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Coordination Compounds of Indium. 37. ^{115}In NMR Studies of Anionic Indium Species in Nonaqueous Solution

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^{115}In NMR studies are reported for InX_4^-, $In_2X_6^{2-}$, and InX_4^- in the presence of X^-, InX_3Y^-, and $InX_2Y_2^-$ anions ($X \neq Y$ = Cl, Br, I) in various nonaqueous solvents. The results confirm and extend previous studies of the nonaqueous solution chemistry of these complexes.

Introduction

The solution chemistry of the complexes of indium, and especially those involving halide ligands, has been the subject of some speculation, much of it founded on evidence which is at best indirect. The results of both spectroscopic and preparative work have been interpreted in terms of the various species presumed to be present, but as pointed out elsewhere, the preparative evidence must be treated with caution in this respect.[1,2] Of the spectroscopic techniques available at the present time, nuclear magnetic resonance offers the distinct possibility of obtaining information not otherwise available. Both ^{115}In (95.72% abundant) and ^{113}In (4.28%) have nuclear spins ($I = {}^9/_2$) which render the technique intrinsically difficult, but previous workers have shown that useful information can be obtained. Three recent papers have been concerned with aspects of the solution chemistry,[3-5] and the literature on this and related topics has been reviewed by Hinton and Briggs.[6]

We have now carried out ^{115}In NMR studies of a number of anionic complexes and related species in nonaqueous solution. As in previous work, the absorption bands are broad, but the chemical shifts due to ligand substitution, changes in coordination number, etc. are sufficiently large to minimize this factor. The spectral results serve both to reinforce earlier work on the solution chemistry of some of the complexes involved and to provide new information on the behavior of others.

Experimental Section

Materials. All organic solvents were refluxed with, distilled from, and stored over calcium hydride.

The preparation of the indium complexes studied in this work has been described in earlier publications in this series.[7-10]

Spectroscopy. ^{115}In spectra were obtained with a Bruker CXP-100 variable-frequency FT spectrometer operating at 19.72 MHz, with a magnetic field of 2.114 T. The instrument was externally locked onto the deuterium resonance of D_2O. No corrections were made for bulk diamagnetic susceptibility differences between solvents; the maximum correction involved (0.66 ppm) is smaller than the uncertainty in determining the position of the narrowest resonance observed.

All samples were run as solutions (approximately 3-cm^3 volumes) in 1-cm (o.d.) tubes, at a temperature of 27 °C.

Table I. Concentration and Solvent Dependence of ^{115}In Resonance of $[(C_6H_5)_4P][InCl_4]$ at 27 °C

solvent	$[(C_6H_5)_4P]$-$[InCl_4]$ concn, M	δ	$\Delta H_{1/2}$,[a] Hz
CH_2Cl_2	0.1–0.5	0 ± 2	370
acetone	0.1	+4 ± 1	180
CH_3CN	0.1	0 ± 2	310
tetrahydrofuran	0.1	−2 ± 2	420
$CHCl_3$	0.1	−3 ± 4	730
methanol	0.1	very broad	

[a] ±30 Hz.

Results and Discussion

As with other elements, changes in molecular structure and environment may affect both resonance frequency and line width in ^{115}In NMR spectroscopy. In particular, the symmetry of the electronic environment at the indium nucleus defines the magnitude of the field gradient whose interaction with the nuclear quadrupole governs the relaxation times and hence the spectral line widths. The narrowest lines are therefore to be expected in tetrahedral or octahedral species, narrow in this context implying half-widths ($\Delta H_{1/2}$) of less than 1000 Hz. In such cases, line broadening on the addition of, for example, halide ion to the solution may indicate the onset of some exchange reaction, although specific ion pair formation, especially with an asymmetric cation, may also cause similar effects.

Previous investigators have reported chemical shifts (δ) in terms of a standard acidified aqueous solution of indium(III) perchlorate. The results in this paper are referred to a standard (zero) corresponding to the ^{115}In resonance of a 0.5 M solution of $InCl_4^-$ in dichloromethane. The difference of 441 ppm between $InCl_4^-$ and $[In(H_2O)_6]^{3+}$(aq) found in the present work is close to the chemical shift of 430 ± 15 ppm for $InCl_4^-$ in various nonaqueous solvents relative to $[In(H_2O)_6]^{3+}$ in water (cf. ref 6 for a compilation of previous results).

