a factor which has been emphasized in the electrochemical syntheses of other metal halides.[8,9,11] We have noted elsewhere that the electrochemical oxidation of metals favors the formation of compounds in which the metal is in a low oxidation state,[8,12,13] and such a situation obviously applies for the thorium/iodine system. An added advantage is that adducts of ThI_2 can be prepared in situ, and of course the uncomplexed compound is easily obtained by thermal decomposition of $ThI_2 \cdot 2CH_3CN$.

The infrared spectrum of solid $ThI_2 \cdot 2CH_3CN$ has two medium-intensity absorptions at 2270 and 2300 cm^{-1}, confirming the presence of acetonitrile; the reason for the presence of this doublet is not obvious at present. The UV-visible spectrum of $ThI_2 \cdot 2CH_3CN$ in acetonitrile at 25 °C shows two strong absorptions at 285 and 325 nm (35 100 cm^{-1}, $\epsilon_{max} = 4.22 \times 10^3$, and 30 800 cm^{-1}, $\epsilon_{max} = 2.94 \times 10^3$).

Electrochemical Efficiency. As in previous work, we have measured the electrochemical yield (E_F), defined as moles of metal dissolved per faraday of electricity. Such experiments are typically carried out at a constant current of 20 mA over 2 h. For the CH_3CN/I_2 systems, we find $E_F = 0.48$ mol faraday^{-1}, implying the anode reaction

$$Th + 2I^- \rightarrow ThI_2 + 2e^- \qquad (1)$$

in keeping with the thorium(II) obtained from acetonitrile solution. This E_F value is equal within experimental error to that required for Faradaic behavior. It is worth noting that this result casts no light on the question of the structure and formulation of ThI_2, although the formation of adducts which are stable at room temperature establishes that the molecule is a Lewis acid. Any discussion of the electronic structure of thorium in these compounds is beyond the scope of the present paper.

Anionic Halogen Complexes. The electrochemical oxidation of a metal into a nonaqueous solution of $R_4NX + X_2$ represents a simple one-step route to the tetraalkylammonium salts of MX_n^{m-} anions.[14] We therefore investigated the oxidation of thorium into a solution of $(C_2H_5)_4NI$ and I_2 in acetonitrile. As the reaction proceeded, an insoluble material was precipitated. Analysis showed an unreasonably high iodine content, and after a number of similarly unsuccessful attempts, we concluded that anionic iodine complexes of thorium cannot be prepared by this method. A similar situation pertains for titanium, zirconium, and hafnium,[7] although anionic chloro and bromo complexes of these elements can be prepared electrochemically, as is the case for thorium(IV).[15]

Reaction of $ThI_2 \cdot 2CH_3CN$ with Dimethyl Sulfoxide. As noted in the Experimental Section, the attempted preparation of a Me_2SO adduct of ThI_2 was foiled by the subsequently demonstrated reaction

$$ThI_2 \cdot 2CH_3CN + (CH_3)_2SO \rightarrow ThOI_2 + (CH_3)_2S + 2CH_3CN$$

The use of low-oxidation-state metal halides (e.g., titanium(III) and vanadium(II)) to reduce organic compounds is well established, and it seems that thorium(II) can now be added to the list. More importantly, the reaction is a very convenient procedure, following electrochemical synthesis, to $ThOI_2$, otherwise only obtained by high-temperature reaction.

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Registry No. $ThI_2 \cdot 2CH_3CN$, 85613-74-7; $ThI_2 \cdot bpy$, 85613-75-8; $ThI_2 \cdot phen$, 85613-76-9; ThI_2, 13779-95-3; $ThOI_2$, 13841-21-9; Th, 7440-29-1; $(CH_3)_2SO$, 67-68-5; $(CH_3)_2S$, 75-18-3.

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Inner-Sphere Coordination of Cl^- by Ni^{2+} As Determined by ^{35}Cl NMR

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Recently the inner- and outer-sphere coordination of Cl^- by Ni^{2+} in aqueous solutions has been studied by NMR, X-ray diffraction, neutron diffraction, Raman spectroscopy, optical spectroscopy, XAFS, and thermodynamic measurements. Values reported for $\bar{n}$, the average number of chloride ions in the inner sphere per nickel ion, range from near zero to 0.4 in a 1 M $NiCl_2$ solution. The problem of determining $\bar{n}$ is difficult because of its small value and the difficulty of interpretation of data due to the indirect nature of some of the methods used. We have attempted to determine $\bar{n}$ by measuring the area of the ^{35}Cl NMR signal since this is a direct method that essentially requires no detailed theory for interpretation. It is based on the fact that in the slow-exchange region the NMR signal arises from free Cl^- only while that due to Cl^- in the inner sphere is unobservable due to shifting and broadening by the contact interaction and quadrupole interaction. Thus measurement of the area of the observed ^{35}Cl resonance will give the concentration of free Cl^- in the solution. The main disadvantages of the method are the need to make rather precise area measurements when $\bar{n}$ is small and the need to go to low temperatures in order to achieve slow exchange.

