units per unit cell.[4,5] (The possibility that $K_7V_5W_8O_{40}\cdot 12H_2O$ has a unit cell edge twice as large as given here is unlikely because of the failure to observe the necessary reflections on long-exposure photographs.) Formulations of the structure in terms of other known complexes (*e.g.*, as double salts) are incompatible with the crystal data and with the solution chemistry involved. Other attempts to indicate whether constitutional water was present were inconclusive or were frustrated owing to the instability of the complex in solution.

The analyses of the three organic ammonium salts all give W/V = 1.88 ± 0.01, which is close to 17/9 = 1.889 or 15/8 = 1.875. Possible formulations based on known tungstovanadates and their stability in relation to the pH are $M'_7V_5W_8O_{40}\cdot M'_6V_4W_9O_{40}\cdot nH_2O$ and $2M'_7V_5W_8O_{40}\cdot 13M'_4V_2W_4O_{19}\cdot nH_2O$ for W/V = 17/9 and $2M'_7V_5W_8O_{40}\cdot 11M'_4V_2W_4O_{19}\cdot nH_2O$ for W/V = 15/8 (M' = univalent cation). However, the infrared spectra of all three salts are very similar to the spectrum of $K_7V_5W_8O_{40}\cdot 12H_2O$ and to the spectra of the salts of $V_4W_9O_{40}^{6-}$, all of which differ systematically from the spectra of the salts of $V_2W_4O_{19}^{4-}$.[1] The formation of the 4:9 complex in these systems is confirmed by the observed crystallization of the potassium salt from solutions of potassium 4-tungsto-2-vanadate(V) in formate buffer solutions. Therefore we retain only the formulation based on a 1:1 combination of $V_5W_8O_{40}^{7-}$ and $V_4W_9O_{40}^{6-}$. With this constitution, the organic and sodium analyses require formulation as acid salts. The formation of acid salts of this type is not unprecedented; previously known acid salts include $K_5H[CoW_{12}O_{40}]\cdot 18H_2O$,[6] $Cs_3H_2[BW_{12}O_{40}]\cdot 2H_2O$, and $Cs_3H[SiW_{12}O_{40}]\cdot 2H_2O$.[7] The nonstoichiometry with respect to cation content is not attributed to partial reduction, since reduction is very slow compared to the time consumed in the preparations. The presumed Keggin-type anions may form a fairly symmetrical packing bound together electrostatically by disordered cations and solvent molecules.[4]

The ion $V_5W_8O_{40}^{7-}$ is unstable in solution; however, it may exist as a minor species in equilibria involving more stable complexes. (The potassium salt was probably first observed as a minor by-product in our preparation of the $V_2W_4O_{19}^{4-}$ salt[3] as small brownish orange square blocks. We have observed a similar phase in very low yield in ammonium salt preparations. The phase is also observed when solutions of $K_4V_2W_4O_{19}$ are acidified, as in the preparation[1] of $K_6V_4W_9O_{40}$, but are allowed to stand for several days at room temperature.) The 5:8 complex decomposes to give the 2:4 complex at pH 4–5. At pH 2–3, it decomposes evidently to condensed species including the 4:9 complex rather than to $VW_5O_{19}^{3-}$, even in solutions less than 10^{-3} *F* in vanadium.

Acknowledgment.—This work was supported by Grant No. 70-1833 from the Air Force Office of Scientific Research.

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
UNIVERSITY OF UTAH, SALT LAKE CITY, UTAH 84112,
AND ADAMS STATE COLLEGE, ALAMOSA, COLORADO 81101

The Reaction of Cobalt(III) with Sodium Salicylate in Aqueous Perchloric Acid

BY RICHARD G. SANDBERG,[1a] JAMES J. AUBORN,[1a]
EDWARD M. EYRING,*[1a] AND KAY O. WATKINS[1b]

