Effect of Halide Complexation of Cadmium(II) on Cadmium-113 Chemical Shifts

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Abstract: A unique combination of solution and solid-state ^{113}Cd NMR experiments has been employed to elucidate the ^{113}Cd chemical shifts of the individual halide complexes of CdX^+, CdX_2, CdX_3^-, and CdX_4^{2-}, where X is Cl^-, Br^-, and I^-. The solution-state experiments made use of standard pulsed Fourier transform NMR techniques to examine the ^{113}Cd chemical shift of aqueous 0.1 M $Cd(ClO_4)_2$ as a function of halide concentration. The solid-state experiments made use of cross-polarization/magic angle spinning techniques to examine the ^{113}Cd chemical shifts of a series of solid Cd(II)–halide complexes. By consideration of the appropriate multiple equilibria in solution together with ^{113}Cd chemical shift "benchmarks" from solid-state Cd(II)–halide complexes, the ^{113}Cd chemical shifts for the individual Cd(II)–halide complexes were derived. The following shielding orders are observed: $Cd^{2+} > CdCl^+ > CdCl_2 > CdCl_6^{4-} \geq CdCl_5^{3-} > CdCl_3^- > CdCl_4^{2-}$ for the Cd(II)–chloride complexes, $Cd^{2+} > CdBr^+ \simeq CdBr_2 > CdBr_3^- \simeq CdBr_4^{2-}$ for the Cd(II)–bromide complexes, and $Cd^{2+} > CdI^+ > CdI_4^{2-} > CdI_3^-$ for the Cd(II)–iodide complexes.

Introduction

Since the initial publication of high-resolution Fourier transform NMR observation of ^{113}Cd,[1] a number of papers have appeared examining the subject in more detail.[2-6] Although this previous research has shown the ^{113}Cd chemical shift to be quite sensitive to changes in chemical environment, with an observed chemical shift range of over 600 ppm,[3] there remains a paucity of information on relationships between chemical shift and structure for specific species. One reason for this is that group 2B 2+ cations form a variety of hydrated complexes in aqueous solutions.[7] For example, an aqueous solution of the salt $CdCl_2$ contains not only the complex $CdCl_2$(aq), but also at least the additional complexes Cd^{2+}(aq), $CdCl^+$(aq), $CdCl_3^-$(aq), and $CdCl_4^{2-}$(aq) (the structures of some of these complexes involve bound water), whose concentrations are determined by a set of multiple equilibria. Thus, it is important to realize that in aqueous solutions of group 2B metal salts the metal-nuclide chemical shift may not be indicative of a single complex. Indeed, under conditions of rapid exchange where a single, time-averaged resonance is observed, the chemical shift will be a weighted average of the individual chemical shifts of the various metal complexes. If one could sort out these individual metal-complex chemical shifts in such cases, the usefulness of metal-nuclide NMR as a means of elucidating structural properties would be greatly increased. In addition, no theoretical treatment of metal-nuclide chemical shifts can hope to advance without definitive structure–shift relationships against which the theory may be compared and guided.

In light of these considerations, we felt it important to try to resolve the individual chemical shifts for the cadmium(II) halide complexes. Also, it is of interest to compare the ^{113}Cd(II) results with those of the analogous ^{67}Zn(II)–halide complexes.[8]

The approach used herein for solutions is similar to that developed earlier[8] and briefly is as follows. Cd(II) is reported to form four distinct halide complexes in aqueous solution,[7,9] CdX^+, CdX_2, CdX_3^-, and CdX_4^{2-}($X = Cl^-, Br^-, I^-$). By use of the known equilibrium constants[9] and the HALTAFALL computer program,[10] the mole fractions of the various complexes may be determined at given analytical Cd(II) and halide concentrations and a constant ionic strength.

Knowing the mole fraction of the various Cd(II) complexes in solution allows one to use the expression for the observed chemical shift under rapid exchange conditions:

$$\delta_{\text{obsd}} = \sum_{i=0}^{4} X_i \delta_i \tag{1}$$

where X_i is the mole fraction (considering Cd(II) species only) of the *i*th Cd(II)–halide complex (e.g., $X_1 = X_{CdCl^+}$) and δ_i is the chemical shift of this *i*th complex, which we wish to determine. Ideally, it is only necessary to make five measurements of δ_{obsd} at different metal ion or halide concentrations to solve for the five individual δ_i shifts. In practice many more observations are required, in part because not all complexes are present at appreciable concentrations at any given total halide concentration. Our procedure was to fix the analytical Cd(II) concentration at 0.1 M and vary the halide concentration to provide an overdetermined system of simultaneous equations. A least-squares treatment was then used to solve the overdetermined system for the individual chemical shifts of the four Cd(II)–halide complexes, relative to the shift of Cd^{2+}(aq) (all chemical shifts are here defined relative to $\delta_{Cd^{2+}(aq)}$ 0 ppm).

A rough check on the validity of the chemical shift values calculated in this way may be obtained by comparing the derived shift values of a tetrahedral complex, CdX_4^{2-}, with the measured shift in a solution containing great excesses of added halide. The assumption here is that the high halide concentration has driven the equilibrium far enough so that all of the Cd(II) is in the tetrahalide form. To this end ^{113}Cd chemical shifts were obtained for a series of 0.1 M Cd(II) aqueous solutions that contained very high concentrations of halide introduced via the appropriate salt or acid. If the above assumption is valid, then the ^{113}Cd chemical shifts of these concentrated halide solutions should equal the derived values for $\delta_{CdX_4^{2-}}$.

