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Metal Complexes in Acetic Acid. I. Kinetics and Mechanism of Reactions of Tetra-μ-acetato-dicopper(II) with Lithium Chloride and Hydrogen Chloride

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Kinetics of reactions of tetra-μ-acetato-dicopper(II) (copper(II) acetate dimer: $Cu_2(OAc)_4$) with lithium chloride and hydrogen chloride (XCl where X denotes Li or H) in acetic acid have been studied spectrophotometrically by using a stopped-flow technique with a computer-assisted averaging device. The rate of decomposition of copper(II) acetate dimer to the monomeric chloro complex is expressed as $-d[Cu_2(OAc)_4]/dt=k^{XCl}[Cu_2(OAc)_4][XCl]$. At 25 °C $k^{LiCl}=(3.5\pm0.6)\times10^5$ mol^{-1} kg s^{-1} ($\Delta H^{\ne}=50\pm10$ kJ mol^{-1} and $\Delta S^{\ne}=30\pm20$ J mol^{-1} K^{-1}) and $k^{HCl}=(4.8\pm1.0)\times10^5$ mol^{-1} kg s^{-1} ($\Delta H^{\ne}=23\pm10$ kJ mol^{-1} and $\Delta S^{\ne}=-60\pm20$ J mol^{-1} K^{-1}). Mechanisms are proposed for the decomposition of copper(II) acetate dimer and some discussions are made on the difference in reactivities of LiCl and HCl.

Acetic acid has been used as a convenient solvent for the titration of weak bases.[2)] It is a non-dissociating solvent having low dielectric constant (D=6.18 at 20 °C[3)]), while it is similar in nature to water for its amphiprotic character. Grunwald and co-workers have studied kinetic behavior of proton exchange and ion-pair exchange (metathesis) in acetic acid.[4)] Although plenty of information has been so far gathered on equilibria of metal complexes in anhydrous acetic acid media,[5–7)] kinetic and mechanistic studies of metal complexes are scarce.[8,9)] It appeared of particular interest for us to make a kinetic and mechanistic study of the reactions of the tetra-μ-acetato-dicopper(II) (henceforth we call it copper(II) acetate dimer) with lithium chloride and hydrogen chloride in acetic acid. The present study should provide some information on the reactivity of the dimeric copper entity.

Experimental

All starting chemicals were of reagent grade. Solutions of reagents were prepared in a glove box filled with dried air.

Reagents. *Acetic Acid*: Potassium permanganate (30 g) was added to acetic acid (3 dm^3) and after refluxing for *ca.* 10 h, the solution was distilled. The distillate was then refluxed again with about 200 g of boron triacetate for 12 h and distilled. Calculated amount of acetic anhydride was added to remove residual water in the acetic acid, and it was allowed to stand for *ca.* 4 d at 110 °C.[10)] The resultant acetic acid contained at most 1.5×10^{-3} mol dm^{-3} of water and presumably the same amount of acetic anhydride as that of remaining water.

Copper(II) Acetate: Copper(II) acetate was recrystallized from water. Then it was recrystallized first from reagent grade acetic acid and then from anhydrous acetic acid, and dried in a desiccator over sodium hydroxide for a few days under a reduced pressure. The copper(II) acetate solution was prepared by weighing crystals, and standardized by EDTA after evaporating excess acetic acid and then adding NH_3 to make the pH buffered at *ca.* 4.3. The determination of copper in copper(II) acetate crystals by electrolysis confirmed the composition of $Cu_2(CH_3CO_2)_4$.

Lithium Chloride: Lithium chloride was recrystallized twice from distilled water and dried at 120 °C. The solution was prepared by weighing. Its concentration was checked by the Mohr method with K_2CrO_4 as indicator.

Hydrogen Chloride Solution: Hydrogen chloride generated from NaCl with concentrated H_2SO_4 was dried with concentrated H_2SO_4 and was led to anhydrous acetic acid. A hydrogen chloride solution was handled as gently and carefully as possible in order to avoid volatilization of hydrogen chloride. The concentration of each hydrogen chloride solution for kinetic measurements was determined by means of mercury(II) thiocyanate method[11)] after dilution of the acetic acid solution with water.