Solvent and Concentration Effects. The tetrahedral structure of the InX_4^- anions, long predicted as the result of Raman studies,[11] has been confirmed by X-ray crystallography in the case of $InCl_4^-$,[12] $InBr_4^-$,[13] and InI_4^-.[14] Such species are expected to give narrow-line spectra (see above), and as a preliminary to an investigation of the spectra of other complexes, we demonstrated that changes in solute concentration or solvent have only a slight effect on the resonance frequency. Table I shows that for a series of solvents, and for concentrations over the range 0.1–0.5 M in dichloromethane, the frequency shifts are identical within experimental error, except for acetone, for which the difference is only a few ppm.

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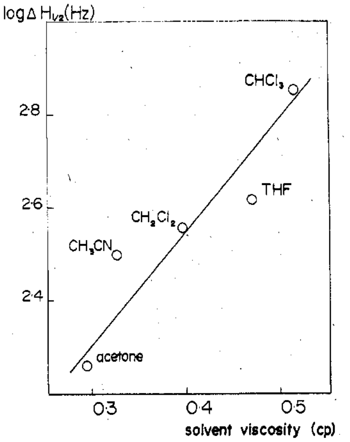

Figure 1. ^{115}In line widths as a function of solvent viscosity (0.1 M solutions of $[(C_6H_5)_4P][InCl_4]$).

Table II. ^{115}In Resonances for InX_4^- Salts and Related Compounds in Nonaqueous Solution

compd	solvent	concn, M	δ^a	$\Delta H_{1/2}$,[b] Hz
$[(C_6H_5)_4P][InCl_4]$	various	various	0	[c]
$[(C_6H_5)_4P][InBr_4]$	CH_2Cl_2	0.1–0.5	−265	290
$[(C_6H_5)_4P][InBr_4]$	CH_3CN	0.1	−258	180
$[(C_4H_9)_4N][InI_4]$	CH_3CN	0.03	−989	250
$[(C_6H_5)_3CH_3As][InI_4]$	CH_2Cl_2	0.1	−1010	430
$InI_3 \cdot 2Me_2SO$	acetone	0.075	−1013	450
$InI_3 \cdot 2CH_3CN$	acetone	0.075	−1013	1000
CH_3InI_2	CH_3CN	0.6	−1005	1120

[a] ±1 ppm for $InCl_4^-$ and $InBr_4^-$; ±5 ppm for iodide species. [b] ±30 Hz. [c] See Table I.

Accordingly, in the later parts of this paper, the frequencies of compounds in different solvents are compared without any correction factor.

The solvent dependence of the line width deserves some comment, since the $\Delta H_{1/2}$ values range from approximately 200 to 800 Hz. The line widths show a significant dependence on viscosity (on the assumption that one can use the available viscosities of the pure solvents rather than those of the experimental solutions), and Figure 1 shows a plot of log $\Delta H_{1/2}$ vs. viscosity. No value is given for methanol, since the absorption is too broad for any significant measurement to be made. This viscosity dependence then shows that a significant contribution to the line narrowing must come from molecular rotation in solution; this rotation may be that of the anion itself or of the ion pair. There is no monotonic dependence of line widths on dielectric constant of the solvent as would be expected if ion pair formation were the only factor affecting the line width, although it has been suggested by previous workers[3-5] that this process alone suffices to explain the line broadening observed with solutions of InX_4^- salts.

Tetrahalogenoindate(III) Anions. Table II shows the ^{115}In resonances of various species known from X-ray or spectroscopic studies to contain tetrahedral InX_4^- anions. We first note that each of the anions $InCl_4^-$, $InBr_4^-$, and InI_4^- shows a relatively sharp single resonance, in keeping with the high symmetry. The chemical shift (δ) is defined as $((\nu - \nu_0)/\nu_0) \times 10^6$ ppm, and the upfield shift in the order $InCl_4^- < InBr_4^- < InI_4^-$ then accords with the increasing electron density around the indium nucleus as the ligand electronegativity decreases along the series; we return to this point below. The observed chemical shifts are in good agreement with those reported in other studies of InX_4^- anions in various aqueous and nonaqueous media,[6] again demonstrating the very small effect of solvent on the resonance frequency. For compounds containing the InI_4^- anion, changes in cation lead to associated changes in δ which are larger than those reported in Table I but which are still only of the order of 1%.

