interpretable polarograms. This work is being continued.

Nitrogen-fixation experiments were attempted by using Cp_2ZrCl_2, $Cp_2Zr(OC_3H_7)Cl$, and $Cp_2Zr(OC_3H_7)_2$. The results (% NH_3) of the nitrogen-fixation experiments for these three compounds are shown as follows: Cp_2ZrCl_2, 2.7, 4.1; $Cp_2Zr(OC_3H_7)Cl$, 1.3; $Cp_2Zr(OC_3H_7)_2$, 0.0.

The yields of ammonia produced are disappointingly small, and any conclusions must be drawn with considerable uncertainty. However, it does appear that the nitrogen-fixing ability of the series decreases as the chloride ligands are replaced by isopropoxide groups. One can only speculate about the effect being related to the ease of the two-electron reduction of Zr(IV)–Zr(II). The speculated "ease-of-reduction" of the series $Cp_2ZrCl_2 > Cp_2Zr(OR)Cl > Cp_2Zr(OR)_2$ may be a result of the relative electron density about the zirconium. As the chlorides are replaced by the more basic alkoxide groups, the electron density about the zirconium should increase and may have the effect of raising the energy of the lowest lying d orbital slightly. Such an effect would make reduction more difficult and would be consistent with the trend seen in the relative nitrogen-fixing abilities of the compounds.

Acknowledgment.—The authors thank the National Institutes of Health for fellowship aid (to D. R. G.) and the National Science Foundation for support under Grants GP-7088X and 17422X.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Mixed-Valence Complexes of Iron(III) with Iron(II) and Mixed-Metal Complexes of Iron(III) with Tin(II) in Aqueous Citrate Media

BY B. BINDER*

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From spectrophotometric absorption data two mixed-valence complexes $Fe^{II}Fe^{III}L^+$ (L^{4-} = citrate ion) and $Fe^{II}Fe^{III}H_2L_2^-$ have been identified in aqueous citrate media. In similar media a mixed-metal complex $Sn^{II}Fe^{III}H_2L_3^{5-}$ has also been found. The formation constant of the last complex has been calculated.

Introduction

As pointed out by Robin and Day,[1] inorganic compounds made up of ions of the same element in two different formal oxidation states constitute an interesting class of substances whose study has been largely neglected. Mixed-valence systems of this kind are of interest because their properties are seldom the sum of the properties of the two metal ions taken separately. One of the most obvious manifestations of this feature is the enhanced optical absorption that usually results when a mixed-valence species is formed. Davidson and coworkers[2] have termed the enhanced absorption "interaction absorption" and have studied the phenomenon in concentrated HCl solutions containing Fe(III) and Fe(II),[3] Sb(V) and Sb(III),[2] and Cu(II) and Cu(I),[3] as well as Sn(IV) and Sn(II).[1] With the copper system[3] they were able to demonstrate that the absorbing species had the empirical formula Cu_2Cl_3; the structure of this compound was postulated to involve a single chloride bridge between the two copper ions. The enhanced absorption apparently results from resonance of a valence electron between the two metal centers.

From a quantitative study of Fe(II)–Fe(III) systems we have found that a number of ligands can bring about interaction absorption at considerably lower concentrations than in the case of chloride ion where 6–12 *M* HCl was required. Among the effective ligands were oxalate, malonate, lactate, glycolate, tartrate, citrate, formate, and glycine. Under similar experimental conditions, Fe(II) and Fe(III) concentrations of 0.03 *M* and ligand concentration of 0.3 *M*, no enhanced absorption was found with acetate, propionate, monochloroacetate, succinate, γ-hydroxybutyrate, and ethylene glycol.

We have also observed what appears to be a similar kind of absorption enhancement when the Fe(II) is replaced by the better electron donor Sn(II) with malonate, tartrate, oxalate, and citrate as ligands. In these media reduction of Fe(III) is slow and the solutions are considerably more intense in color than in the presence of Fe(II).

