Inorg. Chem. **1993**, *32*, 2265–2268

^{115}In NMR Studies of Reactions of Indium Trihalides with Halides and Pseudohalides in Acetonitrile Solution. Complexes with Different Coordination Numbers

M. A. Malyarick* and S. P. Petrosyants

Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky Prospect 31, 117907, Moscow, Russia

Received June 3, 1992

^{115}In NMR studies are reported for the reactions of InX_3 (X = Cl, Br, I) salts with halides (X = Cl, Br, I) and pseudohalides (NCS, NO_2) in acetonitrile. The resonances of InX_4^- anions are observed for InX_3 solutions and InX_3–Y (X = Y = Cl, Br, I; Y = NCS, NO_2) systems. Mixed $InX_nY_{4-n}^-$ anions can be obtained for the mixtures of InX_3 and InY_3 solutions or by the reactions of InX_3 with Y^- (X ≠ Y = Cl, Br, I). In $(NCS)_6^{3-}$ and $In(NO_2)_6^{3-}$ complexes are first detected by ^{115}In NMR, and they are all found to be N-coordinated to indium in solution according to ^{14}N NMR data. The coexistence of six-coordinate $In(NCS)_6^{3-}$ or $In(NO_2)_6^{3-}$ species with tetrahedral InX_4^- anions in solution is a new example of configuration equilibrium in the coordination chemistry of indium.

Introduction

Indium(III) halide complexes exhibit a considerably varied crystal chemistry; structures containing indium in four-up to eight-coordination are known. Only coordination numbers 4 and 6 have been established for the complexes in solution. Mixed halogeno/aqua complexes $InX_n(H_2O)_{6-n}^{3-n}$ (X = F, Cl, Br, I) are formed in aqueous solutions.[1,2] More complicated $InF_nX_m(H_2O)_{6-n-m}^{3-n-m}$ (X = Cl, Br) species have been detected in a recent ^{19}F NMR study of indium fluoride complexes.[3] Six-coordinate $InX_nL_{6-n}^{3-n}$ species can also be obtained in nonaqueous media for L = dimethylformamide, dimethyl sulfoxide, or tributyl phosphate and X = Cl or Br.[4,5] Indium iodide complexes exhibit some differences. Only for iodide in concentrated solutions of HI can the four-coordinate tetrahedral InI_4^- anion be observed.[2] Furthermore, iodide and fluoride ions can be combined in four-coordinate $InFI_m(H_2O)_{3-m}^{2-m}$ species.[3]

When indium is extracted with such solvents as methyl isobutyl ketone, ethyl ether, isopropyl ether, *n*-butyl acetate, cyclohexanone, and ethyl acetoacetate from HCl, HBr, and HI solutions, the species detected in the organic phase by ^{115}In NMR are InX_4^- (X = Cl, Br, I).[2]

The dissolution of $RInX_4$ (R = various organic cations) salts in dichloromethane, acetone, acetonitrile, tetrahydrofuran, and chloroform does not result in indium–solvent bonding or dissociation of the anions. Only InX_4^- or mixed $InX_nY_{4-n}^-$ and $InX_nY_mZ_{4-n-m}^-$ (X ≠ Y ≠ Z = Cl, Br, I) species are identified for mixtures of solutions of different halides.[6]

The only reliably confirmed indium coordination number for complexes with pseudohalide ions is 6, determined by means of an X-ray structural investigation of $(Ph_4As)_3[In(NCS)_6]$.[7] Complex stability measurements have demonstrated the presence of InL_n^{3-n} species (L = NCS,[8,9] NO_2;[10] *n* = 1–6) in aqueous, aqueous organic (NCS), and methanol (NO_2) solutions; however, the overall composition of the complexes has not been determined. Mixed $InF_n(NCS)_m(H_2O)_{6-n-m}^{3-n-m}$ species have been identified in aqueous solutions by ^{19}F NMR spectroscopy.[3]