Perchloric Acid Solution: Aqueous solution of perchloric acid (*ca.* 60%, super special grade, Wako Pure Chemical Industries, Ltd.) was diluted with acetic acid, and acetic anhydride equivalent to water was added dropwise to the perchloric acid solution keeping temperature of the solution below 25 °C. The concentration of perchloric acid was standardized against potassium hydrogen phthalate, Crystal Violet being used as indicator.

Lithium Acetate: Lithium acetate was recrystallized twice from acetic acid. Crystals were dried over sodium hydroxide *in vacuo*. The lithium acetate crystals were dissolved in acetic acid and the concentration was determined with a standard perchloric acid in acetic acid using Crystal Violet as indicator.

Measurements. Spectral measurements were performed on a highly sensitive spectrophotometer (SM 401, Union Giken Co. Ltd., Osaka) which enables us to measure spectra at a full scale of 0.01 optical density. The concentration of water was determined by the Karl-Fisher aquametry.

Dynamic reactions were followed by means of a stopped-flow technique using a highly sensitive stopped-flow spectrophotometer with a computer-assisted averaging device,[12)] which enable us to follow reactions slower than around 1 ms of half-life. Although the sensitivity of the instrument is very high by itself (0.01 absorbance/full scale per cm path length of light), it gives a poor SN ratio when used as a detector of a stopped-flow apparatus. Then by repeating the flow up to 500 times and averaging signals in a microcomputer, it was possible to improve considerably the SN ratio and to obtain a smooth reaction trace even at highest sensitivity of the instrument. The requirement for signal averagers is that the signal be repetitive. In this apparatus, since reactant solutions was driven by nitrogen gas pressure controlled by solenoid valves, the flow was easily controlled for repeated mixing of reactant solutions. Hence a high reproducibility of each signal was attained. In the present study, the averaged trace obtained from 10—50 flows was recorded on an X-Y recorder.

Equilibria. There have been some studies on the monomer-dimer equilibrium of copper(II) acetate in acetic acid

$$Cu_2(OAc)_4 \overset{K_{dim}}{\rightleftharpoons} 2Cu(OAc)_2 \qquad (1)$$

Cheng and Howald,[13] and Grasdalen and Svare[14] determined the monomer-dimer equilibrium constant as a function of the water concentration in acetic acid. According to them, the dissociation constant K_{dim} is less than 5×10^{-6} mol dm^{-3} at 25 °C in dry acetic acid. We have measured the absorbance of copper acetate solution at 680 nm, where the dimer has an absorption maximum and the dissociation products absorb little. Over the copper(II) acetate concentration range from 10^{-5} to 10^{-2} mol kg^{-1}, the molar absorption coefficient of copper(II) acetate remained almost constant (Fig. 1). The spectra of the solution remained unchanged and showed the characteristic absorption maxima at 370 nm and 680 nm, indicating the dimeric structure of copper(II) acetate. We estimated $K_{dim}\leq10^{-7}$ mol dm^{-3}. Thus the copper(II) acetate exists solely as a dimer under our experimental conditions.

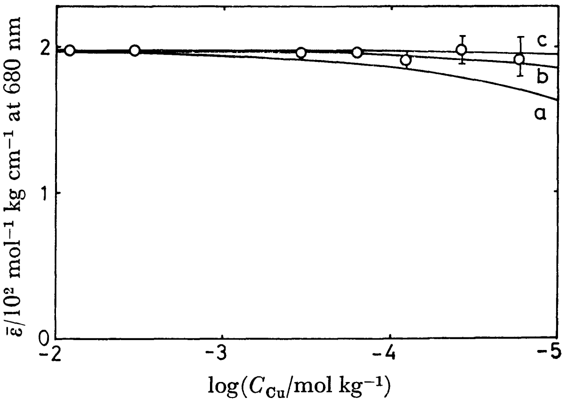

Fig. 1. Dependence of apparent molar absorption coefficient ($\bar{\varepsilon}$) on copper (II) acetate concentration (C_{Cu}). C_{Cu} refers to the concentration per copper atom in mol kg^{-1}. Curves a, b, and c are calculated with $K_{dim}=10^{-6}$, 10^{-7}, and 10^{-8} mol kg^{-1}, respectively.