In this paper we present the results of a quantitative spectrophotometric study of the iron(III)–iron(II)–citrate and the iron(III)–tin(II)–citrate systems. In the former system we were able to identify two mixed-valence complexes which were responsible for the observed interaction absorption; formation constants could not, however, be determined. In the latter case, a single mixed-metal complex predominates; its stability is great enough to permit assessment of its formation constant.

Experimental Section

Reagents and Solutions.—Stock solutions of Fe(II) and Fe(III) were prepared from their perchlorates (G. Frederick Smith Chemical Co.) and were standardized periodically with a standard permanganate solution by the Zimmermann–Reinhardt

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[1] M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, **10**, 247 (1967), and references therein.

[2] J. E. Whitney and N. Davidson, *J. Amer. Chem. Soc.*, **71**, 3809 (1949).

[3] H. M. McConnell and N. Davidson, *ibid.*, **72**, 3168, 5557 (1950).

method. Citric acid and sodium citrate solutions were prepared from weighed quantities of the reagent grade chemicals. A stock sodium perchlorate solution, for adjusting ionic strength, was prepared by neutralization of $HClO_4$ solution with NaOH. Crystalline $SnCl_2 \cdot 2H_2O$ served as a source of Sn(II) ions. It was found experimentally that Sn(II) and Fe(III) citrate complexes are sufficiently stable to be unaffected by the chloride ion introduced in this way.

In order to avoid air oxidation of Fe(II) and Sn(II), all solutions were purged with a stream of nitrogen. A nitrogen blanket was also maintained during transfer and measurement operations.

Measurements.—Most of the spectrophotometric measurements were made with a Beckman Model DU spectrophotometer. When complete spectra were required, a Bausch and Lomb double-beam recording instrument was employed. Both calibrated 1- and 10-cm silica cells were used.

The measurement of pH was carried out with a Beckman Model G pH meter equipped with a glass–calomel electrode pair. The pH meter was standardized with 0.05 *M* solutions of potassium acid phthalate (pH 4.01) and potassium tetraoxalate (pH 1.68). Then the pH scale of the instrument was calibrated *vs.* the analytical hydrogen ion concentration of a series of dilute perchloric acid solutions at the ionic strength of subsequent experiments.

All experiments were carried out at room temperature (25 ± 1°) in an air-conditioned laboratory.

The Iron(III)–Tin(II)–Citrate System

When Sn(II) is added to a citrate solution of Fe(III), a pronounced color change from yellowish green to deep red is immediately observed. Figure 1 shows the corresponding spectral changes where it is seen that there is a decrease in the weak Fe(III) absorption peak at 650 nm but a marked increase in absorption of radiation of shorter wavelengths. Unfortunately the position of the ultraviolet absorption maximum could not be located because it occurs below 300 nm, a region in which the components of the reaction mixture absorb strongly. Thus it was not possible to determine whether the observed spectral changes result from a wavelength shift in the Fe(III) peak alone or from a marked increase in the molar absorbance at other wavelengths as well.

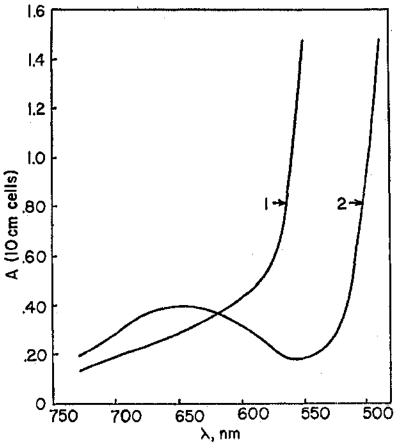

Figure 1.—The effect of added Sn(II) on the spectrum of iron(III) citrate solution, where $[\text{citrate}]_T = 0.309$ *M*, $[Fe^{III}]_T = 0.0285$ *M*, $[Sn^{II}]_T = 0.0274$ *M*, and pH is 3.4: 1, Fe(III) + Sn(II) + citrate; 2, Fe(III) + citrate. Tin(II) citrate and citric acid solutions do not absorb appreciably.