The accuracy of this method is, of course, limited by the accuracy with which the known equilibrium constants describe the system under investigation. Two types of errors should be acknowledged. The first is the usual experimental uncertainty in the determination of the various K_{eq} values that govern the system. The effect of this uncertainty has been discussed before.[8] In order to minimize errors of this type, the solutions used in this study were prepared, taking complex formation into account, to have the same actual ionic strength as that which was used in determining the various equilibrium constants.[9a] Appreciably different K_{eq} values have been obtained for these same systems at different ionic strengths.[9b,c] (A further refinement would be to use a much lower Cd(II) concentration, which would bring the actual ionic strength of each Cd(II)–halide solution even more closely into correspondence with the intended ionic strength of 4.5 M, because variations in the pattern of complex formation would have a smaller effect on the ionic strength. This would require a more sensitive spectrometer than the one available for this study.) The second error is potentially more serious to this type of study, and

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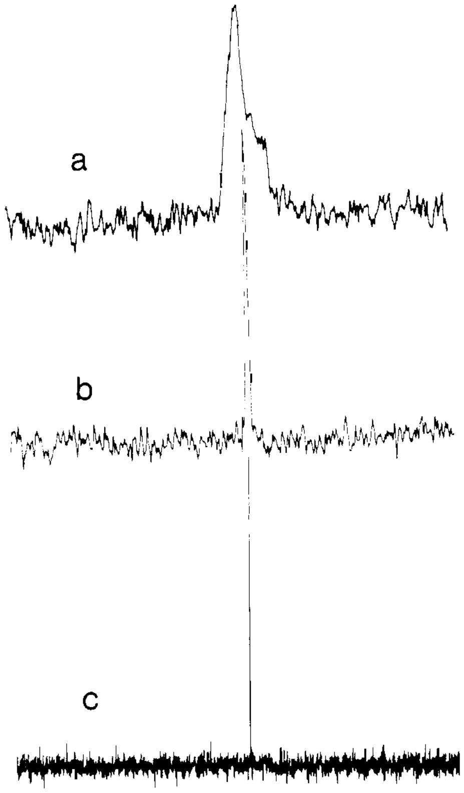


Figure 1. (a) Cross polarization ^{113}Cd spectrum of solid $(Et_4N)_2[CdI_4]$. A 4-kHz spectral width is shown (2300 accumulations). (b) Cross polarization/magic-angle spinning ^{113}Cd spectrum of solid $(Et_4N)_2[CdI_4]$; 4-kHz spectral width (1560 accumulations). (c) Standard pulsed Fourier transform ^{113}Cd spectrum, obtained at 19.9 MHz, of 0.1 M CdI_2 in 5.5 M HI; 4-kHz spectral width (1000 accumulations).

perhaps chemically more interesting, namely, the existence of additional complexes in solution that are unaccounted for by the known equilibrium constants. If present in significant concentration, these additional complexes will contribute to the observed chemical shift, but will not be accounted for in the least-squares analysis. At the highest halide concentrations employed in this study the existence of additional complexes is quite possible (vide infra). Thus, not only could the least-squares analysis be in error, but attempts to estimate $\delta_{CdX_4{}^{2-}}$ from measurements on very concentrated halide solutions may be doomed by the formation of higher order halide complexes.

The availability of "benchmarks", independently determined ^{113}Cd chemical shifts for various discrete Cd(II)-halide complexes, would obviously aid in the evaluation of the solution data. Such ^{113}Cd "benchmarks" can be obtained from NMR experiments on solid Cd(II)-halide complexes of known composition and structure. We have obtained the ^{113}Cd chemical shifts for a number of $CdX_4{}^{2-}$ species in the solid state and have used these shifts as "benchmarks" in the examination of the solution data.

Experimental Section

A. Measurements. ^{113}Cd NMR measurements in the solution state were made in natural abundance at 19.96 MHz on a Bruker HFX-90 spectrometer interfaced to a Digilab FTS/NMR-3 data system, using a multinuclide configuration reported earlier.[11] Field/frequency lock was based on the ^{19}F signal of an external sample of C_4F_8 placed next to the ^{113}Cd receiver insert. Samples were run at 302.5 ± 0.3 K in 10-mm tubes. Typically 300-600 free induction decays were collected for each spectrum, requiring about 0.5-1 h. In all experiments the ^{1}H resonances of water were observed on the same samples immediately before or after the ^{113}Cd measurements were made in order to correct for bulk susceptibility. Such corrections were small.

Solid-sample ^{113}Cd NMR measurements were made using both cross polarization and magic angle spinning techniques.[12] Experiments were performed on a home-built system, operating at 13.3 MHz, based on a Varian HR-60 magnet, and interfaced to a JEOL EC-100 data system. The natural-abundance solid samples were contained in rotors of modified Beams[13] design; the sample chamber was approximately 9 mm in diameter and 18 mm in length. The spinning rate was roughly 2.2 kHz. A typical spectrum, as shown in Figure 1b, employed 1500 scans, with a 1-ms contact time and 6-s delay between scans. Figure 1a shows a corresponding spectrum without magic-angle spinning. The field/frequency lock was achieved with the ^{2}H resonance of an external sample of D_2O. Measurements were made at ambient temperature (about 30 °C). All ^{113}Cd(II) chemical shifts for both solid and liquid samples were referenced to 0.1 M $Cd(ClO_4)_2$ in aqueous solution with ionic strength 4.5 ($NaClO_4$ added) as 0.0 ppm. In the data analysis, the zero chemical shift reference was assumed to correspond to $\delta_{Cd(aq)^{2+}}$ as the concentration of Cd^{2+}(aq) computed by HALTAFALL corresponds to the concentration of the aquated species in a solution environment of 4.5 M $NaClO_4$. Previous studies have shown that the ^{113}Cd chemical shift of aqueous $Cd(ClO_4)_2$ is not very sensitive to the salt concentration.[3] Also, ^{113}Cd data on hydrated Cd^{2+} in the solid state are consistent with this assumption (see Table III). All chemical shifts are reported as $\delta_{ppm} = (\nu_i - \nu_{ref})/\nu_{ref}$, so that shifts to higher frequency are more positive (less shielded).

B. Materials. All chemicals obtained from commercial sources were used without further purification. Lithium chloride, sodium chloride, and sodium bromide were Fisher, A.C.S. certified, reagent grade. Lithium bromide and sodium perchlorate were Fisher purified. Concentrated HI and HCl were Mallinckrodt analytical reagent. Concentrated HBr was Merck reagent grade. Sodium iodide was Baker analyzed reagent and cadmium perchlorate was C. Frederich Smith Chemical Co. reagent.

Solutions of 0.1 M Cd(II) at constant actual ionic strength (4.5) were prepared volumetrically from solutions of cadmium perchlorate (standardized by titration with EDTA), sodium perchlorate (standardized by evaporation to constant weight at 150 °C), and the dried sodium salt of whichever halide was being studied (Cl^-, Br^-, I^-).