The presence of a small amount of water (*ca.* 10^{-3} mol kg^{-1}) is inevitable in the present reaction systems. Water in acetic acid can behave as a base, but it is very weak. Perchloric acid and hydrogen chloride, reacting with water, produce their corresponding hydrates $H_3O^+ClO_4^-$ and $H_3O^+Cl^-$. However, these reactions do not occur to an appreciable extent under our experimental conditions. Judging from the equilibrium constant (0.6 ± 0.3 mol^{-1} dm^3) for the replacement of one of the two acetic acid molecules on the axial sites of the copper(II) acetate dimer by water in acetic acid:[6]

$$Cu_2(OAc)_4(HOAc)_2 + H_2O \rightleftharpoons Cu_2(OAc)_4(H_2O)(HOAc) + HOAc \qquad (2)$$

the monohydrate may be excluded under our experimental conditions. The equilibria of copper(II) acetate dimer with hydrogen chloride, perchloric acid and lithium acetate in acetic acid have been investigated in detail:[7]

$$Cu_2(OAc)_4 + 2HCl \rightleftharpoons 2CuCl(OAc) + 2HOAc \quad (10^{4.7}\ \mathrm{mol^{-1}\ kg}) \qquad (3)$$

$$Cu_2(OAc)_4 + 4HCl \rightleftharpoons 2CuCl_2 + 4HOAc \quad (10^{15.2}\ \mathrm{mol^{-3}\ kg^3}) \qquad (4)$$

$$Cu_2(OAc)_4 + 2HClO_4 \rightleftharpoons 2Cu(OAc)(ClO_4) + 2HOAc \quad (10^{3.5}\ \mathrm{mol^{-1}\ kg}) \qquad (5)$$

$$Cu_2(OAc)_4 + 4HClO_4 \rightleftharpoons 2Cu(ClO_4)_2 + 4HOAc \quad (10^{10.4}\ \mathrm{mol^{-3}\ kg^3}) \qquad (6)$$

$$Cu_2(OAc)_4 + 2LiOAc \rightleftharpoons Li_2Cu_2(OAc)_6 \quad (10^{0.89}\ \mathrm{mol^{-2}\ kg^2}) \qquad (7)$$

$$Cu_2(OAc)_4 + 4LiOAc \rightleftharpoons 2Li_2Cu(OAc)_4 \quad (10^{-0.4}\ \mathrm{mol^{-3}\ kg^3}) \qquad (8)$$

where the values of equilibrium constants for the relevant over-all reactions are given in parentheses. Coordinating solvent molecules are omitted for simplicity. The constant for the formation of chloro copper(II) complex from $Cu_2(OAc)_4$ and LiCl not being available, it was confirmed spectrally that the equilibrium was much favored to the formation of monomeric chloro complex under our experimental conditions. Comparison of the spectrum of $Cu_2(OAc)_4$ with that of the reaction mixture revealed that it was reasonable to follow the rate of the reaction at 300—320 nm, where the change in absorbance was large. Most of the runs were thus performed at 315 nm for LiCl and at 305 nm for HCl. From knowledge of the equilibria mentioned above we were able to set the appropriate conditions for kinetic measurements.

Results

The kinetics have been followed under conditions where the reverse reaction can be neglected in the kinetic study. The increase in absorbance with reaction time in the presence of a large excess of XCl was satisfactorily fitted to a pseudo-first-order rate law. Conditional first-order rate constants, k_0^{XCl}, were obtained from linear plots according to $\ln(A_\infty-A_0)/(A_\infty-A_t) = k_0^{XCl}t$, where A_0, A_t, and A_∞ denote respectively the absorbances at zero, at time t and at infinite time. Thus rate equation for the appearance of monomeric chloro copper complex (Cu–Cl) or decomposition of copper(II) acetate dimer is given by

$$\frac{1}{2}\frac{d[\mathrm{Cu{-}Cl}]}{dt} = -\frac{d[Cu_2(OAc)_4]}{dt} = k_0^{XCl}[Cu_2(OAc)_4], \qquad (9)$$

where $[Cu_2(OAc)_4]$ refers to a concentration of copper(II) acetate dimer ($Cu_2(OAc)_4\cdot2HOAc$), and two solvent molecules coordinated to the axial sites are omitted for simplicity. Conditional rates were found to be unaffected by the initial Cu(II) concentration ($4.31\times10^{-6}-7.48\times10^{-5}$ mol kg^{-1}), while the increase in the XCl concentration resulted in the increase in k_0^{XCl}. The plot of k_0^{XCl} against total concentration of XCl, C_{XCl}, is linear with no intercept (Fig. 2). Then the rate law is