Spectral studies of citrate solutions containing Sn(II), Sn(IV)–Fe(II), Sn(IV)–Fe(III), Sn(II)–Fe(II), Sn(II)–Sn(IV), and Fe(II)–Fe(III) revealed that none of these combinations of ions was responsible for the spectral change just described. Thus the enhanced absorption was logically attributed to a tin(II)–iron(III)–citrate complex. In view of the marked difference in the standard electrode potentials for the two metal ions, the complex shows striking kinetic stability toward decomposition by oxidation–reduction. For example, the absorbances of the solutions were found to decrease only 1% or less in several hours. Furthermore, solutions kept in stoppered bottles become visibly decolorized only after a period of 1 month or more.

A complex of Sn(II), Fe(III), and citrate ion has previously been proposed by Smith[4] in order to explain the inhibiting effect of Fe(III) on the hydrolytic precipitation of Sn(II) from citrate media. From pH titration data, Smith concluded that the ratio of the three components in the complex should be 1:1:1.

The absorbance of our solutions containing the mixed-metal chromophore was found to vary in a complex way when the concentrations of Fe(III), Sn(II), citrate, and hydrogen ion were varied. When the Sn(II) and citrate concentrations were large with respect to the total Fe(III), however, the absorbance becomes essentially independent of the latter three variables. Figure 2 demonstrates the effect of variation in the Sn(II) concentration. Figure 3 shows that under similar conditions the absorbance is directly proportional to the Fe(III) concentration with the straight line intercepting the origin. These observations suggest that essentially all of the Fe(III) in solution is bound (Figure 2) and that a single mole of Fe(III) is contained in each mole of complex (Figure 3). Unfortunately analogous experiments in which concentrations of Fe(III) ≫ Sn(II) were inconclusive because of the relatively high absorbance of iron(III) citrate complexes.

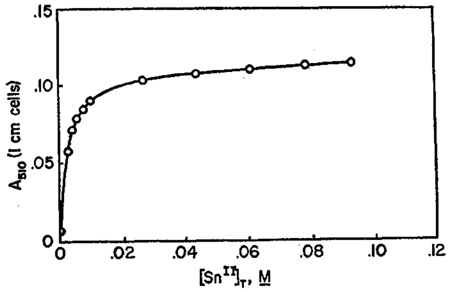

Figure 2.—The effect of Sn(II) additions on interaction absorption (510 nm), where $[Fe^{III}]_T = 2.59 \times 10^{-3}$ *M*, $[\text{citrate}]_T = 0.50$ *M*, and pH is 3.56.

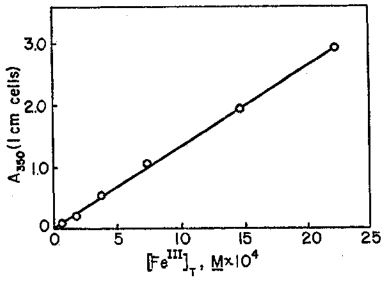

Figure 3.—The effect of Fe(III) additions on interaction absorption (350 nm), where $[Sn^{II}]_T = 0.070$ *M*, $[\text{citrate}]_T = 0.50$ *M*, and pH is 3.67.

In order to characterize further the mixed-metal com-

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[4] T. D. Smith, *J. Chem. Soc.*, 2145 (1965).

plex, the absorbance of a series of solutions was studied in which pH, Fe(III), and Sn(II) were varied. The results are shown in Table I. In treating these data, the raw absorbances were first corrected for the contribution of the Fe(III) not found in the mixed-metal complex in the following way. The concentration, *C*, of the Fe(III)-Sn(II) complex was approximated by employing the molar absorbance coefficient at 510 nm, estimated from experimental data like those shown in Figure 2 (ϵ 51), and assuming that the absorption due to other Fe(III) species was negligible. An approximate value for the interaction absorption, A_I, of the Fe(III)-Sn(II) complex was then obtained from the relationship