The three formally neutral compounds in Table II are all cases in which an ionic dimer formulation has been proposed. Thus for $InI_3 \cdot 2Me_2SO$, X-ray methods[14] established the structure $[InI_2(Me_2SO)_4][InI_4]$, while vibrational spectroscopy indicates that the formulas of the other two compounds in the solid state are $[InI_2(CH_3CN)_4][InI_4]$[10] and $[(CH_3)_2In][InI_4]$.[9] In each case, the NMR results are consistent with the presence of the InI_4^- anion in solution. No resonance could be identified for the cation in any of these systems; this is not surprising in view of the molecular symmetry which will cause large quadrupole broadening which cannot be averaged out by the tumbling motion. For the $[(CH_3)_2In]^+$ cation, solvation may well lead to the formation of $[(CH_3)_2In(CH_3CN)_4]^+$ species in solution, again lowering the symmetry of the cation.

Finally, we note that InI_3, which has the iodine-bridged structure $X_2InX_2InX_2$ in the solid state and in nondonor solvents,[15] also gives a resonance at −1031 ± 5 ppm from $InCl_4^-$ ($\Delta H_{1/2}$ = 1354 Hz) in dichloromethane. The formal charge apparently has little effect on the resonance frequency, given that both InI_4^- and In_2I_6 involve In(III) tetrahedrally bonded to iodine. No resonance was detected for solutions of either $InCl_3$ or $InBr_3$ in acetonitrile or dichloromethane.

Hexahalogenoindate(II) Anions. The $In_2X_6^{2-}$ anions (X = Cl, Br, I) have been prepared as the tetra-*n*-butylammonium salts and shown by vibrational spectroscopy and force constant analysis to have the structure $[X_3In-InX_3]^{2-}$, with a staggered ethane-like configuration in the solid state.[16] The ^{115}NMR spectra of solutions in acetonitrile show a single resonance in each case: $[(C_4H_9)_4N]_2[In_2Cl_6]$, −2.1 ppm, $\Delta H_{1/2}$ 500 Hz; $[(C_4H_9)_4N]_2[In_2Br_6]$, −258 ppm, $\Delta H_{1/2}$ 330 Hz; $[(C_4H_9)_4N]_2[In_2I_6]$, −989 ppm, $\Delta H_{1/2}$ 250 Hz. The chloride and iodide compounds were at (formal) concentrations of 0.1 M, and the bromide compound was at 0.05 M.

The resonances observed are almost identical in frequency with those found for the corresponding InX_4^- anion (cf. Table II). This result finds a ready explanation in the previously proposed[16] disproportionation equilibrium (eq 1). We believe

$$In_2X_6^{2-} \rightleftharpoons InX_4^- + InX_2^- \qquad (1)$$

that the failure to observe resonances from $In_2X_6^{2-}$ or InX_2^- (for which a bent structure has been proposed) is also due to the low symmetry of these species.[16,17]

The intensity of the InX_4^- peak in the spectra of $In_2Cl_6^{2-}$ and $In_2I_6^{2-}$ was compared to that of a solution of InX_4^- of known concentration in the same solvent under identical instrument conditions, thus allowing an estimate of the concentration of each species in eq 1 and hence of the equilibrium constants. We find $K \simeq 0.02$ for $In_2Cl_6^{2-}$ and $K \simeq 0.2$ for $In_2I_6^{2-}$ in acetonitrile, showing that the chloro compound is significantly more stable to disproportionation than is the iodide. This is in keeping with the previous spectroscopic and force constant analysis,[16] which gave a value for K_{In-In} of 0.63 in $In_2Cl_6^{2-}$ and 0.24 in $In_2I_6^{2-}$; this agreement unfortunately reveals nothing as to the mechanism of rupture of the In–In bond of these anions in solution.

InX_4^-/X^- Systems. In an attempt to extend our knowledge of the solution chemistry of anionic indium complexes, we have investigated the effect of added halide ion on the ^{115}In NMR spectra of InX_4^- species. The changes in chemical shift are shown for X = Cl in Figure 2 and for X = Br in Figure 3. In both cases, the experimental limits were those imposed by

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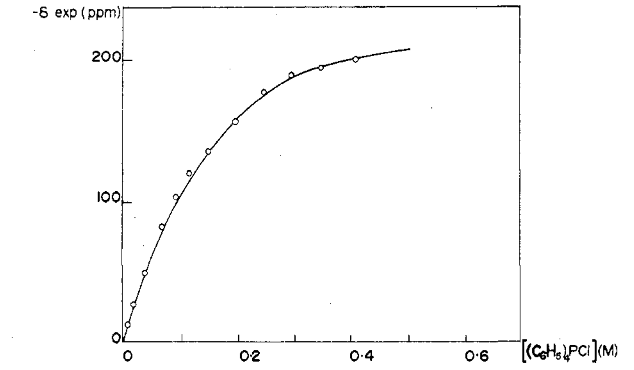

Figure 2. ^{115}In chemical shift as a function of added $(C_6H_5)_4PCl$ (initial solution 0.1 M $[(C_6H_5)_4P][InCl_4]$ in acetonitrile).