Bis(tetraethylammonium) tetrachlorocadmate, $((C_2H_5)_4N)_2[CdCl_4]$, was prepared by published procedures[14] and used without further purification

Bis(tetraethylammonium) Tetrabromocadinate, $((C_2H_5)_4N)_2[CdBr_4]$. To a solution of 4.4 g (0.021 mol) of $(C_2H_5)_4NBr$ in 50 mL of hot 95% ethyl alcohol was added a solution of 3.44 g (0.01 mol) of $CdBr_2{\cdot}4H_2O$ in 100 mL of 80% ethyl alcohol containing 2 mL of 48% HBr. A white precipitate formed, which dissolved on heating and addition of more H_2O. The hot solution was filtered and let stand for crystallization. After filtering, the white, crystalline product was recrystallized from hot 80% ethyl alcohol and dried under vacuum, mp (uncor) 297 °C. Anal. Calcd for $C_{16}H_{40}N_2CdBr_4$: C, 27.75; H, 5.82; N, 4.04; Cd, 16.23; Br, 46.15. Found: C, 27.84; H, 5.59; N, 4.19; Cd, 16.18; Br, 46.16.

Bis(tetraethylammonium) tetraiodocadmate, $((C_2H_5)_4N)_2[CdI_4]$, bis(tetramethylammonium) tetrabromocadmate, $((CH_3)_4N)_2[CdBr_4]$, and bis(tetramethylammonium) tetraiodocadmate, $((CH_3)_4N)_2[CdI_4]$, were prepared using similar procedures as described above. Anal. Calcd for $C_{16}H_{40}N_2CdI_4$ (mp >300 °C): C, 21.82; H, 4.58; N, 3.18; Cd, 12.77; I, 57.65. Found: C, 22.17; H, 4.75; N, 3.90; Cd, 12.71; I, 58.11. Calcd for $C_8H_{24}N_2CdBr_4$ (mp >300 °C): C, 16.56; H, 4.17; N, 4.83; Cd, 19.37; Br, 55.08. Found: C, 16.72; H, 4.28; N, 4.93; Cd, 19.26; Br, 54.81. Calcd for $C_8H_{24}N_2I_4$ (mp >300 °C): C, 12.50; H, 3.15; N, 3.64; Cd, 14.63; I, 66.08. Found: C, 12.71; H, 3.20; N, 3.64; Cd, 14.53; I, 66.26.

Bis(piperidinium) tetrabromocadmate, $(C_5H_{12}N)_2[CdBr_4]$, was prepared by published procedures[15] and used without further purification.

Thiaminium tetrachlorocadmate monohydrate, $C_{12}H_{20}N_4O_2S[CdCl_4]$, was prepared by published procedures.[16]

Hexaamminecobalt(III) pentachlorocadmate, $[Co(NH_3)_6][CdCl_5]$, was prepared by published procedures.[17]

Tris(ethylenediamine)cobalt(III) hexachlorocadmate dichloride dihydrate, $[Co(N_2C_2H_8)_3]_2[CdCl_6]Cl_2{\cdot}2H_2O$, was prepared by published procedures.[18]

Results

A diagrammatic representation of the multiple equilibria in aqueous solutions of Cd(II) and Cl^- is shown in Scheme I.

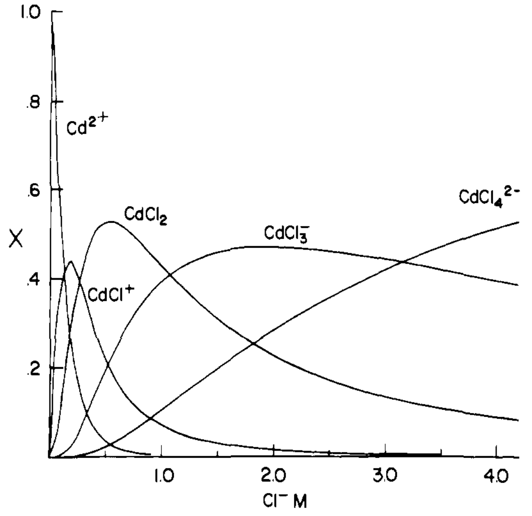
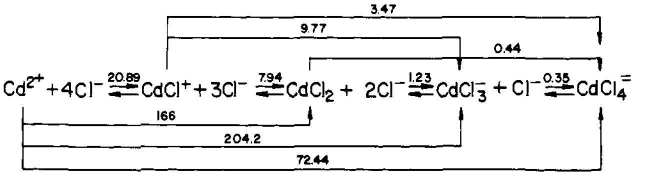
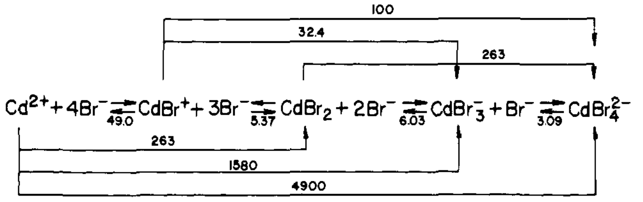


Figure 2. The calculated dependence of the mole fraction of Cd(II) present as various Cd(II) species upon the total added Cl$^-$ concentration, with the total Cd(II) concentration maintained at 0.10 M. The solvent is H_2O with an actual ionic strength of 4.5 M.

Scheme I



Scheme II



The stepwise and overall equilibrium constants shown are for a solution of 4.5 M ionic strength.[9a] Based upon these constants and a computer program (HALTAFALL[10]), kindly provided by Dr. J. Christie, the curves shown in Figure 2 were generated, showing the values of X_0, X_1, X_2, X_3, and X_4 of eq 1 for 0.1 M Cd(II) and the range of Cl$^-$ concentrations used in this study. It is important to note that each of the four chloride complexes reaches a significant mole fraction within the chloride concentration range employed. At no point in Figure 2 does any one complex dominate, even at the highest chloride concentrations. The effect of these chloride complexes on the ^{113}Cd(II) chemical shift is examined in Figure 3, where the experimental ^{113}Cd chemical shift is plotted as a function of chloride concentration. As the mole fractions of the complexes in solution change (Figure 2), there is a pronounced effect on the observed ^{113}Cd chemical shift, resulting in almost a 300-ppm shift to lower shielding at the highest chloride concentration. Using the X_i values and the observed chemical shifts for chloride concentrations up to 2.0 M a least-squares treatment of eq 1 yields the values for δ_1, δ_2, δ_3, and δ_4 given in Table I. The value for δ_0, the ^{113}Cd chemical shift of aqueous Cd(II), is taken to be equal to that of our reference solution, 0.0 ppm.