Experimental Section

The chloride salts were dried in an oven, cooled in a desiccator, weighed, transferred to volumetric flasks, and diluted to volume with deionized water. Aliquots of the chloride solutions were taken and titrated with $AgNO_3$ according to the Mohr method. There was good agreement between concentrations calculated from the weights and the value obtained from titration. In cases where a difference existed, it was assumed to be due to samples gaining water during weighing. The concentrations obtained from titration were used and were known to be better than 1%.

The NMR apparatus has been previously described.[1] Measurements of the ^{35}Cl resonance were made at 8.31 MHz with 10-kHz magnetic field modulation. The modulation frequency was raised from 5 kHz in order to assure no overlap of sidebands even though experiments showed this would not be a problem at the lower modulation frequency. Samples were placed in precision 12-mm NMR tubes and filled with identical volumes of solutions in order to have a constant filling factor. Spectra were taken at four or five rf amplitudes, which were measured with a linear rf voltmeter and fit with digitally computed Lorentzian dispersion curves to obtain the width and the amplitude of the resonance. The line shapes were accurately Lorentzian. Since a linear rf detection method was used, a number proportional to the number of nuclei at resonance was calculated by multiplying the width by the amplitude of the resonance and dividing by the rf amplitude. This number is referred to as the area of the resonance. An average of the areas measured at different rf levels was computed and generally had a standard deviation of about 1% except for the very broad lines.

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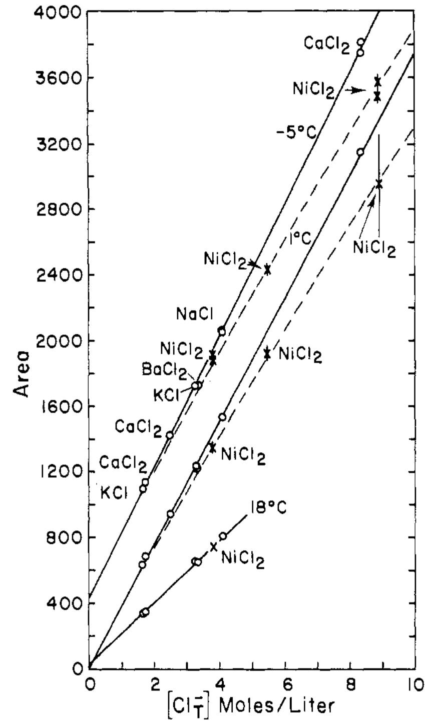

Figure 1. Relative area of resonances vs. total chloride concentration. The data at −5 °C have been displaced vertically by 400 units.

Results and Discussion

Measurements were made at −5, +1, and +18 °C, and the results are shown in Figure 1 as a plot of area vs. total chloride concentration, $[Cl^-]_T$. For NaCl, KCl, $CaCl_2$, and $BaCl_2$ one expects all chloride ions to be observable and therefore a linear relationship with zero intercept should exist between area and $[Cl^-]_T$. The solid lines drawn are the result of a linear least-squares fit of the data for the non-Ni salts, and the equations of the resulting lines are

$$A = (27 \pm 12) + (398.3 \pm 2.7)C \text{ at } -5\ °C \quad (1)$$

$$A = (5 \pm 18) + (273.2 \pm 4.6)C \text{ at } +1\ °C \quad (2)$$

$$A = (27 \pm 10) + (188.5 \pm 3.2)C \text{ at } +18\ °C \quad (3)$$

where A is the area and C is total chloride concentration in moles per liter. The intercepts appear to be slightly greater than zero, and we think this might be due to a slight increase in Q, the quality factor of the tank circuit, with lower electrical conductivity of the solution due to lower salt concentration. The effect of conductivity on Q appears to be slight since the different non-Ni salts have significantly different conductivities but still lie on a straight line. Also $NiCl_2$ has a lower conductivity than $CaCl_2$ at the same concentration and one would expect the $NiCl_2$ areas to lie above the line for non-Ni salts due to an effect of conductivity on Q alone. We are unaware of any mechanism by which the bulk paramagnetism of the $NiCl_2$ solutions could effect the Q of the tank circuit at the ^{35}Cl resonance frequency.