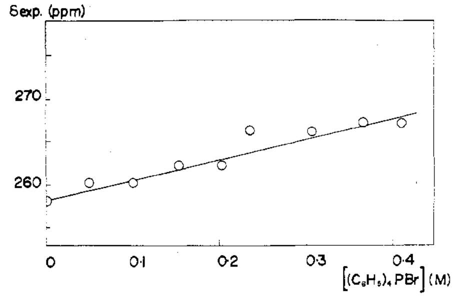

Figure 3. ^{115}In chemical shift as a function of added $(C_6H_5)_4PBr$ (initial solution 0.1 M $[(C_6H_5)_4P][InBr_4]$).

the solubility in acetonitrile of the appropriate tetraphenylphosphonium salts, being those which offered the best solubility properties.

The result which should be noted first is that, for $(C_6H_5)_4PInI_4$, the addition of $(C_6H_5)_4PI$ up to a threefold excess produced no change in either the chemical shift (1007 ± 1 ppm) or the line width ($\Delta H_{1/2} = 147 \pm 26$ Hz) of the InI_4^- resonance. This is in keeping with many previous studies in this laboratory showing that the maximum coordination number for anionic iodoindium(III) species is 4. The result also shows that changes in susceptibility, dielectric constant, etc. due to the addition of excess halide do not influence the ^{115}In chemical shift (cf. Tables I and II), so that the changes observed (X = Cl or Br) can be discussed in this light.

For the $InCl_4^-/Cl^-$ system, the marked change in chemical shift indicates further complexing which may involve one or both of the equilibria shown in eq 2 and 3 for which the

$$InCl_4^- + Cl^- \rightleftharpoons InCl_5^{2-} \qquad (2)$$

$$InCl_5^{2-} + Cl^- \rightleftharpoons InCl_6^{3-} \qquad (3)$$

equilibrium constants K_5 and K_6 apply. The treatment in the standard manner initially assumed a chemical shift δ_6 for $InCl_6^{3-}$ in the order of −220 ppm from $InCl_4^-$ and further assumed that $K_6 \ll K_5$. The best fit to the experimental results gives δ_5 −115 and δ_6 −235 (each ±5) and $K_5 = 350 \pm 100$ and $K_6 = 10 \pm 3$, from which one derives the curve shown (Figure 2) fitting the experimental points satisfactorily.

Both $InCl_5^{2-}$ and $InCl_6^{3-}$ anions have been identified previously. The pentachloroindate(III) anion is a rare example of a main group complex having C_{4v} symmetry in the solid state,[18,19] and equilibrium 2 was proposed earlier to explain experimental results involving the recrystallization of $[(C_2H_5)_4N]_2[InCl_5]$ from nonaqueous solution.[8] For the thallium analogue $TlCl_5^{2-}$, spectroscopic studies[20] of solutions in nitromethane gave $K_5 = 0.2$, significantly smaller than that found above (for acetonitrile). The $InCl_6^{3-}$ anion is also a known species, with the expected octahedral structure in the solid state.[8,20]

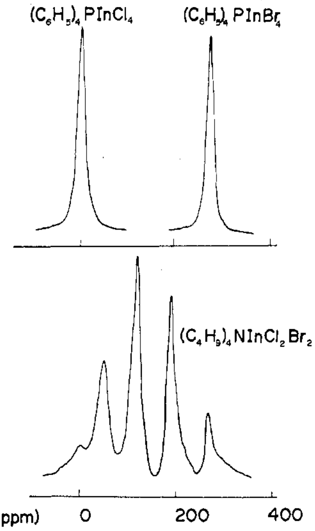

Figure 4. Some typical ^{115}In spectra (salts in dichloromethane, concentration 0.1 mol L^{-1}).