Scheme II describes the multiple equilibria[9] and equilibrium constants for an aqueous solution of 0.1 M $Cd(ClO_4)_2$ and Br$^-$ at an ionic strength of 4.5. The equilibrium constants for formation of Cd(II)-halide complexes are considerably larger for the bromide complexes than for the analogous chloride complexes. This is reflected in Figure 4, where the mole fractions of the Cd(II)-bromide complexes are plotted as a function of bromide concentration. In contrast to the Cd(II)-chloride solutions, the tetracoordinate bromide complex, $CdBr_4^{2-}$, clearly dominates at bromide concentrations greater than 2.0 M. In addition, the $CdBr_2$ complex has a maximum mole fraction of only about 0.275, which is roughly half that attained by the corresponding chloride complex. Figure 5 examines the effects of varying the relative amounts of these Cd(II)-bromide complexes on the ^{113}Cd chemical shift, i.e., it is a plot of the experimental ^{113}Cd chemical shift as a function of bromide concentration. The flattening of the curve at Br$^-$ concentrations greater than about 2.0 M is due to a preponderance of $CdBr_4^{2-}$, a feature not seen as dramatically with the chloride complexes (Figure 3). ^{113}Cd chemical shifts of the individual bromide complexes calculated by a least-squares fit of eq 1 are given in Table I.

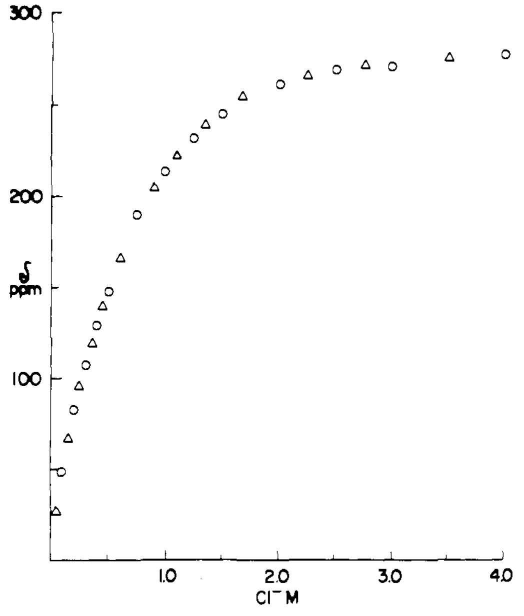
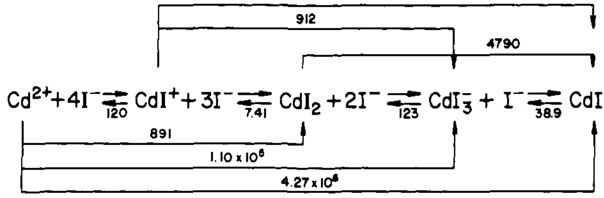


Figure 3. The dependence of the ^{113}Cd chemical shift of a 0.10 M $Cd(ClO_4)_2$ solution on added NaCl, with the total Cd(II) concentration maintained at 0.10 M and the actual ionic strength maintained at 4.5 M. Experimental data are represented by circles while triangles represent values that were derived using eq 1 and mole fractions of Cd(II)-chloride species from known equilibrium constants.[9] The solvent is H_2O.

Scheme III



Scheme III shows the multiple equilibria for aqueous solutions of the Cd(II)-iodide system at an ionic strength of 4.5. The equilibrium constants for formation of iodide complexes are, in general, larger by many orders of magnitude than those for the chloride or bromide complexes. This is reflected in Figure 6, where the very favorable formation of the intermediate Cd(II)-iodide complexes at relatively low iodide concentrations gives way to dominance of the CdI_4^{2-} complex at I$^-$ concentrations greater than about 0.75 M. The CdI_2 complex reaches a maximum mole fraction of only $X_{CdI_2} = 0.070$.

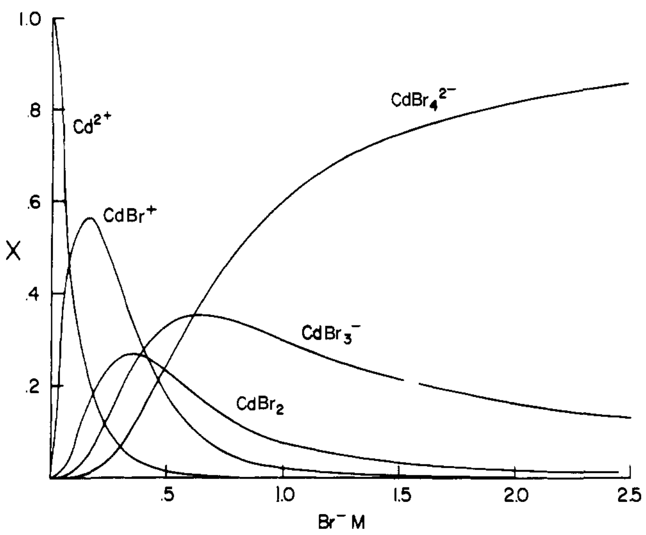


Figure 4. The calculated dependence of the mole fractions of Cd(II) present as various Cd(II) species upon the total added Br^- concentration, with the total Cd(II) concentration maintained at 0.10 M. The solvent is H_2O with an actual ionic strength of 4.5 M.

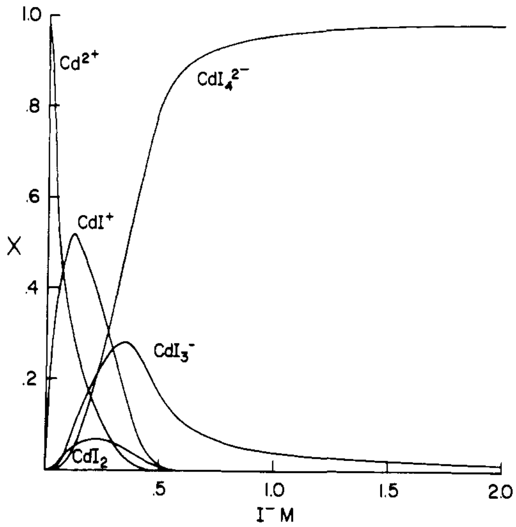


Figure 6. The calculated dependence of the mole fractions of Cd(II) present as various Cd(II) species upon the total added I^- concentration, with the total Cd(II) concentration maintained at 0.10 M. The solvent is H_2O with an actual ionic strength of 4.5 M.