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The instability of perchloric acid solutions of cobalt(III) complicates investigations of oxidation–reduction reactions involving $Co^{3+}(aq)$ and $CoOH^{2+}(aq)$ ions. Although many reactions have been studied,[2] in only a few of these systems has there been any spectrophotometric detection of the formation of intermediate complexes, *e.g.*, the chloride[3] and malic acid systems.[4] In order to obtain additional information on the types of reductant that readily complex cobalt(III), we chose to examine the cobalt(III)–salicylate system. In studying the reaction of cobalt(III) with sodium salicylate, we see not only the formation of a monocoordinated cobalt(III)–salicylate complex but also the formation of a dicoordinated salicylate intermediate complex. The intramolecular transfer of electrons appears to occur at a slow rate at 25°, since only after 1 hr or so do we see the formation of a pink to colorless solution due to formation of cobalt(II).

Experimental Section

Cobalt(III) solutions (0.01–0.02 *M*) were prepared by electrooxidation of stock solutions of cobalt(II) perchlorate hexahydrate (G. F. Smith Chemical Co.) in 3 *M* perchloric acid at 0° and a current density of about 20 mA cm^{-2}. The cobalt(II) and cobalt(III) solutions were standardized spectrophotometrically (ϵ_{max}(Co(III)) 35.3 at 605 nm and ϵ_{max}(Co(II)) 4.84 at 509 nm).[5]

A stock solution of sodium salicylate (0.10 *M*) (The New York Quinine and Chemical Works, Inc.) was always freshly prepared and standardized by titration with cerium(IV). When necessary, the ionic strength was adjusted with sodium perchlorate (G. F. Smith Chemical Co.). All other reagents were of analytical grade, and doubly distilled, deionized, and deoxygenated water was used throughout.

Kinetics were studied at 25° and an ionic strength of 1.5 *M* using the stopped-flow technique (Durrum-Gibson Model D-110). The reductant was present in sufficient excess to ensure pseudo-first-order conditions. The acidity was adjusted with perchloric acid (Baker and Adamson reagent).

On mixing a 10^{-4} *M* cobalt(III) solution with a 10^{-3}–10^{-2} *M* sodium salicylate solution, two distinct changes in absorbance are observed at 400 nm. The initial increase in absorbance is associated with the formation of the monosalicylate complex of cobalt(III) (absorbance ≃0.4) and the subsequent slow decrease in absorbance is attributed to the formation of a disalicylate complex (absorbance ≃0 at 400 nm).

Although the rate of formation of the dicoordinated cobalt–salicylate complex is slower than for the monocoordinated complex, the two rates overlap significantly near the end of the monocomplexation reaction. Thus a plot of our kinetic data in terms of absorbance at 400 nm *vs.* time resembles a Maxwell–Boltzmann distribution curve with the maximum occurring at ~10 sec and ~0.4 absorbance unit. The first-order rate constant for the formation of the monocoordinated cobalt–salicylate intermediate was therefore obtained from the first ~70% (mea-

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[1] (a) University of Utah. (b) Adams State College.

[2] G. Davies and B. Warnquist, *Coord. Chem. Rev.*, **5**, 349 (1970).

[3] T. J. Concocchioli, G. H. Nancollas, and N. Sutin, *Inorg. Chem.*, **5**, 1 (1966).

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sured vertically) of the rising portion of the absorbance *vs.* time curve. The first-order rate constant for dicoordinated cobalt–salicylate intermediate formation was obtained from the declining part of the absorbance *vs.* time curve after absorbance had dropped to less than 75% of peak value. Thus the reported rate constants are either for the monocoordinated intermediate or for the dicoordinated intermediate but are not for a combination of both.