The $InBr_4^-/Br^-$ system shows evidence for the weak formation of complexes with coordination numbers higher than 4, but because of the small changes in δ, the results do not lend themselves to the above analysis. The general conclusion is that K_5 goes in the order Cl ≫ Br ≫ I = 0, a result which parallels the preparative work.[1,8] In this context, it should be noted that the $InBr_5^{2-}$ anion has not been stabilized in the solid state, although $InBr_6^{3-}$ salts are known, and the experimental results in Figure 3 may reflect a similar difficulty in forming five-coordinate In^{III}/Br anionic complexes in solution.

The chemical shifts for $InCl_5^{2-}$ and $InCl_6^{3-}$ deserve some comment. The effect of adding extra chloride ions to the coordination shell of indium(III) is to produce changes in shielding similar to those of replacing chloride by bromide (cf. Table II and the discussion of $InX_nY_{4-n}^-$ species below). Both situations represent potentially increased electron donation to the indium(III) ion as the number of chlorides increases and/or the electronegativity of the ligand decreases. We have at present no experimental method of separating these two effects, but it is worth noting that the NMR results demonstrate such changes much more clearly than do earlier studies of X-ray photoelectron spectra of these anions in the solid state.[22]

Mixed Halogeno Species InX_3Y^-, $InX_2Y_2^-$, and InX_2YZ^-. In a recent paper,[23] we have discussed the preparation of anionic indium(III) complexes of the type InX_3Y^- and $InX_2Y_2^-$ ($X \neq Y$ = Cl, Br, I) by the oxidation reactions

$$In_2X_6^{2-} + Y_2 \rightarrow 2InX_3Y^- \qquad InX_2^- + Y_2 \rightarrow InX_2Y_2^- \quad (4)$$

The vibrational spectra and force constant analysis supported the structural assignment of these anions as having C_{3v} or C_{2v} symmetry, and this has subsequently been confirmed in the case of $InCl_3Br^-$ and $InBr_3Cl^-$ by X-ray crystallography.[13]

The ^{115}In NMR spectra of these anions have now been recorded, in each case with use of 0.1 M solutions in di-

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Table III. Experimental ^{115}In Resonances (in ppm) for $InX_nY_{4-n}^-$ Anions ($X \neq Y$ = Cl, Br, I) in CH_2Cl_2 Solution[a]

	assignt[b]											
parent anion	$InCl_4^-$	$InCl_3Br^-$	$InCl_2Br_2^-$	$InClBr_3^-$	$InBr_4^-$	$InBr_3I^-$	$InBr_2I_2^-$	$InBrI_3^-$	InI_4^-	$InClI_3^-$	$InCl_2I_2^-$	$InCl_3I^-$
$InCl_4^-$	0											
$InCl_3Br^-$	0 (3.5)	−54 (3.5)	−120 (2)	−191 (1)	−269 (tr)							
$InCl_2Br_2^-$	−3 (tr)	−50 (2)	−114 (3)	−183 (3)	−258 (2)							
$InClBr_3^-$	0 (tr)	−54 (1)	−120 (2)	−191 (3.5)	−269 (3.5)							
$InBr_4^-$					−270							
$InBr_3I^-$					−258 (6)	−434 (3)	−626 (1)	−825 (tr)				
$InBrI_3^-$							−614 (2)	−810 (4)	−1010 (4)			
InI_4^-									−1010			
$InClI_3^-$									−1013 (4)	−711 (4)	−440 (2)	
$InCl_3I^-$										−706 (1)	−431 (3)	−191 (6)

[a] Solutions prepared by dissolving tetra-*n*-butylammonium salt of parent anion in CH_2Cl_2 (0.1 mol L^{-1}). [b] Figures in parentheses are approximate relative intensities normalized to a total of 10; tr = detected, in small quantity.

Table IV. Mean ^{115}In Resonances for $InX_4Y_{4-n}^-$ Anions in Dichloromethane

	anion	−δ (±2)
1	$InCl_4^-$	0
2	$InCl_3Br^-$	52
3	$InCl_2Br_2^-$	117
4	$InClBr_3^-$	187
5	$InBr_4^-$	264
6	$InBr_3I^-$	429
7	$InBr_2I_2^-$	616
8	$InBrI_3^-$	812
9	InI_4^-	1010
10	$InCl_3I^-$	190
11	$InCl_2I_2^-$	429
12	$InClI_3^-$	706
13	$InCl_2BrI^-$	258[a]
14	$InClBr_2I^-$	337
15	$InClBrI_2^-$	513