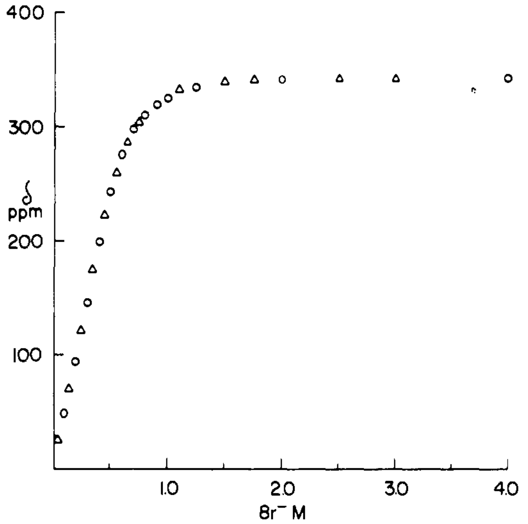


Figure 5. The dependence of the ^{113}Cd chemical shift of a 0.10 M $Cd(ClO_4)_2$ solution on added NaBr, with the total Cd(II) concentration maintained at 0.10 M and the actual ionic strength maintained at 4.5 M. Experimental data are represented by circles while triangles represent values that were derived using eq 1 and mole fractions of Cd(II)-bromide species from known equilibrium constants.[9] The solvent is H_2O.

Table I. Calculated ^{113}Cd(II) Chemical Shifts for the Various Cd(II)-Halide Complexes in Aqueous Solution at Ionic Strength 4.5[a,b]

halide X^-	δ_{CdX^+}, ppm	δ_{CdX_2}, ppm	$\delta_{CdX_3^-}$, ppm	$\delta_{CdX_4^{2-}}$, ppm
Cl^-	92	103	352	252
Br^-	70	76	392	338
I^-	44	(124)[c]	121	75

[a] Chemical shift of a 0.1 M $Cd(ClO_4)_2$ aqueous solution ($I = 4.5$) set at 0.0 ppm; more positive values refer to lower shielding. [b] Least-squares analysis included chloride concentrations to 2.0 M (10 points), bromide concentrations to 2.0 M (12 points), and iodide concentrations to 1.0 M (13 points). [c] This chemical shift value not significant for reasons discussed in text.

This is, of course, due to the very large formation constants of CdI_3^- and CdI^- and small formation constants of CdI_2 from CdI^+ and Cd^{2+}.

Figure 7 plots the observed ^{113}Cd(II) shift of a 0.1 M $Cd(ClO_4)_2$ solution as a function of iodide concentration. The total shift range observed, about 87 ppm, is much less than for either the Cl^- or Br^- systems. The dramatic leveling of the curve at iodide concentrations greater than about 1.0 M is indicative of dominance by the CdI_4^{2-} complex, as is seen in Figure 6. The maximum in the curve at approximately 0.4 M formal iodide concentration is easily understandable in terms of the individual chemical shifts obtained via a least-squares fit of eq 1 and given in Table I. Since $\delta_{CdX_3^-}$ is significantly larger than either δ_{CdI^+} or $\delta_{CdI_4^{2-}}$, the observed δ (plotted in Figure 7) reaches a maximum near the I^- concentration where $X_{CdI_3^-}$ is also greatest. As the iodide concentration increases, the rapid buildup of CdI_4^{2-}, with its smaller chemical shift, in concert with the disappearance of CdI_3^-, produces a decrease in the observed chemical shift according to eq 1. The curve then flattens out as the observed δ approaches $\delta_{CdI_4^{2-}}$. The value of δ_{CdI_2} in Table I (14.8 ppm) is not significant, because the concentration of CdI_2 is very small throughout most of the range of this experiment, and hence the quality of the fit is not sensitive to the value of δ_{CdI_2}.

Table II presents some ^{113}Cd(II) chemical shifts in aqueous solutions of very high halide concentration. The shifts in Table II thus hopefully provide a comparison with the calculated values for $\delta_{CdX_4^{2-}}$ presented in Table I. The comparison is, at best, only approximate, since a constant ionic strength of 4.5 cannot be maintained at such high electrolyte concentrations.

Table III presents the ^{113}Cd chemical shifts of a variety of solid Cd(II)-halide complexes. Considering only the four-coordinate halide complexes, the shielding order $CdCl_4^{2-} < CdBr_4^{2-} < CdI_4^{2-}$ is shown. This same shielding order has been observed for ^{13}C in CX_4,[19] ^{67}Zn in ZnX_4^{2-},[8] and ^{199}Hg in HgX_4^{2-}.[20] In spectra obtained without magic-angle spinning, the $(Et_4N)_2[CdX_4]$ salts gave the narrowest resonance lines of all the four-coordinate complexes studied, implying the least amount of chemical shift anisotropy, and thus the least distorted tetrahedral geometry. The ^{113}Cd chemical shifts for the three $(Et_4N)_2[CdX_4]$ salts ($X = Cl^-$, Br^-, I^-) were therefore taken as "benchmarks" for the $CdCl_4^{2-}$, $CdBr_4^{2-}$, and CdI_4^{2-} complexes, in solution. The least-squares analyses described above were repeated, using only solution data for halide concentrations up to 0.5 M and holding the δ_{X_4} values constant and equal to solid-state