Studies of indium(III) complexes formed in solution have been carried out by various techniques, but only ^{115}In NMR offers the distinct possibility of obtaining information otherwise unavailable. However, since 1965 when Cannon and Richards' study demonstrated that ^{115}In NMR was a very useful technique for the determination of the species and their structures in solution,[11] only a few investigations have been conducted in this area.[2,6,12–14] This may be due to the fact that ^{115}In NMR gives relatively broad line widths, even for complexes with high symmetry, because of the large quadrupole moment of the indium-115 nucleus. The species detectable by ^{115}In NMR until now are the tetrahaloindate anions InX_4^-, $InX_nY_{4-n}^-$, and $InX_nY_mZ_{4-n-m}^-$ (X ≠ Y ≠ Z = Cl, Br, I)[6,13] and the six-coordinate complexes $In(H_2O)_6^{3+}$[2,11,12] and InF_6^{3-}.[14]

In the present work, we have tried to extend the application of ^{115}In NMR. Our data show that this method should be very useful in studies of the reactions of indium trihalides with halides and pseudohalides in acetonitrile solution.

Experimental Section

Materials. $InCl_3$ was prepared by chlorinating In_2O_3 with CCl_4 at ~450 °C. InI_3 was obtained according to literature procedures.[15,16] $(C_4H_9)_4NInX_4$ salts were prepared as insoluble precipitates by mixing aqueous solutions of InX_3 and $(C_4H_9)_4NX$, after which they were recrystallized from acetonitrile and dried in vacuo. Complex thiocyanate salts of $(R_4N)_3In(NCS)_6$ (R = CH_3, C_4H_9) and tetraalkylammonium thiocyanate were synthesized according to the literature.[17,18]

The salts $InBr_3$, R_4NX (R = CH_3, C_2H_5, C_4H_9; X = Cl, Br, I), and MNCS and MNO_2 (M = Na, K) were obtained from commercial sources

---

(1) Wilkinson, G.; Gillard, R. D., McCleverty, J. A., Eds. *Comprehensive Coordination Chemistry*; Pergamon: Oxford, England, 1987; Vol. 3, pp 157–182.

(2) Haraguchi, H.; Fuwa, K.; Fujiwara, S. *J. Phys. Chem.* **1973**, *77*, 1497.

(3) Petrosyants, S. P.; Malyarick, M. A.; Buslaev, Yu. A. *Koord. Khim.* **1989**, *11*, 1493.

(4) Sheka, I. A.; Sheka, Z. A. *Indium Halides and Their Coordination Compounds*; Nauk Dumka: Kiev, 1981.

(5) Skorobogat'ko, E. P.; Mikitchenko, V. F. *Vestn. Kiev Univ. Khim.* **1986**, *27*, 16.

(6) McGarvey, B. R.; Trudell, C. O.; Tuck, D. G.; Victoriano, L. *Inorg. Chem.* **1980**, *19*, 3432.

(7) Einstein, F. W. B.; Gilbert, M. M.; Tuck, D. G.; Vogel, P. L. *Acta Crystallogr.* **1976**, *B32*, 2234.

(8) Golub, A. M.; Keller, X.; Scopenko, V. V. *The Chemistry of Pseudohalides*; Vischa Shkola: Kiev, 1981.

(9) Chaundhari, K. B.; Sudersanan, M. *J. Electrochem. Soc. India* **1983**, *32*, 59.

(10) Golub, A. M.; Akmyradov, R.; Uskova, S. L. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1974**, *17*, 1288.

(11) Cannon, T. H.; Richards, R. E. *Trans. Faraday Soc.* **1966**, *62*, 1378.

(12) Fratiello, A.; Davis, D. D.; Peak, S.; Schuster, R. E. *Inorg. Chem.* **1971**, *10*, 1627.

(13) Colton, R.; Dakternieks, D.; Hauenstein, J. *Aust. J. Chem.* **1981**, *34*, 945.

(14) Kirakosian, G. A.; Loginov, S. V.; Galuzina, T. V.; Tarasov, V. P.; Buslaev, Yu. A. *Zh. Neorg. Khim.* **1990**, *35*, 2306.

(15) Carty, A. J.; Tuck, D. G. *J. Chem. Soc. A* **1966**, 1081.

(16) Gynane, M. J. S.; Wilkinson, M.; Worral, I. J. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 765.