Results

Equilibrium data[2,6,7] as well as the present kinetic data presented in Tables I and II are consistent with the assumption that at the acid concentrations 0.3–1.5 *M* the formation of the monocoordinated cobalt–salicylate and dicoordinated cobalt–salicylate complexes involves the reactions

TABLE I

KINETIC DATA FOR THE FORMATION OF THE MONOCOORDINATED COBALT(III)–SALICYLATE COMPLEX IN AN AQUEOUS PERCHLORATE MEDIUM AT 1.5 *M* IONIC STRENGTH, 25°, AND CONSTANT 10^{-4} *M* COBALT CONCENTRATION

$[H^+]$,[a] *M*	[HA],[b] m*M*	k_{obsd}^{I}, sec^{-1}	k_{obsd}^{II}, M^{-1} sec^{-1}	$[H^+]$,[a] *M*	[HA],[b] m*M*	k_{obsd}^{I}, sec^{-1}	k_{obsd}^{II}, M^{-1} sec^{-1}
0.33	1.00	0.089	72.9	0.80	1.00	0.077	40.6
	3.00	0.215			3.00	0.173	
	6.00	0.406			6.00	0.272	
	10.00	0.747			10.00	0.450	
0.50	1.00	0.098	61.2	1.00	1.00	0.081	32.5
	3.00	0.277			3.00	0.217	
	6.00	0.458			6.00	0.265	
	10.00	0.667			10.00	0.397	
0.60	1.00	0.079	47.5	1.30	1.00	0.071	30.6
	3.00	0.203			3.00	0.143	
	6.00	0.327			6.00	0.236	
	10.00	0.516			10.00	0.348	

[a] Hydrogen ion concentration determined volumetrically.
[b] Initial total concentration of sodium salicylate.

TABLE II

KINETIC DATA FOR THE FORMATION OF THE DICOORDINATED COBALT(III)–SALICYLATE COMPLEX IN AN AQUEOUS PERCHLORATE MEDIUM AT 1.5 *M* IONIC STRENGTH, AND CONSTANT 10^{-4} *M* COBALT CONCENTRATION

$[H^+]$,[a] *M*	[HA],[b] m*M*	k_{obsd}^{III}, sec^{-1}	k_{obsd}^{IV}, M^{-1} sec^{-1}	$[H^+]$,[a] *M*	[HA],[b] m*M*	k_{obsd}^{III}, sec^{-1}	k_{obsd}^{IV}, M^{-1} sec^{-1}
0.33	1.00	0.0109	11.6	0.60	6.00	0.0426	7.22
	3.00	0.0314			10.00	0.0840	
	6.00	0.0645					
	10.00	0.1150		1.00	3.00	0.0214	6.86
					6.00	0.037	
0.50	3.00	0.0208	9.75		10.00	0.069	
	6.00	0.0698					
	10.00	0.1080		1.3	1.00	0.0118	6.06
	15.00	0.141			3.00	0.0232	
					6.00	0.0377	
0.60	1.00	0.0149	7.22		10.00	0.067	
	3.00	0.0355					

[a] Hydrogen ion concentration determined volumetrically.
[b] Initial total concentration of sodium salicylate.