Table II. ^{113}Cd Chemical Shifts for Various Concentrated Halide Solutions of Cadmium(II) Salts

solution (in H_2O)	chemical shift, ppm[a]
0.1 M $CdCl_2$ in 12 M HCl	294.1
0.1 M $Cd(ClO_4)_2$ in 13.5 M LiCl	246.6
0.1 M $Cd(ClO_4)_2$ in 12.0 M LiCl	268.4
0.1 M $Cd(ClO_4)_2$ in 9.0 M LiCl	312.1
0.1 M $Cd(ClO_4)_2$ in 7.0 M LiCl	330.1
0.1 M $Cd(ClO_4)_2$ in 5.25 M LiCl	329.1
0.1 M $Cd(ClO_4)_2$ in 5.25 M NaCl	286.2
0.1 M $CdBr_2$ in 9 M HBr	349.7
0.1 M $Cd(ClO_4)_2$ in 12 M LiBr	310.0
0.1 M $Cd(ClO_4)_2$ in 9 M LiBr	334.1
0.1 M $Cd(ClO_4)_2$ in 7 M LiBr	347.2
0.1 M $Cd(ClO_4)_2$ in 7 M NaBr	334.2
0.1 M CdI_2 in 5.5 M HI	71.2
0.1 M $Cd(ClO_4)_2$ in 8 M NaI	72.1

[a] All shifts referenced to 0.1 M $Cd(ClO_4)_2$ in H_2O (I = 4.5) as 0.0 ppm, with more positive values referring to lower shielding. Bulk susceptibility corrections were applied by further referencing through the solvent ^1H resonances (see Experimental Section).

Table III. ^{113}Cd Chemical Shifts of Solid-State Cd(II)-Halide Complexes

complex	^{113}Cd(II) chemical shift,[a] ppm	complex	^{113}Cd(II) chemical shift,[a] ppm
$(Et_4N)_2[CdCl_4]$	474[b]	$(Me_4N)_2$ $[CdBr_4]$	382
$HThi[CdCl_4]$[c]	451[b]	$(Et_4N)_2$ $[CdBr_4]$	365[b]
$[Co(NH_3)_6][CdCl_5]$	188, 172 (2 peaks?)	$(Me_4N)_2[CdI_4]$	83
$[Co(en_3)]_2[CdCl_6]$-Cl_2·$2H_2O$	162	$(Et_4N)_2[CdI_4]$	70[b]
$pd_2[CdBr_4]$[d]	387	$[Cd(H_2O)_6]$-$(ClO_4)_2$	−9

[a] Referenced to a 0.1 M aqueous $Cd(ClO_4)_2$ solution (formal ionic strength 4.5). Bulk susceptibility corrections were not made. [b] For the reason discussed in the text the tetraethylammonium salts were taken as the benchmarks for use in the calculations summarized in Table IV. [c] Thi (thiamin). [d] pd (piperidinium).

benchmarks. These results are given in Table IV, together for comparison with results from a least-squares analysis using identical data, but in which the $\delta_{CdX_4{}^{2-}}$ values were not held constant. As can be seen, the agreement is quite excellent. However, the differences in the derived ^{113}Cd chemical shifts presented in Table IV, compared with the shifts given in Table I, are quite substantial. In fact, even the shielding order of the complexes is different in Table I from that which is given in Table IV. The discrepancy between the results of Table I and those of Table II is a manifestation of the fact that the main source of error in the chemical shift values given in either table is not errors of experimental measurements, but rather in analysis of the data. The main point is the appropriateness of the equilibria and equilibrium constants[9] included in the analyses. It is not unreasonable to expect that the preferred set of shifts, those given in Table IV, could be in error by as much as 10 or 20 ppm. However, we do not expect the qualitative pattern of shifts given to be incorrect.

Discussion

A great deal of work has been done on the structure of Cd(II) complexes in solution. X-ray diffraction[21,22] studies on liquid samples show that aqueous solutions of $Cd(ClO_4)_2$ and $Cd(NO_3)_2$ involve a Cd(II) cation surrounded by six water molecules, consistent with a postulated octahedral configuration. Although there is sufficient evidence to support the existence of the cadmium(II) monohalide complexes,[9,23,24] extensive structural information is lacking. However, X-ray diffraction studies on aqueous solutions demonstrate the existence of $CdI(OH_2)_5{}^+$.[25] Furthermore, on this basis and on the basis of analogues to X-ray studies[26] of $[HgCl{\cdot}5H_2O]^+$, it seems reasonable that complexes of $CdCl^+$ and $CdBr^+$ involve the replacement of one water molecule from octahedrally coordinated $[Cd{\cdot}6H_2O]^{2+}$ by a halide ion.

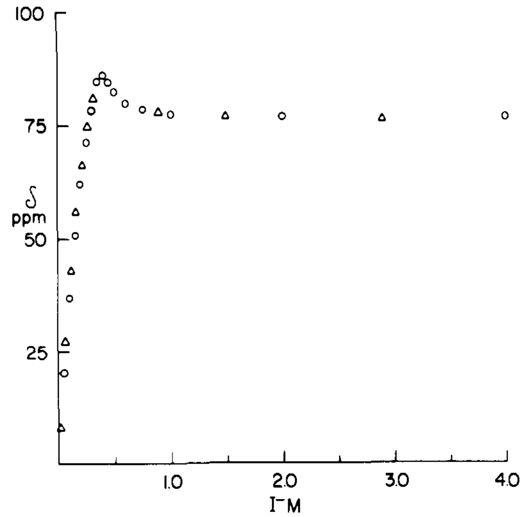


Figure 7. The dependence of the ^{113}Cd chemical shift of a 0.10 M $Cd(ClO_4)_2$ solution on added NaI, with the total Cd(II) concentration maintained at 0.10 M and the actual ionic strength maintained at 4.5 M. Experimental data are represented by circles while triangles represent values that were derived using eq 1 and mole fractions of Cd(II)-iodide species from known equilibrium constants.[9] The solvent is H_2O.

Table IV. ^{113}Cd Chemical Shifts[a] for Various Cd(II)-Halide Complexes Derived by Using a Combination of Solution and Solid-State NMR Data

halide X^-	δ_{CdX^-}, ppm	δ_{CdX_2}, ppm	$\delta_{CdX_3{}^-}$, ppm	$\delta_{CdX_4{}^{2-}}$, ppm
Cl^-	89	114	292	495
Cl^-	89[b]	114[b]	296[b]	474[b]
Br^-	72	75	365	379
Br^-	74[b]	66[b]	380[b]	365[b]
I^-	47	(57)[c]	140	71
I^-	49[b]	(29)[b,c]	148[b]	70[b]

[a] The ^{113}Cd chemical shift of 0.1 M $Cd(ClO_4)_2$ in aqueous solution (I = 4.5) taken to be 0.0 ppm; more positive values refer to lower shielding. Data for halide concentrations up to only 0.5 M were included in the analyses. [b] $\delta_{CdX_4{}^{2-}}$ values held constant at the solid-state "benchmark" values. [c] This chemical shift is not significant for reasons discussed in the text.