(17) Mal'tseva, V. S.; Eriemin, Yu. G. *Zh. Neorg. Khim.* **1974**, *19*, 2323.

(18) Habeeb, J. J.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **1973**, 96.

0020-1669/93/1332-2265$04.00/0

Table I. ^{115}In NMR Resonances in Acetonitrile Solutions of Indium Salts (0.1 M)

	δ, ppm ($\Delta H_{1/2}$, Hz)			
X	InX_3	$InX_3 + X^-$	$[(C_4H_9)_4N][InX_4]$	$R[InX_4]$[6,a]
Cl	8 (1300)	−2 (390)	0 (290)	0 ± 2 (310)
Br	−254 (580)	−260 (320)	−261 (220)	−258 (180)
I	−999 (430)	−1009 (240)	−1007 (240)	−989 (250)

[a] R: $[(C_5H_5)_4P]$ for $InCl_4^-$ and $InBr_4^-$; $[(C_4H_9)_4N]$ for InI_4^-.

without further purification. Acetonitrile rigorously dried and distilled by standard methods was used as the solvent for preparing all solutions. All operations were carried out under a dinitrogen atmosphere.

NMR Spectroscopy. ^{115}In NMR spectra were obtained with a Bruker AC-200 P spectrometer operating at 43.86 MHz. The instrument was externally locked onto the deuterium resonance of D_2O. All samples were studied as solutions in 10-mm (o.d.) tubes at room temperature. For the measurements of chemical shifts, a 0.1 M solution of $(C_4H_9)_4NInCl_4$ in acetonitrile was used as the external standard.

^{14}N NMR spectra were recorded at 14.44 MHz. Chemical shifts were referenced to the external resonance of NO_3^- (aqueous solution of NH_4NO_3 acidified with nitric acid as the standard).

Results and Discussion

InX_3–CH_3CN (X = Cl, Br, I) Systems. Tetrahalogenoindate(III) Anions. Previous authors were not able to observe ^{115}In resonances for acetonitrile solutions of InX_3, with the exception of InI_3.[6] We have now carefully reinvestigated these systems and detected bands almost identical in frequencies with those found for the corresponding InX_4^- anions for all InX_3 solutions (Table I).

Trihalides of the indium neighboring elements aluminum and gallium in acetonitrile solution undergo disproportionation reactions leading to six-coordinate cationic complexes that share the same anion MX_4^-. Thus ^{27}Al NMR data for $AlCl_3$–CH_3CN solutions indicate the three octahedral cations $Al(CH_3CN)_6^{3+}$, $AlCl(CH_3CN)_5^{2+}$, and $AlCl_2(CH_3CN)_4^+$, with the relative concentration of each complex dependent on the $CH_3CN/AlCl_3$ molar ratio.[19] It seems likely that an analogous configuration equilibrium takes place for InX_3–CH_3CN systems. The impossibility of observing cationic indium species by ^{115}In NMR is probably due to the formation of mixed six-coordinate complexes. Unlike the case of aluminum, no ^{115}In resonance could be identified for the cation of $[InI_2(CH_3CN)_4][InI_4]$ in acetone solution. This is not surprising in view of the lowering of the symmetry of the cation, which causes large quadrupole broadening.[6] Even for ^{27}Al, with a significantly smaller Q value compared to that for ^{115}In, a change in molecular symmetry such as $O_h \rightarrow C_{2v}$ causes a sharp increase in line width. Therefore, it may be assumed that the balance between the ionic charges of species in InX_3–CH_3CN solution is established by the formation of only unsymmetric $InX_n(CH_3CN)_{6-n}^{(3-n)+}$ ($n = 1, 2$) cationic species because $In(CH_3CN)_6^{3+}$, like $In(H_2O)_6^{3+}$, would be detectable by ^{115}In NMR.