[a] Estimated. See text.

chloromethane. The case of $InCl_2Br_2^-$ well illustrates the findings; the spectrum (Figure 4) consists of five distinct lines, the extreme of which corresponds to the ^{115}In resonance frequencies of $InCl_4^-$ and $InBr_4^-$, respectively, and the intermediate lines are therefore assigned to $InCl_3Br^-$, $InCl_2Br_2^-$, and $InBr_3Cl^-$. The same resonances were obtained from solutions prepared from either $InCl_3Br^-$ or $InBr_3Cl^-$, although the relative intensities differed significantly in each of these three cases. Repetition of such experiments with other anions led to the results shown in Table III; results are not available for solutions of $InBr_2I_2^-$ or $InCl_2I_2^-$, but the ^{115}In frequencies in these ions could be deduced from the spectra of other salts. We have also shown experimentally that the multiline spectrum of any given $InX_nY_{4-n}^-$ salt can be reproduced by mixing solutions in the ratio $nInX_4^-:(4-n)InY_4^-$ and in the ultimate case obtained a twelve-line spectrum by mixing equal volumes of 0.1 M solutions of $InCl_4^-$, $InBr_4^-$, and InI_4^-. The analysis of all these experimental results leads to Table IV. Three pairs of ions clearly overlap in the twelve-line case, but only for $InCl_2BrI^-$ is there an absence of information from other experiments.

These results are similar to those reported for mixed AlX_4^-/AlY_4^- anions by Kidd and Truax,[24] using ^{27}Al NMR. Like these authors, we find that the line widths of the C_{3v} and C_{2v} species are significantly greater than those of the tetrahedral anions, an effect which they ascribe to the lower molecular symmetry of the former. Redistribution reactions in the isoelectronic tin(IV) halides have also been studied by NMR methods,[25] and the half-life for establishment of the equilibrium involving the series SnX_4, SnX_nY_{4-n}, SnY_4 is estimated at between 10^{-3} and 10 s. Almost identical values apply in the present case; the maximum separation between adjacent lines defined the lower limit, and the establishment of the separate line spectrum within the minimum time of approximately 30 s needed for mixing the solutions fixes the upper limit.

Since the ^{115}In resonance frequency reflects the electron density at the nucleus, which is itself at the center of the molecule, one might expect some simple dependence on ligand electronegativity. The results in Figure 5 show that such a relationship indeed holds, with the results falling on a series of three curves, one for each InX_4^-, InY_4^- series, using the Allred–Rochow values for χ. It has been suggested previously[22,26] that both X-ray photoelectron spectra and vibrational stretching force constants for anionic indium(III) complexes demonstrate the strongly ionic nature of the In–X bond, and

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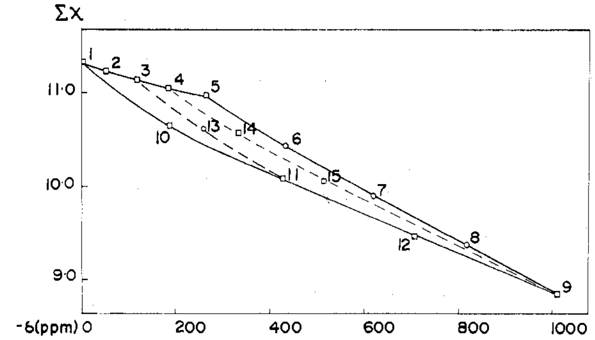

Figure 5. ^{115}In chemical shifts as a function of total ligand electronegativity for $InX_nY_{4-n}^-$ and InX_2YZ^- anions. Key numbers refer to entries in Table IV.

the data in Figure 5 generally confirm such a model. The curves are nonlinear, and markedly so for the chloride–iodide complexes, so that in any given series, an $InX_nY_{4-n}^-$ complex has a lower chemical shift than would be estimated by interpolation from the appropriate InX_4^-/InY_4^- pair results on the assumption of a linear dependence of δ on $\sum\chi$. The results for InX_2YZ^- anions show similar general trends, and the set $InClBr_3^-$, $InClBr_2I^-$, $InClBrI_2^-$, $InClI_3^-$ lie on a smooth curve. All in all, it is obvious that factors over and above ligand electronegativity are involved in determining δ, demonstrating that the ionic model is not a completely accurate description of the bonding. As expected, the effects of a significant covalent contribution show up most clearly in anions containing In–I bonds. We hope to discuss this point more fully elsewhere.

