from sodium benzophenone ketyl under argon. Dichloromethane is distilled from $LiAlH_4$ under argon. Benzene-d_6 is obtained in ampules, and NMR samples are prepared under inert atmosphere conditions in a Vacuum Atmospheres drybox.

The infrared spectral samples are all made in a drybox and the spectra are obtained on a Perkin-Elmer 283 instrument.

The ^{13}C NMR spectra are obtained from a Varian CFT-20 instrument and the ^1H NMR spectra are recorded on a Varian XL-100 Nicolet FT-100 instrument in 5-mm tubes. Molecular weight measurements are done in benzene with equipment described by Shriver.[11] The mass spectrum is obtained on an AEI MS-902 double focusing spectrometer.[12]

Preparation of 1,3-Dimethyl-2-methyleneimidazoline. To a 40-mL ether suspension of 2-chloro-1,3-dimethylimidazolidinium chloride[13] at −10 °C is added 31.2 mL of CH_3Li in ether over a 3-h period. The mixture is stirred at 0–10 °C for 5 h until no further methane is evolved. The mixture is filtered from LiCl and excess ether is removed under vacuum to give a pale yellow oil, 3.0 g (86%), bp 70–75 °C. Mass spectrum at 70 eV: $(M + 1)^+$ calcd for $C_6H_{13}N_2^+$, *m/e* 113.1079; found, *m/e* 113.1074.

Zeise's Dimer and 1,1-Bis(dimethylamino)ethylene. To a yellow-orange suspension of $Pt_2Cl_4(C_2H_4)_2$ (250 mg, 0.042 mmol) in 15 mL of benzene at 5 °C is added 1,1-bis(dimethylamino)ethylene (97 mg, 0.085 mmol) in 5 mL of benzene. The mixture becomes deep yellow and the $Pt_2Cl_2(C_2H_4)_2$ dissolves. After 4 h the solution is orange. It is filtered and excess benzene is sublimed away to give a bright yellow powder, 260 mg (77%), mp 111 °C dec. Further recrystallization can be accomplished from dichloromethane. Anal. Calcd for $[C_6H_{14}Cl_2N_2Pt]_2$: C, 18.96; H, 3.71; Cl, 18.65; mol wt, 756. Found: C, 18.48; H, 3.36; Cl, 19.39; mol wt, 856.

Zeise's Dimer and 1,3-Dimethyl-2-methyleneimidazoline. To a yellow-orange suspension of $Pt_2Cl_4(C_2H_4)_2$ (250 mg, 0.043 mmol) in 10 mL of benzene at 5 °C is added 1,3-dimethyl-2-methyleneimidazoline (209.2 mg, 1.87 mmol) in 5 mL of benzene. The mixture becomes bright yellow and the suspended material goes into solution. After 2 h the evolution of ethylene ceases, and the mixture is filtered. Sublimation of the excess benzene gives a bright yellow solid, 260 mg (79%), mp 145 °C dec. Anal. Calcd for $C_6H_{12}Cl_2N_2Pt$: C, 19.06; H, 3.20. Found: C, 22.98; H, 3.26.

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Registry No. 1, 815-62-3; η^1-**2**, 68757-84-6; η^2-**2**, 68757-85-7; **3**, 68738-47-6; η^1-**4**, 68757-86-8; η^2-**4**, 68757-87-9; $[Pt(C_2H_4)Cl_2]_2$, 12073-36-8; 2-chloro-1,3-dimethylimidazolium chloride, 37091-73-9.

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Contribution from the Department of Physical Chemistry,
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Complex Formation between Aluminum Ion and 5-Nitrosalicylic Acid. Mechanism and Equilibrium Constant

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The Eigen mechanism for the formation of labile complexes is today universally accepted for divalent cations; according to this mechanism, water loss from the inner coordination sphere is rate determining, and the rate constant is ligand independent.[1] Tervalent cations present a much less clear-cut picture.[2] For Al(III) there is some evidence[3] that it should follow the same mechanism as the divalent cations, whereas energetic considerations argue against this dissociative mechanism.[4] Further knowledge about the ligand dependence—or independence—of the rate constant is therefore desirable. To this aim, we consider it especially promising to compare ligands which have identical active sites and differ only in their basic strength. In this note, we report the results concerning 5-nitrosalicylic acid, to be compared with the weaker 5-sulfosalicylic,[5] and salicylic,[6] acids.