TABLE I
INTERACTION ABSORPTION (AT 25°) AS A FUNCTION OF $[H^+]$, $[Fe^{III}]_T$, AND $[Sn^{II}]_T$ AT $[CITRATE]_T = 0.154\ M$

$[Fe^{III}]_T$, *M*	$[Sn^{II}]_T$, *M*	$10^4[H^+]$, *M*	A_{510}(obsd) (1-cm cells)	A_I(estd at 510 nm)
0.0285	0.0274	4.47	0.706	0.682
0.0285	0.0274	2.46	0.735	0.732
0.0285	0.0274	2.09	0.784	0.762
0.0285	0.0274	1.51	0.796	0.774
0.0285	0.0274	1.35	0.823	0.802
0.0285	0.0274	1.20	0.841	0.821
0.0285	0.0274	1.05	0.881	0.862
0.0285	0.0274	0.853	0.884	0.865
0.0285	0.0274	0.725	0.878	0.858
0.0228	0.0274	1.05	0.753	0.739
0.00800	0.0274	1.32	0.314	0.311
0.00456	0.0274	1.32	0.190	0.188
0.00342	0.0274	1.35	0.150	0.149
0.0285	0.0205	2.63	0.594	0.566
0.0285	0.0137	1.70	0.441	0.408

$$A_I = A_{obsd} - ([Fe]_T - C)\epsilon_{Fe} \qquad (1)$$

where $[Fe]_T$ is the total Fe(III) concentration and ϵ_{Fe} is the average molar absorbance coefficient of the iron(III) citrate complexes. The latter coefficient was determined from a blank which had a known Fe(III) concentration with citrate and hydrogen ion concentrations identical with those of the solution under study. As will be seen from columns 4 and 5 of Table I, the corrections were small at the wavelength used; as a consequence a second approximation to improve the correction factor was unnecessary.

Equilibrium quotients for the more important equilibria involving Fe(III), Sn(II), and citrate not bound in mixed complexes are listed in Table II. These quotients were employed to calculate approximate concentrations for the various species in the solutions being studied. Unfortunately, literature data could not be found at a single ionic strength and it was necessary to assume that the quotients listed would apply at the ionic strength chosen for our measurements (0.3 *M*). This assumption undoubtedly introduces some uncertainty in the value obtained for the formation constant of the Fe(III)-Sn(II) complex. However, it was found that the absorbances neither of the mixed-metal solutions nor of the individual tin(II) and iron(III) citrate solutions were significantly affected by variations in ionic strengths between 0.1 and 1.0 *M*. This fact plus the consistency of the calculated formation constants leads us to believe that the final results are accurate to at least an order of magnitude and that our conclusions relative to the composition of the Sn(II)-Fe(III) complex are valid.

TABLE II
EQUILIBRIUM QUOTIENTS FOR CITRATE SYSTEMS AT 25°

Equilibrium quotient[a]	Lit. value	Ionic strength, *M*	Ref
$K_{a1} = \frac{[H^+][H_3L^-]}{[H_4L]}$	8.45×10^{-4}	0.3	*b*
$K_{a2} = \frac{[H^+][H_2L^{2-}]}{[H_3L^-]}$	1.74×10^{-5}	0.3	*b*
$K_{a3} = \frac{[H^+][HL^{3-}]}{[H_2L^{2-}]}$	4.10×10^{-7}	0.3	*b*
$K_1 = \frac{[FeH_2L^+]}{[Fe^{3+}][H_2L^{2-}]}$	2.0×10^{6}	1.0	*c*
$K_2 = \frac{[FeHL]}{[Fe^{3+}][HL^{3-}]}$	7.1×10^{11}	1.0	*c*
$K_3 = \frac{[FeL^-][H^+]}{[Fe^{3+}][HL^{3-}]}$	2.9×10^{9}	0.1	*d*
$K_D = \frac{[Fe_2L_2^-][H^+]^2}{[Fe^{3+}]^2[HL^{3-}]^2}$	1.5×10^{21}	0.1	*e*
$K_4 = \frac{[SnHL^-]}{[Sn^{2+}][HL^{3-}]}$	2.35×10^{7}	0.1	*f*
$K_5 = \frac{[Sn(HL)_2^{4-}]}{[SnHL^-][HL^{3-}]}$	2.69×10^{5}	0.1	*f*
$K_6 = \frac{[FeH_2L]}{[Fe^{2+}][H_2L^{2-}]}$	1.32×10^{2}	1.0	*c*
$K_7 = \frac{[FeHL^-]}{[Fe^{2+}][HL^{3-}]}$	1.20×10^{3}	1.0	*c*