$$Co^{3+} + H_2O \overset{K_h}{\rightleftharpoons} CoOH^{2+} + H^+$$

$$Co^{3+} + HA \xrightarrow{k_1} CoHA^{3+}$$

$$CoOH^{2+} + HA \xrightarrow{k_2} CoOHHA^{2+}$$

$$CoHA^{3+} + H_2O \overset{K_3}{\rightleftharpoons} CoOHHA^{2+} + H^+$$

$$CoHA^{3+} + HA \xrightarrow{k_4} Co(HA)_2^{3+}$$

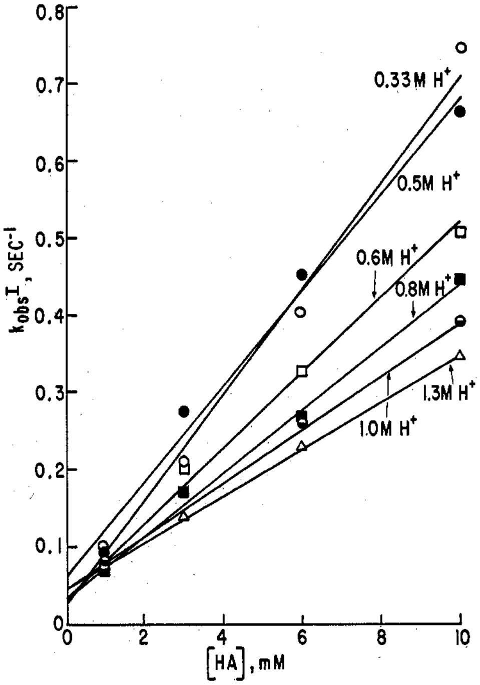

Figure 1.—Plot of the first-order observed specific rate of monocoordinated intermediate complex formation *vs.* total salicylate molarity for several hydrogen ion concentrations (in water at 25° and 1.5 *M* ionic strength adjusted with $NaClO_4$). The experimental points are for the following H^+ molarities: ○, 0.33 *M*; ●, 0.5 *M*; □, 0.6 *M*; ■, 0.8 *M*; ◒, 1.0 *M*; △, 1.3 *M*.

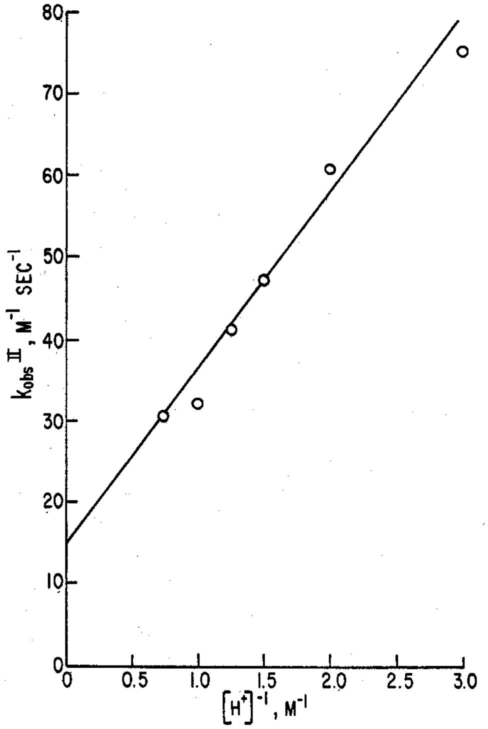

Figure 2.—Plot of the second-order observed specific rate of monocoordinated intermediate complex formation *vs.* reciprocal hydrogen ion molarity (at same conditions as in Figure 1).

$$CoOHHA^{2+} + HA \xrightarrow{k_5} CoOH(HA)_2^{2+}$$

From the plots of k_{obsd}^{I} *vs.* [HA] (Figure 1) and k_{obsd}^{III} *vs.* [HA] (Figure 2) it is seen that the intercepts are small and nearly acid independent, thus k_{-1}, k_{-2}, k_{-4}, and k_{-5} may be neglected. The rate expression for the

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rate of formation of the monocoordinated cobalt–salicylate CoHA is given by

$$\frac{\mathrm{d(mono\ complexes)}}{\mathrm{d}t} = k_1[\mathrm{Co}^{3+}][\mathrm{HA}] + k_2[\mathrm{CoOH}^{2+}][\mathrm{HA}]$$

Assuming that there is a fast equilibrium between $[\mathrm{Co}^{3+}]$ and $[\mathrm{CoOH}^{2+}]$ with a hydrolysis constant K_h[2,6,7] the rate expression becomes

$$\frac{\mathrm{d(mono\ complexes)}}{\mathrm{d}t} = k_1[\mathrm{Co}^{3+}][\mathrm{HA}] + \frac{k_2K_h}{[\mathrm{H}^+]}[\mathrm{Co}^{3+}][\mathrm{HA}]$$

The first-order rate may be expressed as

$$\mathrm{rate} = k_{\mathrm{obsd}}{}^{\mathrm{I}}[\mathrm{Co}^{3+}]_{\mathrm{tot}}$$