Experimental Section

The materials and methods were those described in our previous paper.[5] The nitrosalicylic acid was Fluka, "purum". The ionic strength was again 0.1 M. The temperature was 25 °C throughout. All measurements were carried out at 355 nm where the difference between the absorptivity of the complex and that of the ligand was found to be at its maximum.

At pH ≥1.9, the kinetic results were obtained by mixing two solutions, each containing one of the reactants at the appropriate pH. For runs at pH <1.9, the complex present in less acid solution was decomposed by acidification. The stopped-flow technique was used when the pH was ≥3.1; at lower pH, the reaction was too slow for this method and was monitored by an ordinary spectrophotometer and recorder.[5]

Results

Equilibrium Constants. We again[5] define an apparent, pH-dependent formation constant of our complex, which we assume to be AlL^+, namely

$$K_{app} = \frac{[AlL^+][H^+]}{[Al(III)]([HL^-] + [H_2L])} = \frac{K_1 K_{H1}[H^+]}{(K_{H1} + [H^+])(K_{OH} + [H^+])} \quad \text{(I)}$$

where K_{H1} is the dissociation constant of the carboxylic group, K_{OH} the hydrolysis constant of Al(III), and K_1 the equilibrium constant of the reaction

$$Al^{3+} + HL^- \rightleftharpoons AlL^+ + H^+ \quad (1)$$

(The relative concentration of L^{2-} is so small[7,8] that its contribution to K_{app} can be neglected.)

At three values of pH—1.94, 2.13, and 2.46—the absorbance was measured at ligand concentrations of 0.5×10^{-4} or 10^{-4} M and four to five different metal ion concentrations ranging from 5×10^{-4} to 4.8×10^{-3} M. For each value of pH, K_{app} was obtained by the graphical method of our previous paper.[5]

In addition, at the same values of $[H^+]$ and reactant concentrations, we measured the pseudo-first-order rate constant, k_{obsd}, given by

$$k_{obsd} = d \ln ([AlL^+] - [AlL^+]_\infty)/dt = k_f a + k_d[H^+] \quad \text{(II)}$$

where a is the mean concentration of Al(III), and k_f and k_d are the formation and dissociation rate constants, respectively,

Table I. Comparison of Equilibrium and Rate Constants for Al(III) and Salicylic, and Substituted Salicylic, Acids

acid	10^3K_{H1}	K_1	K_{H2}[a]	K_1/K_{H2}	$10^{-3}k_4$	k_1	$10^{-3}k_2$	$10^{-3} \times k^*_{AlOH}$	k_1	k_3	ref
salicylic[b]	2.04	1.33	5×10^{-14}	3×10^{13}	3.90	≤2.5	≤1.4	1.95	~1.4		6
5-sulfosalicylic	3.75	7.60	8×10^{-13}	1×10^{13}	2.50	≤1.9	≤2.0	1.22	~1.5	$<2 \times 10^{-2}$	5
5-nitrosalicylic	5.70	13.0	7×10^{-11}	2×10^{11}	1.54	≤0.9	≤1.4	0.77	~0.7	$<8 \times 10^{-3}$	this work

[a] From ref 8. This reference refers to 31 °C. Since we are chiefly interested in a *comparison* between the three acids, the difference in temperature is not relevant. [b] Recalculated as described in the text.