We have investigated InX_3 solutions over the concentration range 0.1–1.0 M, which corresponds to CH_3CN/InX_3 molar ratios of about 230–12. The concentration of indium trihalide has a great influence on the ^{115}In line width (Figure 1), and for salt concentrations exceeding 0.5 M ($InCl_3$) and 0.7 M ($InBr_3$, InI_3), the absorptions become too broad for any significant measurements to be made. The order of the slopes of the lines (Figures 1) deserves some comment. Besides the viscosity, which affects the signal line width, one more factor can be considered. Increasing the InX_3 salt concentration lowers the CH_3CN/InX_3 molar ratio so that some associating processes can take place. Taking into account that $InCl_3$ and $InBr_3$ have analogous polymeric sheet lattices in the solid state, with each indium surrounded octahedrally by halide atoms, and that InI_3, which has a dimeric iodine-bridged structure involving In(III) tetrahedrally bonded to iodine,[20] the decrease in the slopes of the lines in Figure 1 in the order Cl > Br > I could be correlated with the sequence for the stabilities of complexes with coordination numbers higher than 4.

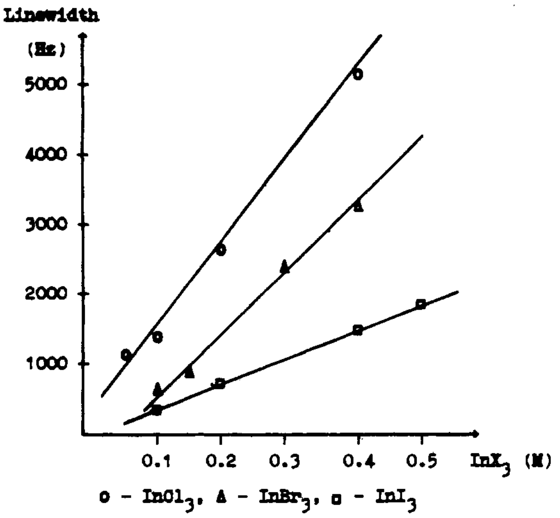

Figure 1. ^{115}In line width as a function of indium trihalide concentration.

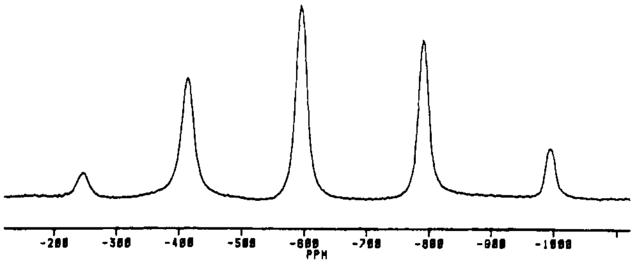

Figure 2. ^{115}In NMR spectrum of an equimolar mixture of $InBr_3$ and InI_3 acetonitrile solutions (0.3 M indium salts).

A similar order relative to the halide ligands was determined for InX_3–X^- systems. The addition of R_4NX salts to InX_3 solutions up to a molar ratio of $X^-/InX_3 = 1$ produced no changes in the resonance frequencies of InX_4^-, but the line widths were significantly sharper (Table I). Further increases in X^- concentrations affected the spectra of chloride, bromide, and iodide salts in different ways. Our results are consistent with data for InX_4^-/X^- systems[6] and indicate further indium complexation with chloride and formation of $InCl_5^{2-}$ and $InCl_6^{3-}$ anions, a weak interaction of $InBr_4^-$ with the bromide ion, and a lack of complex formation, with the exception of InI_4^-, for the iodide system. This corresponds to many previous studies demonstrating that the maximum coordinating number for anionic indium species with iodide in nonaqueous solution is 4.

Mixed Halogeno Species $InX_nY_{4-n}^-$. The formation of InX_4^- anions in acetonitrile solutions of indium trihalides leads to an easy preparation of mixed $InX_nY_{4-n}^-$ (X ≠ Y = Cl, Br, I) complexes. The case of an equimolar mixture of $InBr_3$ and InI_3 solutions serves as a good example: The spectrum (Figure 2) consists of five distinct lines, corresponding to the ^{115}In NMR frequencies of $InBr_nI_{4-n}^-$ anions. All of the possible forms are also observed for $InCl_3$–$InBr_3$ and $InCl_3$–InI_3 solutions (Table II).