Assuming that $[\mathrm{CoOH}^{2+}]$ is small compared with $[\mathrm{Co}^{3+}]$, then $[\mathrm{Co}^{3+}]_{\mathrm{tot}} = [\mathrm{Co}^{3+}]$. The first-order rate is therefore

$$\mathrm{rate} = k_{\mathrm{obsd}}{}^{\mathrm{I}}[\mathrm{Co}^{3+}]$$

$$k_{\mathrm{obsd}}{}^{\mathrm{I}} = \left\{k_1 + \frac{k_2K_h}{[\mathrm{H}^+]}\right\}[\mathrm{HA}]$$

$$k_{\mathrm{obsd}}{}^{\mathrm{II}} = k_1 + \frac{k_2K_h}{[\mathrm{H}^+]}$$

In Figure 1, $k_{\mathrm{obsd}}{}^{\mathrm{I}}$ is plotted *vs.* sodium salicylate concentrations and values for second-order $k_{\mathrm{obsd}}{}^{\mathrm{II}}$ are obtained from the slopes. In Figure 2, $k_{\mathrm{obsd}}{}^{\mathrm{II}}$ is plotted *vs.* $[\mathrm{H}^+]^{-1}$ and k_1 is obtained from the intercept and k_2K_h from the slope of the line. Since K_h comes from spectral data[2] for high-spin hydroxo and fluoro complexes and is not well known, the rate constant k_2 should be quoted as k_2K_h. We thus find $k_1 = 14.1\ M^{-1}\ \mathrm{sec}^{-1}$ and $k_2K_h = 20.2\ \mathrm{sec}^{-1}$.

The rate expression for the rate of formation of the dicoordinated cobalt(III)–salicylate intermediate ($[\mathrm{Co(HA)}_2]$) is equal to the rate of disappearance of the monocoordinated cobalt–salicylate intermediate

$$\frac{-\mathrm{d(mono\ complexes)}}{\mathrm{d}t} = k_4[\mathrm{CoHA}^{3+}][\mathrm{HA}] + k_5[\mathrm{CoOH(HA)}^{2+}][\mathrm{HA}] = k_4[\mathrm{CoHA}^{3+}][\mathrm{HA}] + \frac{k_5K_3}{[\mathrm{H}^+]}[\mathrm{CoHA}^{3+}][\mathrm{HA}]$$

The first-order rate may be expressed as

$$\mathrm{rate} = k_{\mathrm{obsd}}{}^{\mathrm{III}}[\mathrm{CoHA}^{3+}]_{\mathrm{tot}}$$

Assuming that $[\mathrm{CoOH(HA)}^{2+}]$ is small compared with CoHA^{3+}, then $[\mathrm{CoHA}^{3+}]_{\mathrm{tot}} = [\mathrm{CoHA}^{3+}]$. The first-order rate is, therefore

$$\mathrm{rate} = k_{\mathrm{obsd}}{}^{\mathrm{III}}[\mathrm{CoHA}^{3+}]$$

and

$$k_{\mathrm{obsd}}{}^{\mathrm{III}} = \left\{k_4 + \frac{k_5K_3}{[\mathrm{H}^+]}\right\}[\mathrm{HA}]$$

with

$$k_{\mathrm{obsd}}{}^{\mathrm{IV}} = k_4 + \frac{k_5K_3}{[\mathrm{H}^+]}$$

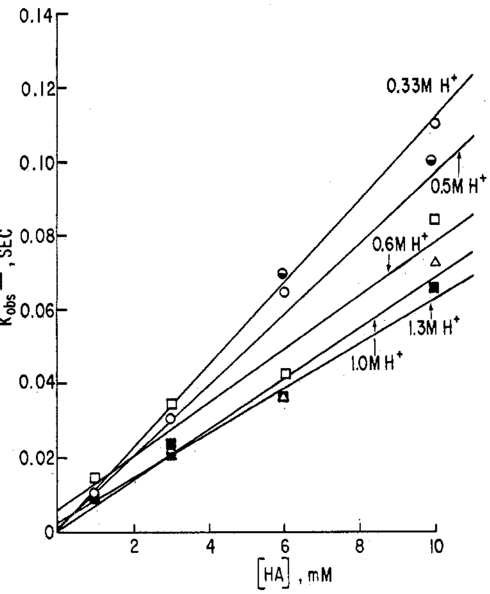

Figure 3.—Plot of the first-order observed specific rate of dicoordinated intermediate complex formation *vs.* total salicylate molarity for several hydrogen ion concentrations (at same conditions as in Figure 1). The experimental points denote the following hydrogen ion molarities: ○, 0.33 *M;* ◒, 0.5 *M;* □, 0.6 *M;* △, 1.0 *M;* ■, 1.3 *M*.