$$-\frac{d[Cu_2(OAc)_4]}{dt} = k^{XCl}[Cu_2(OAc)_4][XCl], \qquad (10)$$

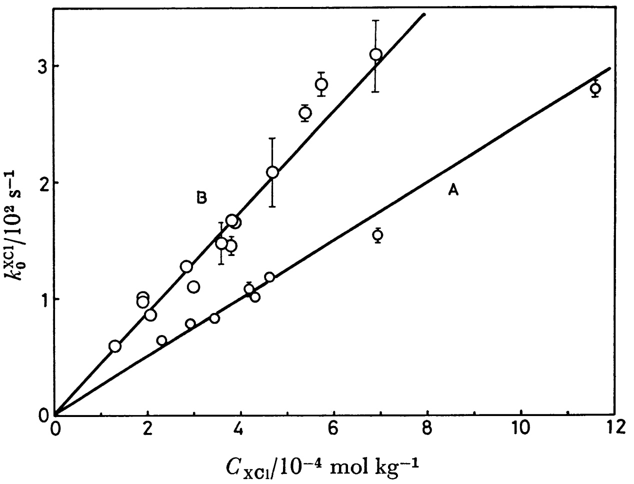

Fig. 2. Plots of conditional first-order rate constant (k_0^{XCl}) against the concentration of XCl (C_{XCl}). A: LiCl, B: HCl, at 20 °C.

Table 1. Effect of added water on the conditional rate constants

LiCl system[a]		HCl system[b]	
$10^2C_{\mathrm{H_2O}}$/ mol kg^{-1}	k_0^{LiCl}/s^{-1} ($\pm$10)[c]	$10^2C_{\mathrm{H_2O}}$/ mol kg^{-1}	k_0^{HCl}/s^{-1} ($\pm$15)[c]
<0.2[d]	151±25[e]	<0.2[d]	120±25[e]
0.43	151	0.28	108
1.3	170	0.61	105
2.3	177	0.89	105
3.4	191	1.4	106
6.1	233	1.9	119
9.8	244	3.1	140
		3.9	156

a) Conditions: $C_{\mathrm{Cu}}=9.64\times10^{-6}$ mol kg^{-1}, $C_{\mathrm{LiCl}}=4.31\times10^{-4}$ mol kg^{-1}, 25 °C. b) Conditions: $C_{\mathrm{Cu}}=8.52\times10^{-6}$ mol kg^{-1}, $C_{\mathrm{HCl}}=2.50\times10^{-4}$ mol kg^{-1}, 25 °C. c) Deviation from an average value of several experimental points. d) No added water. The concentration of water was less than 2×10^{-3} mol kg^{-1}. e) This value was estimated from data at 25 °C in Table 2.

where k^{XCl} is a second-order rate constant. Some kinetic experiments were carried out to have an idea of the effect of added water in the present reaction (Table 1). There was no effect of water at least up to 10^{-2} mol kg^{-1}. As the amount of water in our reaction systems is at most 3×10^{-3} mol kg^{-1}, the contribution of water to reaction rates can be neglected. From the temperature dependence of k^{XCl} (Eyring's plot), the activation parameters are calculated, and tabulated in Table 2.

The reaction of copper(II) acetate dimer ($C_{\mathrm{Cu}}=9.39\times10^{-6}$ mol kg^{-1}) with LiCl ($C_{\mathrm{LiCl}}=4.95\times10^{-4}$ mol kg^{-1}) was followed in the presence of lithium acetate over the concentration range from 3.59×10^{-5} to 1.20×10^{-4} mol kg^{-1}, which does not appreciably favor equilibria 7 and 8 to the right. We found no kinetic effect of lithium acetate, which is one of the strongest bases in acetic acid. The kinetic run of $Cu_2(OAc)_4$ (8.45×10^{-6} mol kg^{-1}) with HCl (2.72×10^{-4} mol kg^{-1}) was carried out in the presence of up to 1.2×10^{-5} mol kg^{-1} of $HClO_4$. Perchloric acid at such a concentration level does not appreciably favor equilibria of $Cu_2(OAc)_4$ shown in Eqs. 5 and 6. The rate constant remained unchanged in the presence of such amounts of $HClO_4$, which is the strongest acid in acetic acid.