[a] L^{4-} = citrate ion. [b] R. G. Bates and G. D. Pinching, *J. Amer. Chem. Soc.*, **71**, 1274 (1949). [c] R. E. Hamm, S. M. Shull, Jr., and D. M. Grant, *ibid.*, **76**, 2111 (1954). [d] R. C. Warner and I. Weber, *ibid.*, **75**, 5086 (1953). [e] C. F. Timberlake, *J. Chem. Soc.*, 5078 (1964). [f] Reference 4.

The Iron(III)-Iron(II)-Citrate System

Evidence of Fe(III)-Fe(II) mixed-valence complexes in citrate media is observed when Fe(II) is added to iron(III) citrate solution: the greenish yellow color is visibly intensified. Spectral changes, which are less dramatic than in the case of the Fe(III)-Sn(II) system, are shown in Figure 4. Absorption enhancement in the visible region of the spectrum is evident. Spectral enhancements of this kind are not unusual. They have been observed by us also when such ligands as oxalate, malonate, lactate, glycolate, and tartrate were used in place of citrate. Furthermore, similar enhancements have been reported in a number of other mixed-valence systems by several investigators.[1]

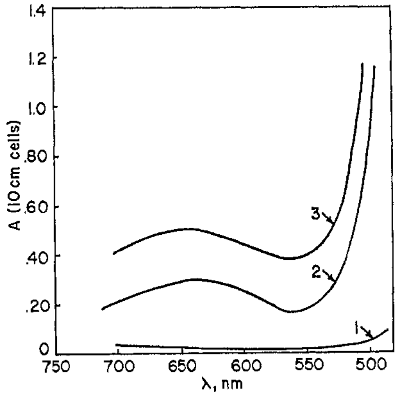

Figure 4.—The effect of added Fe(II) on the spectrum of iron(III) citrate solution: 1, $[citrate]_T = 0.154\ M$, $[Fe^{III}]_T = 0$, $[Fe^{II}]_T = 0.0249M$; 2, $[citrate]_T = 0.154\ M$, $[Fe^{III}]_T = 0.0285M$, $[Fe^{II}]_T = 0$; 3, $[citrate]_T = 0.154\ M$, $[Fe^{III}]_T = 0.0285M$, $[Fe^{II}]_T = 0.0249M$. pH is 4.6, and absorbance of citric acid is negligible.

Mixed-valence Fe(III)–Fe(II) chromophores found in chloride media have been proposed previously[3] in order to explain this type of absorption enhancement. However, when the chloride ligand is replaced by perchlorate, there is no mixed-valence absorption. This effect suggests that the ligand plays a major role in mixed-valence chromophores. All of the ligands we investigated lead to the same conclusion.