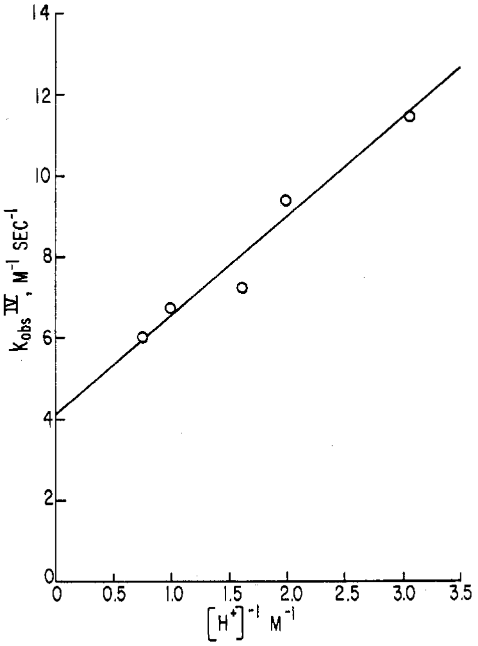

Figure 4.—Plot of the second-order observed specific rate of dicoordinated intermediate complex formation *vs.* reciprocal hydrogen ion molarity (at same conditions as in Figure 1).

In Figure 3, $k_{\mathrm{obsd}}{}^{\mathrm{III}}$ is plotted *vs.* sodium salicylate concentrations and values for second-order $k_{\mathrm{obsd}}{}^{\mathrm{IV}}$ are obtained from the slope. In Figure 4, $k_{\mathrm{obsd}}{}^{\mathrm{IV}}$ is plotted *vs.* $[\mathrm{H}^+]^{-1}$ and k_4 is obtained from the intercept and k_5K_3 is obtained from the slope of the line. Since the equilibrium constant K_3 is uncertain, k_5 cannot be expressed. Our results show $k_4 = 4.1\ M^{-1}\ \mathrm{sec}^{-1}$ and $K_3k_5 = 2.6\ \mathrm{sec}^{-1}$.

Discussion

Ligand field effects are useful in describing the d electrons of a metal that are involved in electron transfer and in ligand bonding.[8] The gain of an electron by a metal ion is much easier when it is in the high-spin state than when it is in the low-spin state because electron transfer can then occur without change of electron spin state, *i.e.*, without change of multiplicity and also without extensive reorganization of the metal–ligand bonds.[9]

The lowest empty orbitals (t_{2g}) of the high-spin form of a metal have lobes between the ligands which are more accessible to overlap with π or p orbitals of a reducing agent than are the only empty orbitals (e_g) of the low-spin form, which have lobes directed along the metal–ligand bond direction. The result of the overlap of a filled ligand π orbital with a half-filled low-energy t_{2g} orbital is the transfer of an electron from ligand to metal without change of multiplicity.

The effects of π bonding *via* the filled t_{2g} orbitals of a metal need to be considered.[10] These effects will vary depending on the energy of the ligand π orbitals relative to the energy of the metal t_{2g} orbitals and upon whether the ligand π orbitals are filled or empty. Consider the case where there are empty ligand π orbitals of higher energy than the filled metal t_{2g} orbitals. The net result of the π interaction is to stabilize the metal t_{2g} orbitals, which have acquired some ligand orbital character in the process. In effect, the π interaction causes the *Dq* value for the complex to increase, thus making the complex more stable.