Table 2. Second-order rate constants and activation parameters

Temp/°C	$10^{-5}k^{\mathrm{LiCl}}$/ mol^{-1} kg s^{-1}	$10^{-5}k^{\mathrm{HCl}}$/ mol^{-1} kg s^{-1}
17	1.9±0.3 (8)[a]	4.0±0.7 (6)
20[b]	2.5±0.5 (8)	4.2±0.9 (14)
25	3.5±0.6 (22)	4.8±1.0 (19)
30	4.8±0.8 (2)	6.0±1.5 (4)
35	6.0±1.0 (2)	7.3±1.5 (4)
$\Delta H^{\ddagger}$/kJ mol^{-1}	50±10	23±10
$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	30±20	−60±20

a) Figure in parenthesis indicates number of runs carried out at different XCl concentrations. b) Data for this are given in Fig. 2.

The reaction of copper(II) acetate dimer with perchloric acid ($Cu_2(OAc)_4+4HClO_4 \rightarrow 2Cu(ClO_4)_2$) was followed at 680 nm where the difference in absorbance of $Cu_2(OAc)_4$ and $Cu(ClO_4)_2$ is maximum. The reaction was too fast to be followed in the present conditions ($C_{\mathrm{HClO_4}}=10^{-3}$ mol kg^{-1}, $C_{\mathrm{Cu}}=10^{-4}$ mol kg^{-1}, 25 °C). Judging from the dead time of our apparatus, we presume the half life time is less than 0.5 ms. Then, provided the order is first with respect to $HClO_4$, the second-order rate constant ($k^{\mathrm{HClO_4}}$) seems to be larger than 3×10^6 mol^{-1} kg s^{-1}.

Discussion

The values of activation enthalpy and entropy for k^{LiCl} and k^{HCl} are very different. We shall consider the present results in the light of the exchange of acetic acid at the axial positions of copper(II) acetate dimer. Grasdalen[15] has studied the exchange rate of acetic acid at the axial positions of the dimeric copper(II) acetate by measuring ^{1}H NMR line width and line shift in acetic acid/ethanol solutions ($k_{\mathrm{ex}}=3.0\times10^4$ s^{-1} (25 °C), $\Delta H_{\mathrm{ex}}^{\ddagger}=44.8$ kJ mol^{-1} and $\Delta S_{\mathrm{ex}}^{\ddagger}=9.2$ J mol^{-1} K^{-1}). We have also made measurements of the temperature dependence of the solvent acetic acid proton line broadening and shift for solutions of copper(II) acetate dimer in acetic acid, acetic acid/chloroform and acetic acid/dichloromethane solutions. Activation parameters for acetic acid exchange were determined to be $k_{\mathrm{ex}}=(1.2\pm0.2)\times10^4$ s^{-1}, $\Delta H_{\mathrm{ex}}^{\ddagger}=50\pm4$ kJ mol^{-1} and $\Delta S_{\mathrm{ex}}^{\ddagger}=2\pm5$ J mol^{-1} K^{-1} for both HOAc/$CDCl_3$ solution ([HOAc]=5.24 mol kg^{-1}) and HOAc/CD_2Cl_2 solution ([HOAc]=1.79 mol kg^{-1}).[16] The values of activation enthalpy $\Delta H_{\mathrm{ex}}^{\ddagger}$ for the exchange of acetic acid are the same even in different diluent solvent (ethanol, chloroform and dichloromethane) and even for different concentration of acetic acid in the bulk. The fact clearly indicates that the rate-determining step for k_{ex} should be the same in these mixed solvents and also, most probably in pure acetic acid solution.

In ethanol solution the axial ethanol molecule on the copper acetate dimer is readily replaced by acetic acid.[14] This is contrary to the prediction based on the difference in the basicity between acetic acid and ethanol: the latter is much more basic than the former. The geometry should thus favor the coordination of acetic acid by an extra hydrogen bonding with the bridging acetate.[14] This hydrogen bonding appears to account for the unexpectedly slow exchange rate of acetic acid at the copper acetate dimer without recourse to the exchange between axial and bridging ligands.[15,17]

In view of the fact that the activation enthalpy for the reaction of copper acetate dimer with lithium chloride is the same as that for the acetic acid exchange, it seems reasonable to suppose that the reaction of copper acetate dimer with lithium chloride is a dissociative interchange mechanism: in the transition state the chloride ion in LiCl[18] enters the apical coordination site vacated in the solvent dissociation. Positive activation entropy for k^{LiCl} is in harmony with this dissociative mode of activation. The coordination of chloride to copper initiates the decomposition of the dimeric structure, followed by fast reactions leading to monomeric chloro complexes.