In order to determine the composition of the mixed-valence Fe(III)–Fe(II) complexes causing the observed spectral changes, the absorbance of a series of solutions was studied over a wide hydrogen ion concentration range while the total concentrations of Fe(III), Fe(II), and citrate were held constant. However, the extent of complexing of Fe(III) and Fe(II) by citrate depends on pH. Consequently, free ferric ion, ferrous ion, and the various anionic citrate concentrations vary whenever changes in hydrogen ion concentration occur. Experimental results obtained from these solutions are summarized in Table III. Comparison of columns 2 and 3 shows that at the wavelength chosen (510 nm) the interaction absorption, A_I, of the mixed-valence complexes is a significant part of the total absorbance observed. Estimates of interaction absorption were obtained by subtracting from the observed absorbance iron(III) citrate and iron(II) citrate blanks under the assumption that the concentration of mixed-valence chromophores present in these solutions is relatively small. Such an assumption appears to be in agreement with Hush's interpretation[5] of this type of mixed-valence absorption, provided enhanced single ion absorption enhancement is negligible. Furthermore, the consistency of our results and rough estimates of the stability of the chromophores make this assumption appear valid.

TABLE III

INTERACTION ABSORPTION (AT 25°) AS A FUNCTION OF pH[a]

$10^4[H^+]$, M	A_{510}(obsd) (10-cm cells)	A_I(at 510 nm) (10-cm cells)	Based on equilibrium calculations: $10^3[H_2L^{2-}]$, M	$10^3[FeL^-]$, M	$10^3[Fe^{2+}]$, M
66.1	0.848	0.134	0.0374	5.93	24.8
41.7	0.778	0.171	0.0880	6.52	24.6
26.9	0.764	0.212	0.193	6.90	24.3
18.2	0.755	0.233	0.384	7.13	23.7
12.9	0.751	0.247	0.655	7.28	22.9
5.50	0.749	0.256	2.25	7.49	19.2
2.75	0.726	0.234	5.25	7.57	14.6
1.32	0.745	0.232	11.3	7.61	9.83
1.02	0.745	0.221	14.3	7.62	8.40
0.677	0.788	0.245	20.5	7.63	6.45
0.617	0.781	0.235	22.2	7.63	6.07
0.501	0.790	0.232	26.1	7.63	5.30
0.447	0.799	0.234	28.4	7.63	4.92
0.372	0.818	0.245	32.4	7.64	4.37

[a] $[Fe^{III}]_T = 0.0285\ M$, $[Fe^{II}]_T = 0.0249\ M$, $[\text{citrate}]_T = 0.154\ M$, and $[Fe^{3+}] < 10^{-6}\ M$; thus $[FeOH^{2+}]$ and $[Fe(OH)_2^+]$ are negligible.

Approximate concentrations for the various species in the solutions studied were calculated employing equilibrium quotients listed in Table II. As was the case in the iron(III)–tin(II)–citrate system, deviations in ionic strength were assumed to affect these quotients to a negligible extent. Experimentally it was found that varying ionic strength between 0.2 and 0.6 M did not alter the absorbance of the solutions.

Discussion

Data Treatment.—In an effort to determine the composition of the mixed chromophores responsible for the observed interaction absorption, approximate equilibrium concentrations of all species were calculated. First, the total reagent concentration in each solution was expressed as the sum of the equilibrium concentrations of all species present. Expressions of this type, together with the equilibrium quotients shown in Table II, result in a set of nonlinear equations. To solve each set of equations the Newton–Rapheson[6] method of successive approximations was incorporated into a FORTRAN program. Representative computer answers are shown in Table III, columns 4, 5, and 6.

To interpret the spectrophotometric data, plots of interaction absorption *vs.* the equilibrium concentrations of the various species were constructed. Satisfactory linear plots, shown in Figures 5 and 6, were found only when mixed-metal or mixed-valence complexes were postulated.

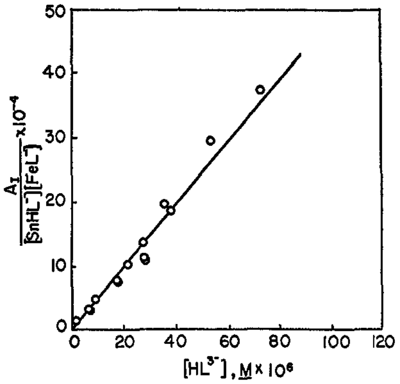

Figure 5.—Determination of mixed-metal complex formation constant; slope = kK_5.