Previous experiments[2] have shown that at −5 and +1 °C $NiCl_2$ solutions are in the slow-exchange region whereas solutions at 18 °C are in the fast-exchange region. The areas for the $NiCl_2$ solutions lie below the lines for the noncomplexing salts at −5 and +1 °C, and the difference is interpreted as due to Cl^- bound in the inner sphere of Ni^{2+}. At 18 °C the $NiCl_2$ area at 1.89 M lies on the line as expected. Measurements could not be made at higher concentrations because of the extreme width of the resonance. The observed areas for $NiCl_2$ were used to calculate free chloride ion concentrations from eq 1 and 2, and then K_1 and n_{Cl^-} were calculated from eq 4 and 5. The results are shown in Table I. A plot

$$K_1 = [NiCl^+]/[Ni^{2+}][Cl^-] \quad (4)$$

$$n_{Cl^-} = [NiCl^+]/([Ni^{2+}] + [NiCl^+]) \quad (5)$$

of n_{Cl^-} vs. total $NiCl_2$ concentration is shown in Figure 2. In Figure 1 the dashed lines are computed areas for $NiCl_2$ solutions from eq 1 and 2 and the weighted average K_1's from Table I. In Figure 2 the lines were calculated by using the weighted average K_1's. All errors given are standard deviations and were calculated by using standard statistical methods.

Table I

[$NiCl_2$], M	+1 °C		−5 °C	
	K_1	n_{Cl^-}	K_1	n_{Cl^-}
1.89	0.031 ± 0.015	0.10 ± 0.05	0.022 ± 0.011	0.07 ± 0.04
1.89			0.007 ± 0.007	0.03 ± 0.03
2.74	0.030 ± 0.011	0.13 ± 0.05	0.038 ± 0.005	0.16 ± 0.02
4.45			0.036 ± 0.005	0.22 ± 0.03
4.45	0.037 ± 0.032	0.23 ± 0.20	0.049 ± 0.005	0.27 ± 0.03
weighted av	0.031 ± 0.009		0.035 ± 0.003	

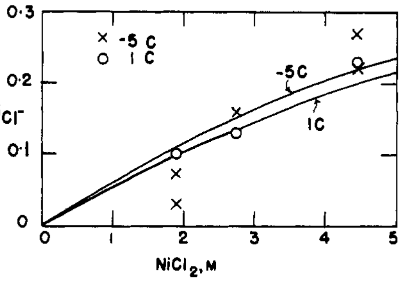

Figure 2. Average number of inner-sphere-bound chlorides per nickel vs. the total $NiCl_2$ concentration.

Although these measurements of necessity were made at low temperatures, they support the conclusions from XAFS, X-ray, and neutron diffractions that the degree of complexing is small at 25 °C since there is little evidence for a significant temperature coefficient for K_1. At 25 °C some previous results for 4.5 m $NiCl_2$ solutions set an upper limit of $n_{Cl^-} = 0.2 \pm 0.2$ by neutron diffraction,[3] 0.53 ± 0.09 by ^1H and D NMR,[4] and 0.62 by ^{35}Cl NMR.[5] A comparison of XAFS and diffraction results has been presented recently.[6] These studies indicate no Cl^- in the inner sphere of Ni^{2+} in 1–4 m solutions of $NiCl_2$, but the sensitivity for detecting $n_{Cl^-} < 0.5$ is limited. In the case of the NMR results it seems likely that the large number of correlated parameters needed in fitting relaxation data makes derivation of the degree of complexing difficult. The NMR relaxation studies[1,5] indicate the presence of more than one complex species such as $NiCl^+$ and $NiCl_2$. The points in Figure 2 suggest the rise in n with concentration may be faster than can be accounted for by a monochloro species, but the accuracy of the points makes this conclusion tentative.

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Registry No. **1**, 85664-79-5; **5**, 85664-80-8; ·CN, 2074-87-5; $TCNE^{-}\cdot$, 34512-48-6; CH_2Cl_2, 75-09-2; O_2, 7782-44-7.

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