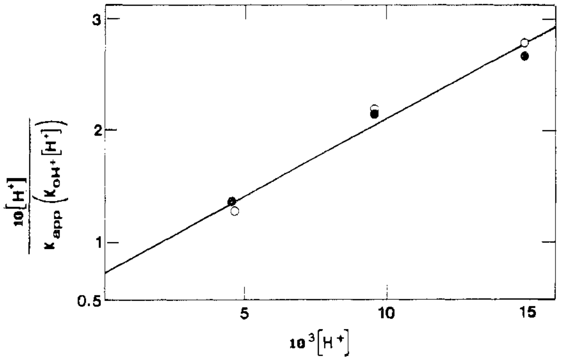

Figure 1. Dependence of $[H^+]/K_{app}(K_{OH} + [H^+])$ on $[H^+]$ (see eq I): circles, kinetic results; dots, spectrophotometric results.

and depend on pH. Their ratio[9] equals K_{app}.

Taking the reciprocal of eq I we see that a plot of $[H^+]/K_{app}(K_{OH} + [H^+])$ as a function of $[H^+]$ should be a straight line. This is shown in Figure 1. The spectrophotometric and kinetic results are seen to coincide within the limit of experimental accuracy. From the intercept and slope we get the results shown in Table I. Our value for K_{H1} is in good agreement with the data given in the literature.[7,8] No values for K_I seem to be reported.

Rate Constants. In addition to reaction 1 we have to consider the reactions

$$AlOH^{2+} + H_2L \rightleftharpoons AlL^+ + H^+ + H_2O \quad (2)$$

$$\upharpoonleft\downharpoonright$$

$$Al^{3+} + H_2L \rightleftharpoons AlL^+ + 2H^+ \quad (3)$$

$$\upharpoonleft\downharpoonright$$

$$AlOH^{2+} + HL^- \rightleftharpoons AlL^+ + H_2O \quad (4)$$

where the vertical, protolytic equilibria are rapid in comparison with the rate of complex formation. Reactions 1 and 2 have the same pH dependence. We can write k_{obsd} in the form

$$k_{obsd} = (k_1K_{H1} + k_2K_{OH} + k_3[H^+] + k_4K_{H1}K_{OH}/[H^+])B \quad \text{(III)}$$

with[10]

$$B = \frac{a[H^+]}{(K_{H1} + [H^+])(K_{OH} + [H^+])} + \frac{[H^+]}{K_1K_{H1}} = \frac{K_{app}a + [H^+]}{K_1K_{H1}} \quad \text{(IV)}$$

Figure 2 shows k_{obsd}/B as a function of $1/[H^+]$, for 28 experiments carried out at 17 values of pH between 1.1 and 3.4; the concentrations of the reactants were in the same range as stated above. A straight line is seen to be obtained[11] with no tendency to curve upward at low values of $1/[H^+]$; this means that $k_3[H^+]$ is small in comparison with the other members in parentheses in eq II. The intercept and slope of Figure 2 are equal to

$$k_1K_{H1} + k_2K_{OH} = (5.0 \pm 0.3) \times 10^3 \text{ s}^{-1}$$

and

$$k_4K_{H1}K_{OH} = (3.11 \pm 0.05) \times 10^{-5} \text{ M s}^{-1}$$

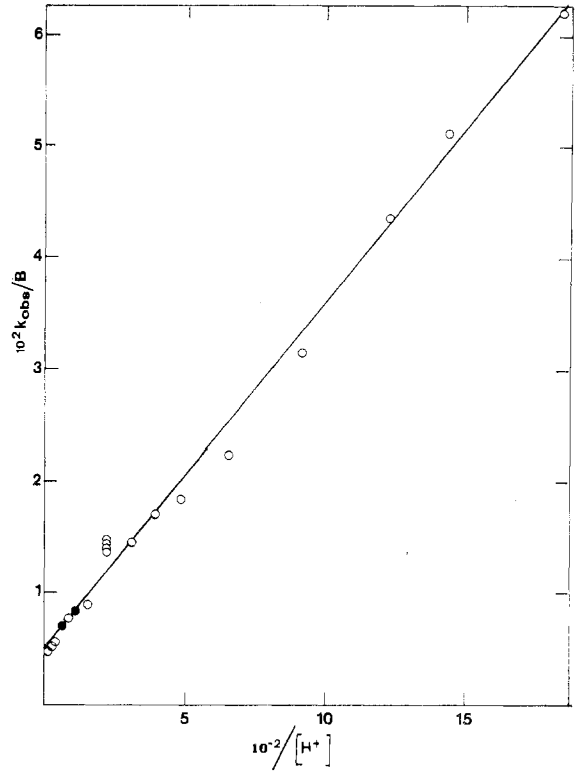

Figure 2. Values of k_{obsd}/B as a function of $1/[H^+]$ (where B is defined in eq III). The dots comprise five experiments each.