Mixed halide anions $InX_nY_{4-n}^-$ may be also obtained by adding Y^- to InX_3 solutions for molar ratios $Y^-/InX_3 \leq 1$. The typical ^{115}In NMR spectrum (Figure 3) displays bands of indium anionic species for the case of the Cl^-/InI_3 system.

Further increasing the Y^- concentrations variously influenced the spectra of the trihalide solutions in a manner similar to that

---

(19) Dalibart, M.; Derouault, J.; Granger, P.; Chapelle, S. *Inorg. Chem.* **1982**, *21*, 1040.

(20) Carty, A. J.; Tuck, D. G. *Prog. Inorg. Chem.* **1975**, *19*, 243.

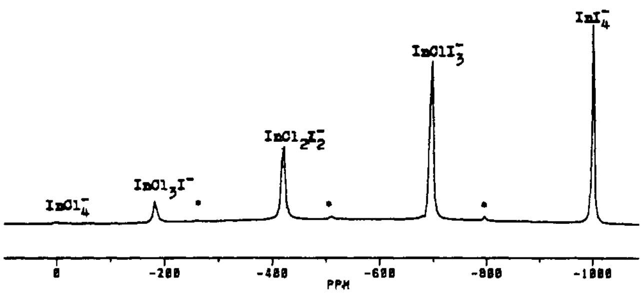

Figure 3. ^{115}In NMR spectrum of an InI_3 acetonitrile solution with added $(C_2H_5)_4NCl$ (Cl/InI_3 = 0.7; 0.3 M InI_3). * = impurity peaks of $InI_nBr_{4-n}^-$.

Table II. Mean ^{115}In Resonances for Mixed $InX_nY_{4-n}^-$ Anions in Acetonitrile Solutions

anion	$-\delta$, ppm	anion	$-\delta$, ppm
$InCl_3Br^-$	45	$InClI_3^-$	698
$InCl_2Br_2^-$	107	$InBr_3I^-$	417
$InClBr_3^-$	176	$InBr_2I_2^-$	600
$InCl_3I^-$	183	$InBr_3I^-$	795
$InCl_2I_2^-$	420		

for the above mentioned X^-/InX_3 systems. No bands assigned to mixed $InX_nY_{4-n}^-$ species were observed for $Y^-/InX_3 > 1$ (Y = Cl, Br) molar ratios. The spectra displayed one broad ($\Delta H_{1/2}$ = 2.5–7.0 kHz) line with the chemical shift depending on the Y^- concentration, which may be determined by fast exchange between a few forms and/or by formation of five- and six-coordinate complexes.

The addition of iodide up to $I^-/InX_3 = 3$ produced no changes in either chemical shift or line width of $InX_nI_{4-n}^-$ resonances, suggesting that I^- is too weak compared to Cl^- and Br^- to displace them from mixed species and that the formation of complexes with coordination numbers higher than 4 is impossible.

InX_3–MNCS–CH_3CN (X = Cl, Br, I; M = Na, K, $(C_4H_9)_4N$) Systems. Spectra of Bu_4NNCS–InX_3 solutions display three resonances, only one of which (–504 ppm; $\Delta H_{1/2}$ = 1050 Hz) is not dependent on the dilution of the solution and whose intensity increases with increasing NCS/In.

A different result was obtained for MNCS–InX_3 (M = Na, K) systems. The precipitate of MX formed with the first portions of added NCS^-. It then fully dissolved in a short period because of an In–X interaction, and the bands of InX_4^- anions were detected for all solutions independently of the halide. When the thiocyanate concentration was increased, one more band (–504 ppm; $\Delta H_{1/2}$ = 580–920 Hz) was detected along with the InX_4^- resonance. A line with almost identical parameters (–505 ppm; $\Delta H_{1/2}$ = 450–680 Hz) was observed for acetonitrile solutions of $(R_4N)_3In(NCS)_6$ (R = CH_3, C_4H_9; C = 0.1–0.5 M) with octahedral coordination of the indium anion. Therefore, the following reactions take place in the InX_3–MNCS–CH_3CN solutions:

$$k\mathrm{InX_3} + l\mathrm{MNCS} \rightarrow n\mathrm{InX_4}^- + m\mathrm{In(NCS)_6}^{3-} + p\mathrm{MX}\downarrow \quad (1)$$

Not dissolving more precipitate of MX forms with molar ratio $l/k \geq 1.5$. Typical spectra for these systems are presented in Figure 4. Increasing the NCS concentration shifts the equilibrium toward $In(NCS)_6^{3-}$ formation, and for $l/k = 6$, bands of InX_4^- anions are not observed.