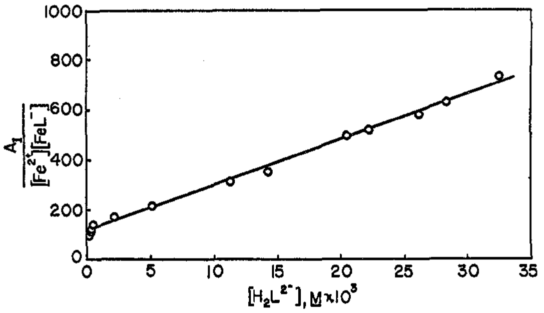

Figure 6.—Determination of composition of mixed-valence complexes; intercept = k_1; slope = k_2K_6.

Mixed-Metal Iron(III)–Tin(II)–Citrate Complex.—The dependence of the observed interaction absorption on the changing concentration of a mixed-metal complex has been plotted in Figure 5. The equation describing this line is

$$\frac{A_I}{[SnHL^-][FeL^-]} = kK_5[HL^{3-}]$$

where k is the product of molar absorbance coefficient and formation constant for the mixed complex. Since the plotted line intercepts the origin, only one absorbing

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[5] N. S. Hush, *Progr. Inorg. Chem.*, **8**, 391 (1967).

[6] K. J. Nielson, "Methods of Numerical Analysis," Macmillan, New York, N. Y., 1956, p 200.

citrate complex containing both Fe(III) and Sn(II) should be present in significant amounts. Dividing k by the estimated molar absorbance coefficient (ϵ 51; see Figure 2), the formation constant may be calculated for the mixed-metal complex. When the formation equilibrium is written in terms of uncomplexed metal ions

$$Sn^{2+} + Fe^{3+} + 3HL^{3-} = FeSnH_2L_3^{5-} + H^+$$

the formation constant equals 6.6×10^{24}.

In view of this relatively large equilibrium quotient,[7] it was confirmed experimentally that under conditions where the concentrations of citrate and Sn(II) far exceed the Fe(III) concentration, virtually all the iron was found in the mixed-metal complex. Under such conditions Beer's law, as shown in Figure 3, is obeyed when small increments of Fe(III) are added. Absorbance spectra recorded for these solutions indicate that a large absorption maximum is located at a wavelength shorter than 300 nm.

Mixed-Valence Iron(III)–Iron(II)–Citrate Complexes.—A linear relationship between interaction absorption and the concentration of mixed-valence complexes is shown in Figure 6. In this case the equation describing the line is

$$\frac{A_{\mathrm{I}}}{[Fe^{2+}][FeL^-]} = k_1 + k_2K_6[H_2L^{2-}]$$

where intercept k_1 is the product of the molar absorbance coefficient and formation constant for one mixed-valence complex while slope k_2K_6 contains an analogous product for the other complex. As may be seen, at very low H_2L^{2-} concentration the line curves toward the point of origin. Although experimental error in this region is greatest, there is a possibility that at low pH additional mixed-valence complexes may be found. Unfortunately, the molar absorbance coefficient for neither of the two mixed-valence complexes was available; consequently formation constants could not be calculated.

In terms of the uncomplexed metal ions the formation equilibria for the two mixed-valence complexes in the solutions studied are

$$Fe^{2+} + Fe^{3+} + HL^{3-} = Fe^{II}Fe^{III}L^+ + H^+$$
$$Fe^{2+} + Fe^{3+} + 2HL^{3-} = Fe^{II}Fe^{III}H_2L_2^-$$

Acknowledgment.—The author wishes to thank Professor D. A. Skoog for his valuable cooperation in this work.