respectively. With[5,12] $K_{OH} = 3.55 \times 10^{-6}$ M, this yields the value of k_4 shown in Table I.

Discussion

In Table I, we present a comparison between salicylic, sulfosalicylic, and nitrosalicylic acids. The first two columns show K_{H1} and K_1. It seems at first sight as if the complex were stronger the higher the acidity of the complexing ligand. However, in the complex the last proton is expelled. Therefore, the appropriate comparison is not between K_1 and K_{H1} but rather between $[AlL^+]/[Al^{3+}][L^{2-}] = K_1/K_{H2}$ and K_{H2} (where K_{H2} is the dissociation constant of the phenolic group). This is shown in the third column of Table I. The complex is seen to be stronger the more basic the ligand, as expected.

Although the contribution of reaction 3 cannot be detected, an approximate upper limit for k_3 can be estimated as described previously;[5] the result is shown in the table. On the basis of the rate of water exchange[3] we should expect a somewhat higher value, namely, ~4 × 10^{-2} M^{-1} s^{-1}. However, since the rate constants predicted from the rate of water exchange are frequently higher than those found experimentally,[13] we cannot say that our values of k_3 are definitely reduced below the "normal" value. Such a reduction, if significant, could be ascribed to the presence of an internal hydrogen bond, whose decelerating effect on the rate of formation of more labile complexes is well-known.[14]

In order to get comparable values for k_4 we recalculated the results of Secco and Venturini[6,15] according to the method described in this note. Disregarding the points at the lowest values of pH, which lie somewhat below the straight line corresponding to our Figure 2, and using the same value of K_{OH} as above, we get the result reported in the table. Although the values of k_4 are seen to be all of the same order of magnitude, they vary somewhat more strongly than might be expected for a series of very similar ligands. Taking K_{out}, the formation constant of the outer-sphere complex, from the Fuoss equation,[16] we calculated the rate constants for the exchange between the ligand and a coordinated water molecule; these constants are designated by k^*_{AlOH} in the table. No data on the rate of water exchange on $AlOH^{2+}$ are available for comparison; our results do confirm, however, the labilizing influence of OH.

Owing to the proton ambiguity of reactions 1 and 2, we cannot evaluate k_1 and k_2 separately. We calculated the value to be assigned to k_1 if pathway 2 were nonexistent, and vice versa for k_2. These values obviously constitute upper limits for the corresponding rate constants. They are also given in Table I, with values for salicylic acid recalculated as explained above. If we want to proceed further, we must make some assumption about either k_1 or k_2. Assuming k^*_{AlOH} to be the same for reaction 2 as for reaction 4, and again taking K_{out} from the Fuoss equation,[16] we estimated the contribution of reaction 2 to the intercept of Figure 2. From the difference, we calculated the values of k_1 given in the table.

From the rate of water exchange[3] on Al^{3+} we should predict[5] a value of $\sim 0.6\ M^{-1}\ s^{-1}$ for k_1. The somewhat higher value found for sulfosalicylic acid had previously[5] been discussed in terms of internal hydrolysis.[17] An alternative explanation would be the assumption of a concerted mechanism. This assumption would be compatible with the slight increase of the rate constant with increasing basicity of the ligand which can be discerned from our table. It can also explain the existence of more specific effects which become apparent when we compare the rate constants reported for water–ligand exchange between the inner and outer coordination spheres when[18] $Co(CN)_6^{3-}$,[19] SO_4^{2-}, and[20] $Fe(CN)_6^{3-}$ serve as ligands. This alternative assumption is further strengthened by the fact that an associative interchange mechanism has recently been assigned to the formation of Fe^{3+} complexes on the basis of the negative[21] or zero[22] values found for the volume of activation. If this is correct, then the fact that complex formation is accelerated by the presence of OH^- in the inner coordination sphere can no longer serve as a criterion for the dissociative mechanism of the *un*hydrolyzed species, and it would be reasonable to assume an associative mechanism for all tervalent cations in their unhydrolyzed form.[23,24]