Water is a particularly important ligand in that although the Co^{3+}(aq) ion is spin paired, it requires very little excitation energy to achieve the high-spin state.[11] This energy may be further decreased if the ion is slightly hydrolyzed and one water molecule is replaced by OH^-, which has a smaller ligand field. Cobalt(III), when in the low-spin state, exchanges its ligands slowly.[12] The rapid exchange of water[13] and of organic hydroxy compounds with cobalt(III) ions requires their excitation to the high-spin state. This ligand-exchange step might conceivably determine the rate of an oxidation.

The cobalt(III)–salicylate system may be considered as a strong-field or low-spin state. This would make it more difficult for electron transfer from ligand to metal, since the lowest t_{2g} orbitals are filled. One of the t_{2g} electrons would have to be excited to the e_g orbitals in order for the cobalt(III) t_{2g} orbitals to be able to accommodate an electron donated from a ligand π orbital, but if the two oxygens of the salicylate ligand have empty π orbitals that can overlap with the filled t_{2g} orbitals of cobalt(III), then the t_{2g} orbitals (which obtain some ligand orbital character in the process) are stabilized. In effect, the π interaction causes the *Dq* value for the complex to increase, thus making the complex more stable.

We observe spectrophotometrically the formation of intermediate complexes, which are relatively stable, and then after 1 hr or so, the appearance of the pink to colorless solution at 25°, which is due to the formation of cobalt(II). After the appearance of the pink to colorless solution, a sample was run on the Cary 14 spectrophotometer to see if we could observe the oxidized salicylate. We observed a large peak at 260 nm, which is possibly attributable to the formation of the oxidized form of salicylic acid. This oxidized species may be *cis,cis*-muconic acid, which has an absorbance maximum at 260 nm.

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Contribution from the Department of Chemistry,
The Ohio State University, Columbus, Ohio 43210

Fast Kinetics of Formation of Ternary Copper(II)–Ethylenediamine–Histamine Complexes

By V. S. Sharma and D. L. Leussing*[1,2]

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Compared to the abundant literature which is available concerning the rates of formation of binary complexes of labile metal ions, relatively little is yet known about the rates of formation of ternary complexes with these metal ions. Ternary, or mixed-ligand, complexes have particular interest because these often occur as precursor and successor complexes in metal ion mediated reactions between two ligands.

To date several categories of reactions have been uncovered for the formation of mixed-ligand complexes of Cu(II): (I) solvent substitution reactions,[3–6] $(L)Cu(H_2O)_2{}^{2+} + L' \rightleftarrows (L)Cu(L') + 2H_2O$, $k_f \sim 10^8\text{–}10^9\ M^{-1}\ \text{sec}^{-1}$; (II) solvent substitution reactions with release of a proton to solvent,[6] $(L)Cu(H_2O)_2{}^{2+} + HL' \rightleftarrows (L)Cu(L') + 2H_2O + H^+$, $k_f \sim 10^4\ M^{-1}\ \text{sec}^{-1}$; and (III) ligand substitution reactions accompanied by transfer of a proton from entering to leaving ligand,[5] $(L)Cu(L) + HL' \rightleftarrows (L)Cu(L') + HL$, $k_f \sim 10^3\text{–}10^7\ M^{-1}\ \text{sec}^{-1}$. Another category (IV), direct replacement of one ligand by another, is important at high pH ($\sim$10) in the presence of excess ligand and has been observed in nmr exchange studies of binary complexes,[7] $(L)Cu(L) + L^* \rightleftarrows (L)Cu(L^*) + L$, $k_f \sim 10^4 - 10^6\ M^{-1}\ \text{sec}^{-1}$, for bidendate ligands.

Earlier we have reported[5] on the rates of formation of $Cu^{II}(hm)(ser)^+$ and $Cu^{II}(en)(ser)^+$ (hm = histamine, ser = serinate, and en = ethylenediamine), and in this paper we describe the kinetics of formation of Cu^{II}(en)-

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[2] Support of this research by the National Science Foundation is gratefully acknowledged.

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