Such a configuration equilibrium between complexes with different coordination numbers was known earlier only for the $In(ClO_4)_3$–HI–H_2O–acetone system when $In(H_2O)_6^{3+}$ and InI_4^- species were simultaneously present in solution.[12] The InX_3–MNCS–CH_3CN systems are remarkable because of the coexistence of four- and six-coordinate anionic complexes; this is the reason for examining the equilibria for all the halides, not just for iodide.

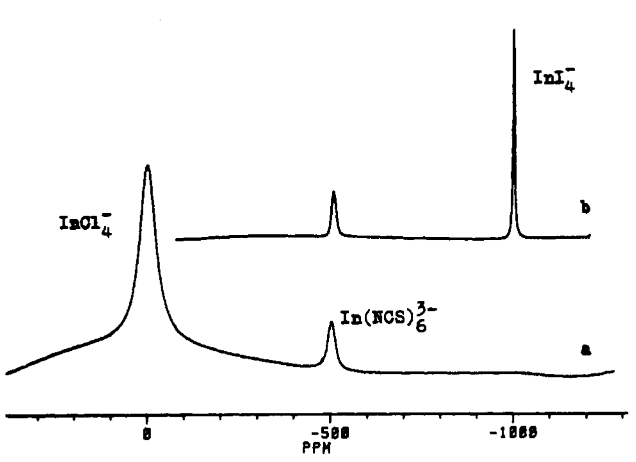

Figure 4. ^{115}In NMR spectra of InX_3–KNCS–CH_3CN systems (0.3 M indium salts): (a) X = Cl and $NCS/InCl_3$ = 1.8; (b) X = I and NCS/InI_3 = 2.7.

Table III. ^{14}N NMR Resonances for NCS^-- and NO_2^--Containing Solutions

compd	solvent	δ, ppm	$\Delta H_{1/2}$, Hz
KNCS	H_2O	–166	106
$[(CH_3)_4N]_3[In(NCS)_6]$	CH_3CN	–208	353
KNO_2	H_2O	236	210
$In(NO_2)_6^{3-}$	CH_3CN	–6	60

The interactions of aluminum and gallium trihalides with thiocyanate in acetonitrile solutions are significantly different from the indium reaction. The resonances of $MX_n(NCS)_{4-n}^-$ together with MX_4^- anions (M = Al^{3+}, Ga^{3+}; X = Cl^-, Br^-, I^-) can be observed by ^{27}Al and ^{71}Ga NMR for MX_3–KNCS–CH_3CN systems.[21] A change in polyhedron configuration and formation of $M(NCS)_6^{3-}$ as the NCS^-/MX_3 ratio increases take place only for aluminum, whereas complete displacement of X^- from four-coordinate halide complexes of gallium does not occur. The lack of four-coordinate indium(III) thiocyanate species can probably be associated with the strong preference of In(III) for octahedral coordination by small, electronegative, and hard ligands.[20]

Being an ambidentate functional group, the NCS^- anion is usually able to realize two ways of bonding—via nitrogen or sulfur. According to the literature, only In–N bonds are formed in the octahedral anion $In(NCS)_6^{3-}$.[7] Because nitrogen NMR shifts are well-known as a criterion for establishing the mode of linkage,[22] we have used ^{14}N NMR to verify that In–N bonding is retained in solution. It was shown for a number of metals in the thiocyanate complexes that the nitrogen shielding increased for ligating nitrogen (about 15–40 ppm upfield of the signal for the free anionic ligand) but coordination shifts for terminal nitrogen were relatively small and were of either sign. Table III shows that the NCS band of $[(CH_3)_4N]_3In(NCS)_6$ is shifted toward high field by 42 ppm compared to that of an aqueous solution of KNCS. We therefore conclude that the InN_6 kernel of the indium thiocyanate complex is also stabilized in solution.