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[7] One of the reviewers pointed out that the difference in magnitude of the formation constant determined in this work and the constant which follows (derived from literature data) may serve to illustrate the unusual stability of the mixed-metal complex: $K = [FeL^-][Sn(HL)_2^{4-}][H^+]/[Fe^{3+}][Sn^{2+}][HL^{3-}]^3 \approx 1.8 \times 10^{22}$.

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Nitrosyl–Nitrite Interconversion in Ruthenium Complexes

BY JOHN B. GODWIN AND THOMAS J. MEYER*

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The series of nitrosyl complexes $Ru(AA)_2(NO)X^{3+}$ (AA = 2,2′-bipyridine, 1,10-phenanthroline; X = Cl^-, Br^-, NO_2^-, pyridine) react with OH^- to give the corresponding nitro complexes $Ru(AA)_2(NO_2)X^+$, which have been isolated and characterized. For the equilibrium $Ru(bipy)_2(NO)Cl^{2+} + 2OH^- = Ru(bipy)_2(NO_2)Cl + H_2O$, $K_1 = (1.6 \pm 0.4) \times 10^9\ M^{-2}$ at 25.0° in 1.0 M NaCl. The nitro complexes can be reconverted into nitrosyl complexes by reactions with the Lewis acids BF_3, $SnCl_4$, or H^+. The nitro–nitrosyl conversions are chemically reversible.

Introduction

We have reported the preparation of the series of nitrosyl complexes $Ru(AA)_2(NO)X^{3+}$ (AA = 2,2′-bipyridine and 1,10-phenanthroline; X = Cl^-, Br^-, NO_2^-, py)[1]. The complexes act as a controlled source of nitrosonium ion (NO^+) in that they react with hydroxide ion to give the corresponding nitro complexes[1] and with azide ion to liberate N_2 and N_2O.[2] Here we describe in detail the conversion of the nitrosyl complexes into nitro complexes, the measurement of the equilibrium constant for the reaction

$$Ru(bipy)_2(NO)Cl^{2+} + 2OH^- = Ru(bipy)_2(NO_2)Cl + H_2O$$

at 25° in 1 M NaCl, and the reconversion of coordinated nitrite into nitrosyl by reaction with either BF_3 or $SnCl_4$.

Experimental Section

Stannic chloride was distilled before use and boron trifluoride was used as the gas. All other reagents were of reagent or analytical grade and used without further purification. The preparations of the ruthenium-nitrosyl complexes were reported earlier.[1] Infrared spectra were recorded on Perkin-Elmer 421 or Beckman Model IR12 spectrophotometers as KBr pellets. Ultraviolet-visible spectra were recorded on a Cary Model 14 spectrophotometer equipped with a thermostated constant-temperature cell block.

Preparations. 1. $Ru(AA)_2NO_2X \cdot H_2O$ (X = Cl, Br; AA = bipy, phen).—Two general procedures were used. A. One-tenth gram of the appropriate nitrosyl complex as its hexafluorophosphate salt, $[Ru(AA)_2(NO)X](PF_6)_2$, was suspended in 5–10 ml of water and 1–2 ml of 2 M NaOH was added slowly with stirring. The suspended pale brown solid immediately began to turn red-brown and the solution color deepened. Stirring was continued for 15 min. The red-brown solid was then collected on a frit, washed twice with ice-cold water, twice with 1,2-dimethoxyethane, and several times with ether, and air-dried with suction.

B. One-tenth gram of the appropriate nitrosyl complex as its hexafluorophosphate salt was suspended in 25 ml of ethanol at 40–50° and 3 ml of 2 M aqueous sodium hydroxide was added slowly with vigorous stirring. The complex slowly dissolved and the solution turned deep red. After about 10 min a red-brown solid began to precipitate. Ether was added carefully

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[1] T. J. Meyer, J. B. Godwin, and N. Winterton, *Chem. Commun.*, 1872 (1970); J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, **10**, 471 (1971).

[2] F. J. Miller and T. J. Meyer, *J. Amer. Chem. Soc.*, **93**, 1294 (1971).