Raman and infrared studies have led a number of workers to conclude that the $CdCl_2$, $CdBr_2$, and CdI_2 complexes are linear,[27,28] although evidence exists for the polymerization of $CdBr_2$[23] and $CdCl_2$[24] in aqueous solutions. Davies and Long[27] have assigned a symmetry of D_{3h} to the $CdCl_3{}^-$ and $CdI_3{}^-$ complexes on the basis of vibrational spectra, but a Raman study suggests that $CdBr_3{}^-$ is pyramidal. All researchers seem to agree that the $CdCl_4{}^{2-}$, $CdBr_4{}^{2-}$, and $CdI_4{}^{2-}$ complexes are tetrahedral.[22,23,27-29] The structural role of water molecules in Cd(II)-halide complexes remains uncertain.[23]

Ahrland has invoked a transformation from octahedral to tetrahedral geometry at the third complexation step ($CdX_2 \rightarrow CdX_3{}^-$) to account for the unusually large values of $\Delta S°$

and ΔH° observed for this step. If such a change did occur, it would be characterized by an abnormally high dehydration energy and by the liberation of an abnormally large number of water molecules.[30] This would lead to unusually high values of both ΔS° and ΔH° for such a step,[30] as has been observed. (Unusually large values of ΔS° and ΔH° for the third complexation step are not as apparent for I^- as for Cl^- and Br^-.[30])

If water molecules do indeed occupy coordination sites not taken by halide ions, then it is reasonable to predict overall octahedral geometries for the $Cd^{2+}(aq)$, $CdX^+(aq)$, and $CdX_2(aq)$ complexes.[30] Although vibrational spectroscopy studies have demonstrated the involvement of water with these Cd(II) halide complexes only in the iodide cases,[23,25] the thermodynamic data seem to support a stepwise replacement of water molecules by halide ion for all three halides, thus maintaining overall octahedral geometry up to the trihalide, where a very large dehydration occurs.[30] This idea may be further refined by the inclusion of a single water molecule in the coordination shell of CdX_3^-, which could change the geometry from pyramidal to approximately tetrahedral. (A similar situation has been observed for the approximately tetrahedral HgI_3^-.)[30]

As discussed in the Introduction, the existence of Cd(II)-halide complexes unaccounted for by the known equilibrium constants could produce serious errors in the least-squares analysis presented herein. For example, $CdCl_2$ may polymerize in solution,[27] but the chemical shift of the polymer is not accounted for in our analysis since the K_{eq} governing its formation is unknown. More direct evidence for the existence in solution of higher order halide complexes such as $CdCl_5^{3-}$ and $CdCl_6^{4-}$ is found in the existence of solid complexes with these same stoichiometries.[17,18] Intuitively one might expect these higher order Cd(II)-halide complexes to form at high halide concentrations, such as those in Table II and perhaps at the upper concentrations of the data represented in Figures 3, 5, and 7.

One interpretation for the wide scatter in ^{113}Cd chemical shifts in the Cd(II)-bromide and Cd(II)-chloride systems of Table II is the existence of these higher order halide complexes in solution. If such complexes are involved, then one is not simply measuring the ^{113}Cd chemical shift of $CdCl_4^{2-}$ or $CdBr_4^{2-}$ in such solutions. Supporting this view are the solid-sample ^{113}Cd chemical shifts of the pentachloride and hexachloride species, which are roughly 300 ppm more shielded than the tetrachloride complex (Table III). If these complexes exist in appreciable amounts at the chloride concentrations represented in Table II, the observed $^{113}Cd(II)$ chemical shifts for the solutions in Table II should be lower than that of $CdCl_4^{2-}$, which is just what is observed. Similarly, the derived value of $CdCl_4^{2-}$ of Table I (252 ppm) is also much lower than the value observed for the solid complex, suggesting the presence of the pentachloride and hexachloride species at the upper concentration of Figure 3.

Because of these uncertainties as to the presence of higher order complexes in concentrated halide solutions, the least-squares analysis was repeated by including only data from solutions of 0.5 M or less halide concentration. For comparative purposes the analysis was performed both with and without $\delta^{113}{}_{CdX_4{}^{2-}}$ held constant at the solid-state "benchmark" values. The fact that these two sets of results (Table IV) are very similar and are quite different from those in Table I suggests that complexes of the type $CdCl_5^{3-}$ and $CdCl_6^{4-}$ may be involved in the solutions of Figure 3 corresponding to the highest formal Cl^- concentrations.

The shielding order for the Cd(II)-chloride complexes is found in Table IV to be $Cd^{2+} > CdCl^+ > CdCl_2 > CdCl_3^- > CdCl_4^{2-}$, with the largest changes at the third and fourth chloride complexation step. The implication, based on the previous discussion of geometries, is that the octahedral Cd(II) chlorides are more shielded than the tetrahedral chlorides. If the solid-state shifts for the penta- and hexachlorides are included, the complete shielding order becomes $Cd^{2+} > CdCl^+ > CdCl_2 > CdCl_6^{4-} \geq CdCl_5^{3-} > CdCl_3^- > CdCl_4^{2-}$. The $CdCl_5^{3-}$ complex is a trigonal bipyramid,[17] while the $CdCl_6^{4-}$ complex has considerably distorted octahedral geometry.[18]

Some of the considerations of higher order halide complexes may also apply to the bromide case, although comparison of data from Tables I-IV suggests that such involvement is less serious than for the chloride case. The shielding order for the Cd(II)-bromide complexes is seen from Table IV to be $Cd^{2+} > CdBr^+ \simeq CdBr_2 > CdBr_3^- \simeq CdBr_4^{2-}$. The octahedral species are again more shielded than the tetrahedral species. However, a striking contrast to the Cd(II)-chloride complexes is the approximate equality in ^{113}Cd shielding between the mono- and dibromide and between the tri- and tetrabromide complexes.