InX_3–MNO_2–CH_3CN (M = Na, K; X = Cl, Br, I) Systems. The spectra of InX_3–MNO_2 and InX_3–MNCS solutions in acetonitrile largely coincide; besides the resonances of InX_4^- anions, a band (–513 ppm; $\Delta H_{1/2}$ = 1300–3000 Hz) whose intensity increases with increasing MNO_2 concentration was detected for NO_2^- systems (Figure 5). The fact that its chemical shift is close to that of the $In(NCS)_6^{3-}$ resonance leads us to assume formation of $In(NO_2)_6^{3-}$. Therefore, InX_3–MNO_2 solutions also demonstrate configuration equilibrium between four- and six-coordinate indium anions.

---

(21) Tarasov, V. P.; Petrosyants, S. P.; Kirakosian, G. A.; Buslaev, Yu. A. *Koord. Khim.* **1980**, *6*, 52.

(22) Mason, J. *Chem. Rev.* **1981**, *81*, 205.

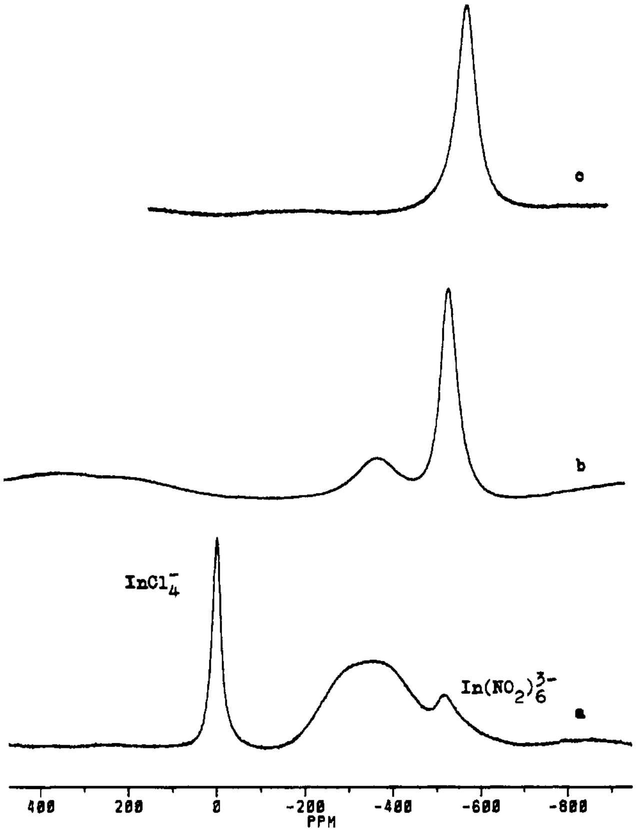

Figure 5. ^{115}In NMR spectra of $InCl_3$–KNO_2–CH_3CN systems (0.3 M of indium salt): (a) $NO_2/InCl_3$ = 3.4; (b) $NO_2/InCl_3$ = 2.7; (c) $NO_2/InCl_3$ = 8.3.

Unlike thiocyanate, NO_2^- is an ambidentate group for which there is a large difference in nitrogen shifts depending on the geometrical differences in the two modes of linkage. The N-bonded nitro ligand (in $M–NO_2$ or RNO_2 compounds) resonates at medium field in the region of $MeNO_2$ and NO_3^-, and the bent nitrite with a two-coordinate nitrogen (only RONO compounds are known) resonates some 200 ppm downfield.[22] We have now measured ^{14}N chemical shifts for NO_2^- solutions. Table III shows a high-field shift of 240 ppm for the nitrogen resonance of $InCl_3$–NO_2^- systems compared with that of the free anion. Analogous differences have been observed for a number of transition metal complexes with NO_2^- (coordination shift of about 250 ppm for $NaNO_2$[23]) and indicate N-bonding in the complexes. Thus $In(NO_2)_6^{3-}$ is also a nitro species.

