration while the intensity of the ν_8 band of free CD_3CN at 348 cm^{-1} stays essentially the same. The band at 371 cm^{-1} is attributed to the ν_8 CCN deformation mode of CD_3CN coordinated to the cationic species ($\text{In}(\text{CD}_3\text{CN})_x^{3+}$).¹⁴

The frequencies of other three bands (321 , 112 , and 89 cm^{-1}) are consistent with the previous values reported for InCl_4^- by Woodward and Taylor in Raman studies for InCl_3 extracts from aqueous solutions of indium chloride containing hydrochloric acid.⁵ They are, therefore, attributed to A_1 symmetric stretching, F_2 antisymmetric deformation, and E symmetric deformation bands of InCl_4^- , respectively. Much weaker F_2 antisymmetric stretching band at 337 cm^{-1} is covered by the stronger ν_8 band

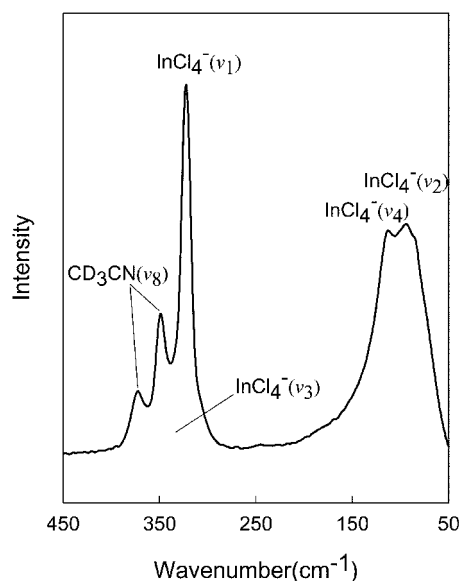


Fig. 1. Raman spectrum in the range of $450\text{--}50\text{ cm}^{-1}$ of InCl_3 solution in CD_3CN at 4.0 m. The CCN deformation bands of CD_3CN free and coordinated are observed at 347 and 371 cm^{-1} , respectively. The A_1 symmetric stretching (ν_1), E symmetric deformation (ν_2), and F_2 antisymmetric deformation (ν_3) bands of InCl_4^- are located at 321 , 94 , and 113 cm^{-1} , respectively. The F_2 antisymmetric stretching band (ν_3), expected at about 337 cm^{-1} , is apparently overlapped by the ν_7 CCN deformation band of free CD_3CN and the ν_1 A_1 symmetric stretching band of InCl_4^- . No other considerable bands are observed in the spectrum, suggesting that InCl_4^- is the primary anion present in the solution.

of free CD_3CN and the A_1 symmetric stretching band of InCl_4^- at 348 and 321 cm^{-1} , respectively, as shown in Fig. 1.

InCl_4^- with T_d symmetry has four vibrational modes, A_1 symmetric stretch (ν_1), E symmetric deformation (ν_2), F_2 asymmetric stretch (ν_3), and F_2 asymmetric deformation (ν_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.⁵ 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

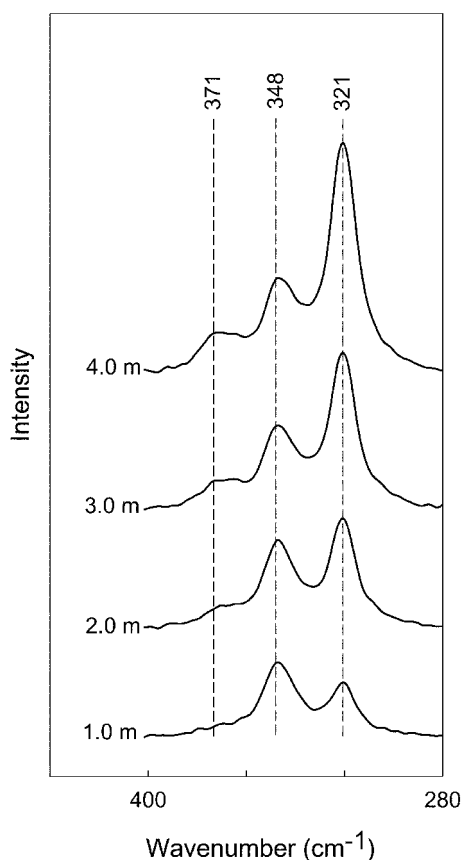
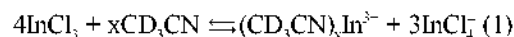


Fig. 2. The emerging bands on the both side of the ν_8 CCN deformation band of free CD_3CN with increasing InCl_3 concentration. The emerging band at 371 cm^{-1} is believed to arise from the coordinated CD_3CN to In^3 ($\text{In}(\text{CD}_3\text{CN})_x^3$). The strong A_1 symmetric stretching band of InCl_4^- at 321 cm^{-1} grows proportionally with InCl_3 concentration.

low frequency region even at high concentration as shown in Fig. 1, indicating that InCl_4^- 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 ligating group, such as carbonyl group.¹⁵

InCl_4^- is formed via disproportionation reaction of InCl_3 as shown in reaction (1).



The stability of InCl_4^- in solution originates from the low energy, which is 285.8 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 InCl_3 is 64.2 kcal/mol more stable than the reactants. InCl_5^- and InCl_6^- 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_4^- , compared with those of 2.543 Å for InCl_3 , 2.375 and 2.714 Å for InCl_5^- , and 2.464 and 2.494 Å for InCl_6^- .

It is also notable that the measured frequencies are essentially the same as the previous values, indicating that the vibrational characteristics of 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 CD_3CN solution containing InCl_3 ^a

Obs ^b	Calc ^c	Obs/Calc	Int ^d	Description ^e
346.9 (-0.6) ^c				CD_3CN ν_8 CCN deform
370.7 (23.2) ^{d,e}				CD_3CN coordinated to In^3 ν_8
321	306	1.05	25	InCl_4^- A_1 sym. str.
89	85	1.05	2	InCl_4^- E sym. deform
337 ^f	328	1.03	10	InCl_4^- F_2 antisym. str.
112	115	0.97	3	InCl_4^- F_2 antisym. deform

^aAll frequencies are in cm^{-1} .

^bNumbers in parantheses are the frequency shifts relative to the frequencies of free CD_3CN in the pure CD_3CN .

^cPredicted frequencies with B3LYP/6-311++G(3df, 3pd)/SDD

^dPredicted Raman scattering activity in $\text{\AA}^4/\text{amu}$.

^eBrief description of the vibrational mode.

^fValue taken from Ref.[5]. Frequencies could not be determined in this study because of severe overlap by the CCN deformation bands of free CD_3CN 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 (In^{3+}).^{14,16}

In conclusion, relatively strong bands are observed in the low frequency region of the Raman spectrum of acetonitrile containing InCl_3 . The frequencies match with the previously observed tetrachloroindate anion (InCl_4^-) in extracts from indium chloride solution containing hydrochloric acid.⁵ No other considerable bands are observed in the region, indicating that 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 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.³⁻¹⁵

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