Registry No. AlL^+, 68813-17-2; H_2L, 96-97-9; Al^{3+}, 22537-23-1.

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Molecular Stereochemistry of Iodo(*meso*-tetraphenylporphinato)iron(III)

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The molecular stereochemistry of iodo(*meso*-tetraphenylporphinato)iron(III), FeTPPI, was examined to determine if the axial ligand has any substantial influence on the coordination geometry of the iron(III) atom in this high-spin porphinato derivative. After completion of this work, the structure of the related bromide complex, FeTPPBr, was reported.[1] We are thus able to compare the structures of the chloro,[2] bromo, and iodo derivatives of $[FeTPP]^+$.

Experimental Section

FeTPPI was prepared by the reaction of a $CHCl_3$ solution of $(FeTPP)_2O$[3,4] with a 100-fold excess of aqueous KI/H_2SO_4. The aqueous layer was removed, the $CHCl_3$ solution was filtered and concentrated, and crystals were grown by allowing pentane to diffuse into the solution.

Preliminary examination of a crystal of FeTPPI with dimensions of 0.27 × 0.20 × 0.53 mm established that the Laue symmetry and systematic absences were consistent with the monoclinic space group $P2_1/n$. Lattice constants $a = 10.118$ (3) Å, $b = 16.352$ (4) Å, $c = 21.211$ (7) Å, and $\beta = 89.56$ (2)° came from a least-squares refinement that utilized the setting angles of 60 reflections. These constants led to a calculated density of 1.51 g/cm^3 for a cell content of four FeTPPI molecules; the experimental density was 1.49 g/cm^3. All measurements were made at the ambient laboratory temperature of 20 ± 1 °C.

Diffracted intensities were measured by θ–2θ scanning using graphite-monochromated Mo Kα radiation. The scan range used was 1.0° below Kα_1 to 1.0° above Kα_2. Backgrounds were collected at the extremes of the scan for 0.5 times the time required for the scan itself. All independent data to $(\sin\theta)/\lambda \leq 0.648$ Å^{-1} were measured. Four standard reflections, measured periodically, showed no trend with time. Variable 2θ scan rates were used as described previously;[5] the slowest was 2.0°/min and the fastest was 12.0°/min. Net intensities were reduced to relative squared amplitudes, $|F_o|^2$, with correction for the absorption of x-radiation ($\mu = 1.34$ mm^{-1}). Reflections having $F_o > 3\sigma(F_o)$ were taken to be observed. A total of 6175 unique data, 77% of the theoretical number possible, were used in the subsequent solution and refinement of the structure.

The structure was solved by the usual heavy-atom method.[6] Isotropic block-diagonal least-squares refinement smoothly converged.[7] A difference Fourier synthesis gave the approximate positions of all hydrogen atoms in the asymmetric unit of the structure; these atoms were then assigned to theoretically calculated positions (C–H = 0.95 Å, $B(H) = B(C) + 1.0$ Å^2), and their contributions to the calculated structure amplitudes were included in subsequent cycles of refinement. Anisotropic temperature factors and the imaginary component of anomalous scattering were now included, and the structure was refined to convergence. This led to a conventional residual (R_1) of 0.049, a weighted residual (R_2) of 0.059, and an error of fit of 1.90. A final difference Fourier synthesis had one peak of ~ 1.1 e/Å^3 near the iodide and several peaks of 0.5–0.7 e/Å^3 near the iron and iodide, but it was otherwise featureless. Final atomic coordinates and associated thermal parameters are reported in Table I. A listing of the final observed

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