Apart from the similarities between the systems containing MNCS and MNO_2, the latter solutions exhibit some peculiarities. An insoluble phase is present for the entire range of the NO_2^-/InX_3 molar ratio. The $In(NO_2)_6^{3-}$ complex is unstable in solution, preventing us from obtaining and investigating $M_3(NO_2)_6$ compounds in the solid state. There are also some differences in spectra of the NO_2^- solutions dependent on the halide. Thus only InX_4^- and $In(NO_2)_6^{3-}$ resonances were observed when X = Br and I for all NO_2^- concentrations whereas one more broad band ($\Delta H_{1/2}$ = 3.7–10 kHz) with a chemical shift in the range between $InCl_4^-$ and $In(NO_2)_6^{3-}$ signals was detected for some interval of NO_2^-/InX_3 for the indium trichloride solution (Figure 5). It may be supposed that this band is due to mixed chloro/nitro complexes. The large line width together with the tendency of indium to form six-coordinate species with N-donor atoms allowed us to assign this line to $InCl_n(NO_2)_{6-n}^{3-n}$ complexes.

Notwithstanding the fact that both thiocyanate and nitrate are N-bonded to indium, the differences between their geometries and efficient charges on the nitrogen atoms[8] result in the NCS^- ligand being stronger than NO_2^-; thus the formation of $In(NCS)_6^{3-}$ does not involve intermediate species.

It seems likely that of all acido ligands considered (Cl^-, Br^-, I^-, NCS^-, NO_2^-), only chloride and nitrite can be combined in the coordination sphere of indium because of the similarity of their donor characteristics with respect to In^{3+}. For all other possible anion-pair combinations in solutions, only extreme homoligands (InX_4^- and InL_6^{3-}) are formed.

Conclusions

Trihalides of indium undergo a coordination disproportionation reaction in acetonitrile solution as do aluminum and gallium salts.[19,24] However in contrast to the cases of aluminum and gallium, a $M(CH_3CN)_6^{3+}$ cation has not been detected for indium. It seems likely that the equilibrium with InX_4^- is established by mixed halogeno/solvent cationic species $InX_n(CH_3CN)_{6-n}^{(3-n)+}$. This distinction among solutions of Al^{3+}, Ga^{3+}, and In^{3+} trihalides may be a result of an increase of metal ion softness for the series Al^{3+}–Ga^{3+}–In^{3+} and a weakening of M–N (CH_3CN) bonds as compared to M–X (X = Cl^-, Br^-, I^-) bonds.

The interaction of InX_3 with halide ions results in the formation of four coordinate InX_4^- or mixed $InX_nY_{4-n}^-$ anions. Similar halide complexes are produced by aluminum and gallium,[25-27] for which MX_4^- anions (X = Cl^-, Br^-, I^-) are the highest complex forms, whereas indium has the ability to form species with the coordination numbers exceeding 4 (for X = Cl^-, Br^-).

Indium forms six-coordinate InL_6^{3-} complexes with pseudohalides (NCS^-, NO_2^-) which are in equilibrium with InX_4^- anions. We have not been able to observe four-coordinate indium species with halide and pseudohalide anions; if mixed complexes are formed, they are six-coordinate. This distinguishes indium from aluminum and gallium, for which the presence of halide ions (Cl^-, Br^-, I^-) in the coordination sphere stabilizes the four-coordinate polyhedron.[21]

---

(23) Bramley, R.; Figgis, B. N.; Nyholm, R. S. *J. Chem. Soc. A* **1967**, 861.

(24) Buslaev, Yu. A.; Tarasov, V. P.; Petrosyants, S. P.; Melnikov, N. N. *Zh. Strukt. Khim.* **1974**, *15*, 617.

(25) Kidd, R. G.; Traux, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 6867.

(26) Buslaev, Yu. A.; Tarasov, V. P.; Melnikov, N. N.; Petrosyants, S. P. *Dokl. Akad. Nauk SSSR* **1974**, *216*, 796.

(27) Dechter, J. P. *Prog. Inorg. Chem.* **1982**, *29*, 285.