The activation enthalpy for k^{HCl} is smaller than for k_{ex}, while the activation enthalpy for k^{LiCl} is identical with that for k_{ex} within experimental errors. The rate for the reaction of $\mathrm{Cu_2(OAc)_4}$ with $\mathrm{HClO_4}$ is much faster than that with HCl. At this stage it is of interest to consider the role of ionization and dissociation of reactants in the present reaction systems. Dissociation of AB is written as

$$\mathrm{AB} \rightleftarrows \mathrm{A^+B^-} \rightleftarrows \mathrm{A^+} + \mathrm{B^-}$$

with the overall dissociation constant K_{D}:

$$K_{\mathrm{D}} = \frac{[\mathrm{A^+}]+[\mathrm{B^-}]}{[\mathrm{AB}]+[\mathrm{A^+B^-}]} = \frac{K_{\mathrm{i}}K_{\mathrm{d}}}{1+K_{\mathrm{i}}}$$

where K_{i} is an ionization constant and K_{d} is a dissociation constant.[19] Available values of K_{d} are $10^{-7.10}$ for LiCl,[20,21] $10^{-6.78}$ for LiOAc,[20,22] $10^{-8.55}$ for HCl,[20] $10^{-10.1}$ for $\mathrm{H_2O}$,[20] and $10^{-5.87}$ for $\mathrm{HClO_4}$.[20] K_{d} can be calculated by an equation of the type derived by Fuoss for ion-pair formation.[23] Therefore unknown K_{d} values may be predicted, at least to a correct order of magnitude. On this basis, K_{d} is estimated to be about $10^{-6}\ \mathrm{mol\ dm^{-3}}$ for all of these 1 : 1 electrolytes. Then values of K_{i} for LiCl, LiOAc, HCl, and $\mathrm{H_2O}$ can be estimated to be $10^{-1.1}$, $10^{-0.8}$, $10^{-2.6}$, and $10^{-4.1}$, respectively. Hydrogen chloride and water are largely unionized, while lithium chloride and lithium acetate are to a considerable extent in the form of undissociated ion-pair. It should be noted that the extent of ionization is largest for perchloric acid.

It seems likely that the rate-determining step for HCl and $\mathrm{HClO_4}$ is the proton-assisted cleavage of a copper-oxygen bond. Since perchloric acid is ionized to a much larger extent than hydrogen chloride, it may act more effectively on copper–oxygen bond than un-ionized HCl molecule. The addition of a proton from HCl to a bridged oxygen results in a polarized transition state leading to the cleavage of a copper–oxygen bond. Subsequent formation of monomeric chloro copper(II) complexes should be fast. The negative activation entropy for k^{HCl} is consistent with preequilibrium involving HCl addition: polarized transition state should favor the solvation of the activated complex.

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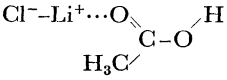
17) The exchange between axial and bridging ligands has been proposed as the rate-determining step in the trifluoroacetate exchange with tetrakis(μ-trifluoroacetato)dimolybdenum in acetonitrile (K. Teramoto, Y. Sasaki, K. Migita, M. Iwaizumi and K. Saito, *Bull. Chem. Soc. Jpn.*, **52**, 446 (1979)). It is unfortunate that no separate NMR signal of acetic acid attached to copper acetate dimer can be observed in any solvents studied because of the low solubility

of the dimer.

18) Grunwald *et al.* showed molecular structure of ion-pairs in acetic acid from electric dipole moments. The solvated ion-pair of LiCl is best described as monodentate attachment of *cis*-HOAc to cation:



$\mathrm{Cl^{-}{-}Li^{+}\cdots O{=}C(CH_3){-}O{-}H}$

(E. Grunwald, M. R. Crampton, A. Effio, and T.-P. I, *J. Am. Chem. Soc.*, **98**, 1716 (1976).

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