Finally we note that these NMR results cast an interesting light on the earlier preparative and spectroscopic work. First, insofar as the solution chemistry is concerned, the behavior of a mixture of InX_4^- anions is identical with that of the corresponding $InX_nY_{4-n}^-$ anion, so that the elaborate preparative route was probably unnecessary in such cases, although it may have merit elsewhere. Second, we have shown that a sample of $[(C_4H_9)_4N][InCl_3Br]$ of known vibrational spectrum dissolves in ethanol to give a five-line ^{115}In NMR spectrum, which is not significantly changed by raising of the temperature. On crystallization, the $InCl_3Br^-$ salt is again obtained, and the residual liquor still shows a five-line spectrum. Thus the present work and that described earlier[23] are experimentally compatible, and all that remains is to find a satisfactory explanation. Work on this is proceeding.

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Registry No. $[(C_6H_5)_4P][InCl_4]$, 30862-70-5; $[(C_6H_5)_4P][InBr_4]$, 68091-45-2; $[(C_4H_9)_4N][InI_4]$, 33752-36-2; $[(C_6H_5)_3CH_3As][InI_4]$, 33752-37-3; $[InI_2(Me_2SO)_4][InI_4]$, 30420-18-9; $[InI_2(CH_3CN)_4][InI_4]$, 74684-22-3; $[(CH_3)_2In][InI_4]$, 39042-62-1; $[(C_4H_9)_4N][InCl_4]$, 32965-21-2; $[(C_4H_9)_4N][InCl_3Br]$, 71785-24-5; $[(C_4H_9)_4N][InCl_2Br_2]$, 74684-23-4; $[(C_4H_9)_4N][InClBr_3]$, 71749-62-7; $[(C_4H_9)_4N][InBr_4]$, 33751-01-8; $[(C_4H_9)_4N][InBr_3I]$, 71749-64-9; $[(C_4H_9)_4N][InBrI_3]$, 71749-67-2; $[(C_4H_9)_4N][InClI_3]$, 71749-65-0; $[(C_4H_9)_4N][InCl_3I]$, 71749-61-6; $InBr_2I_2^-$, 71749-72-9; $InCl_2I_2^-$, 71749-70-7; $InCl_2BrI^-$, 74684-24-5; $InClBr_2I^-$, 74684-25-6; $InClBrI_2^-$, 74684-26-7; $[(C_4H_9)_4N]_2[In_2Cl_6]$, 59643-22-0; $[(C_4H_9)_4N]_2[In_2Br_6]$, 59643-24-2; $[(C_4H_9)_4N]_2[In_2I_6]$, 59643-26-4.

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The Cluster Approach to Exchange Coupling in Diamminecopper(II) Carbonate, $Cu(NH_3)_2CO_3$

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The layer structure of $Cu(NH_3)_2CO_3$ consists of carbonate-bridged chains of copper(II) ions linked together into sheets by hydrogen bonding. The susceptibility data for this magnetically condensed compound have been analyzed by using a cluster approach in which the two different kinds of exchange-coupling interactions were included explicitly. Clusters of six copper ions give the best representation of the experimental data, with the intrachain coupling constant being -5.2 cm^{-1} and the interchain coupling constant being -2.6 cm^{-1}.

Introduction

The magnetic properties of exchange-coupled polymeric compounds such as chains or sheets can be calculated only for a limited number of cases. These include the Ising chain, the *XY* chain, the Ising sheet, and the Heisenberg chain with infinite spin.[2a] In other cases the approach that has been taken in the calculations is illustrated by the work of Bonner and Fisher[2b] on the Heisenberg chain with $S = {}^1/_2$. They carried out exact calculations on small rings and short chains of $S = {}^1/_2$ ions and extrapolated their results to the limit of an infinite one-dimensional chain to obtain an approximation for the magnetic properties at that limit. Weng[3] followed Bonner and Fisher's cluster approach in his calculations of the magnetic properties of Heisenberg chains with $S \geq 1$. Recently the magnetic properties of linear Heisenberg chains with nearest- and next-nearest-neighbor exchange[4] and of alternating Heisenberg chains[5] have also been investigated by using the cluster approach.

The recent reevaluation of the magnetic data for $Cu(NH_3)_2CO_3$ from this laboratory[6] by Kamase, Osaki, and Uryu[7] was based on a misinterpretation of the published data.

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