Comparison of data for the iodide systems in Tables I-IV gives no evidence of higher order iodide complexes of the types discussed above for chloride. From Table IV, the shielding order for the Cd(II)-iodide complexes is seen to be $Cd^{2+} > CdI^+ > CdI_4^{2-} > CdI_3^-$, where the ^{113}Cd chemical shift of the CdI_2 complex could not be determined for reasons discussed above. Here the octahedral species are also more shielded than the tetrahedral species, as was the case for the Cl^- and Br^- complexes. However, the tetra- and triiodide shielding order is now reversed from that of the chloride complexes.

Another feature of these results is that, in general, the iodide complexes are more shielded than the corresponding bromide complexes which are more shielded than the corresponding chloride complexes, e.g., $CdI_n{}^{(2-n)+} > CdBr_n{}^{(2-n)+} > CdCl_n{}^{(2-n)+}$, where $n = 1$-4. The exception to this shielding order occurs for the trichloride and tribromide complexes where the shielding order is $CdCl_3^- > CdBr_3^-$ (Table IV). In addition to having the highest shieldings, the Cd(II)-iodide system has a much smaller chemical shift range than either the Cd(II)-chloride or Cd(II)-bromide systems.

It should be noted that the Cd(II)-iodide-water complexes may have markedly different overall geometries than their chloride and bromide counterparts. There is some thermodynamic evidence (fairly uniform values for stepwise ΔH° and ΔS°) that suggests that the changeover from octahedral geometry $[Cd^{2+}\cdot 6H_2O]$ to tetrahedral geometry $[CdX\cdot 3H_2O]$, occurs at the first complexation step for higher polarizable (soft) ligands such as CN^-.[30] Since iodide is the most polarizable of the halides studies in this work, a similar situation may exist (although the stepwise sequences of ΔH° and ΔS° for $Cd(II)$-I^- complexes are not nearly as smooth as for the CN^- complexes[30]), implying small overall geometrical changes between the several similar overall tetrahedral geometries for all I^- complexes.

Although both Zn(II) and Cd(II) are closed-shell (d^{10}) cations, Zn(II) is considered a hard or class a acceptor, while Cd(II) is considered a mildly soft class b acceptor.[30] Only very soft ligands such as CN^- will coordinate to either Zn(II) or Cd(II) by bonds that are appreciably covalent.[30] Although halides are harder than the pseudohalides, covalent bonding is still important for the formation of Cd(II)-halide complexes.[30] Covalent bonding plays a very small role in the essentially ionic Zn(II)-halide complexes.[30] This greater polarizability of the Cd(II) cation as compared to the Zn(II) cation is reflected in the higher stabilities of the Cd(II)-halide complexes.[9]

Earlier work from this laboratory[8] found the Zn(II)-halide complex shielding order to be $Zn^{2+} > ZnX^+ > ZnX_3^- > ZnX_4^{2-} > ZnX_2$. As has been summarized before,[8] the Zn^{2+}, ZnX^+, and ZnX_4^{2-} aqueous complexes are structurally similar to the aqueous Cd(II) complexes. However, unusually large stepwise $\Delta S°$ and $\Delta H°$ values for the second Zn(II)-halide complexation step ($ZnX^+ \rightarrow ZnX_2$) suggests a switch from octahedral to tetrahedral symmetry at this step, as compared to the third complexation step for Cd(II)-halide complexes.[30] Raman studies of Zn(II)-bromide complexes[23] indicate a very unsymmetrical bent structure (C_{2v}) for $ZnBr_2$, where the role of water is not specified. The structure of $ZnBr_3^-$ has been suggested as pyramidal,[23] C_{3v}, and as a trigonal bipyramid[30] with water molecules occupying the apices. Thus, the overall general shielding order for Zn(II)-halide complexes may be described as octahedral (Zn^{2+}) > approximately octahedral (ZnX^+) > trigonal bipyramidal > (ZnX_3^-) > tetrahedral (ZnX_4^{2-}) > C_{2v} (ZnX_2). Although the assignment of such definitive structures to the various Zn(II)-halide complexes is not rigorous, it is clear that, as with Cd(II), the octahedral Zn(II)-halide species are more shielded than the tetrahedral species.

Conclusion

The availability of "benchmark" chemical shift data on solids is highly useful in the interpretation of chemical shift results for liquid solutions. Using ^{113}Cd data on solid CdX_4^{2-} systems greatly enhances the reliability of the least-squares analysis of the weighted-average data on Cd(II)-halide complexes. Analogous use of solid-state chemical shift benchmarks for interpreting liquid solution data should see greatly increased popularity, e.g., for studies of organometallic species.

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Trifluoromethanol (CF_3OH) and Trifluoromethylamine (CF_3NH_2)

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Abstract: Synthesis and properties of CF_3OH and CF_3NH_2 are described. Both are made from the corresponding chloro compounds CF_3OCl and CF_3NCl_2, respectively, by reaction with HCl. Both are unstable at room temperature because of elimination of HF. While CF_3OH is a typical protonic acid, CF_3NH_2 is a base, in spite of the inductive effect of the CF_3 group.

In general hydrogen can be formally substituted by fluorine in organic compounds. Thus a huge number of compounds of that type are known or are capable of existence. But if a partly or fully fluorinated organic material contains acidic hydrogen the β position, HF elimination is observed and is responsible for difficulty in synthesizing α-fluoro alcohols.[2-6] Only $c\text{-}C_4F_7OH$ is stable and well characterized;[7] the reason for this will be discussed later.

Fluoromethanol (CF_2FOH) was claimed several times, although never isolated or characterized,[8,9] but the protonated form has been reported[10] recently.

Here we describe the preparation and characterization of CF_3OH, the first fully fluorinated primary alcohol, which because of its acidity could also be named trifluoroorthocarbonic acid.

As with the alcohols, perfluorinated primary amines $R_FCF_2NH_2$ were also unknown hitherto. Yet CF_3NH_2 can be prepared in the same manner as CF_3OH. Some of these results have been presented in short communications.[11,12]

Experimental Section

General. ^1H and ^{19}F NMR spectra were recorded on a JEOL 60 HL and ^{13}C spectra on a Bruker 90-MHz instrument. For Raman spectra, a Corderc PH1 with He-Ne laser excitation (190 W), for IR spectra,

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