the electrochemically generated species must be Cr(V), we conclude that the active species in both Scheme II and eq 1 and 2 is a Cr(V) oxo-porphyrin.

Relevance to Natural Systems

As given in Scheme I, the active species in the cytochrome P-450 mechanism is supposed to be an Fe(IV)-oxo porphyrin radical cation, a formal Fe(V) species. Our electrochemically generated $[(CrTPP)O]^+$ state is reactive in a formally similar fashion. There are, of course, considerable differences between cytochrome P-450 and the present work, notably that cytochrome P-450 is able to activate dioxygen to form its active state and is kinetically faster. It was mainly because of the slow $[(CrTPP)O]^+$ reaction kinetics that we were able to study it effectively. The dimer chemistry proposed in Scheme II has no analogue in cytochrome P-450 chemistry, but free heme also shows a rich oxo-bridged dimer chemistry. It seems likely that immobilization of the metalloporphyrin in the polypeptide is important in preventing dimer formation, as has been shown for hemoglobin and myoglobin.[13]

In principle, it should be possible to extend the $[(CrTPP)O]^{+/0}$ strategy to different metal ions, specifically iron and manganese. Also, the methods described here should be useful in extending oxo-porphyrin reactivity to other substrates besides olefins.

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Equilibria and Mechanism of the Interaction of Indium(III) with the Indicator 1-(2-Pyridylazo)-2-naphthol (PAN)

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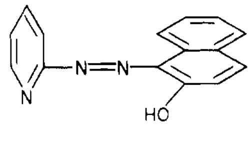
The interaction between In(III) and the indicator PAN (HL) has been investigated at 25 °C, ionic strength 0.2 M ($NaClO_4$), and $[H^+] = 0.003$–0.2 M in methanol-water mixtures of different composition. One complex, InL^{2+}, has been observed, with $K = [InL^{2+}][H^+]/[In^{3+}][HL] \simeq 1.2$ in pure water. The formation of this complex proceeds mainly via three parallel paths, one involving $InOH^{2+}$ and HL, and two proton-ambiguous paths, involving In^{3+} and HL, and $InOH^{2+}$ and H_2L^+, respectively. Rate constants for these processes (upper limits only for the proton-ambiguous paths) are reported. The unusually low values of the forward rate constants are interpreted in terms of an internal hydrogen-bond mechanism.

Introduction

Whereas the mechanism of complex formation of divalent metal ions is quite well established,[1] the position with respect to tervalent cations is much less clear. This is mainly due to the extensive hydrolysis and polymerization,[2] which seriously limit the range of concentrations and acidity that can be investigated. In addition, the presence of differently protonated forms of both metal ions and ligands introduces proton ambiguity,[3] which often makes it impossible to assign the observed rate constants uniquely to a given reaction path.

Furthermore, as far as tervalent metal ions of the group 13[21] atoms such as Al(III), Ga(III), and In(III) are concerned, there is the additional difficulty of finding ligands suitable for spectrophotometric monitoring of their complexation.

This difficulty can be overcome by using metallochromic indicators, and we have done so[4,5] in the course of our program of studying substitution reactions at tervalent cations. In the present paper, we present the results of an investigation of the reaction of In(III) with PAN (1-(2-pyridylazo)-2-naphthol)



a diprotic acid that, in its monoprotonated, neutral form, we shall designate by HL. Unfortunately, this indicator does not dissolve in pure water; the experiments therefore had to be carried out in the presence of methanol.

Experimental Section

Chemicals. All reagents were analytical grade. PAN was Carlo Erba RP and was used without further purification. Indium perchlorate solutions were prepared by dissolving the pure metal in perchloric acid. The resulting solution was titrated as described previously.[5] Triply distilled water was used to prepare the solutions. The temperature was 25.0 ± 0.1 °C. The ionic strength was 0.2 M obtained with sodium perchlorate. Stock solutions of PAN were 10^{-3} M in 60% aqueous methanol.

Methods. (a) Equilibria. Spectrophotometric titrations were carried out by using a Perkin-Elmer E 200 double-beam spectrophotometer. Increasing amounts of $In(ClO_4)_3$ were added with a microsyringe to a solution of the ligand already thermostated in the spectrophotometric cell.

The acid concentration and solvent composition were kept constant at the desired values during each titration. A wavelength of 545 nm was chosen since in this region the spectrum of the complex shows a broad shoulder whereas the absorptivity of the ligand is low and the relative difference of absorptivities is most favorable.

(b) Kinetics. Kinetic runs were carried out in a Durrum-Gibson stopped-flow apparatus. All experiments were performed under pseudo-first-order conditions ($c_M \gg c_L$, where c_M and c_L are the stoichiometric concentrations of metal and ligand, respectively), either by mixing two solutions containing metal ion and ligand, respectively, or by mixing a solution containing both constituents with a solution of perchloric acid. In the latter case the decrease of absorbance owing to the decomposition of the complex was recorded. The agreement between the two procedures was within the limit of experimental error. The data were evaluated with the aid of a microcomputer (Radio Shack TRS 80). The signal from the stopped-flow apparatus was fed into a Biomation 802 transient recorder and from there, through an appropriate interface, was transferred in digital form to the computer and processed as described elsewhere.[6] The maximum spread between repeated runs (four to seven) never exceeded 10%.

Measurements were again carried out at a wavelength of 545 nm.

Results

Equilibrium Constants. The equilibria of the In(III)-PAN system have been identified, and the relevant equilibrium pa-

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* To whom correspondence should be addressed at the University of Pisa.

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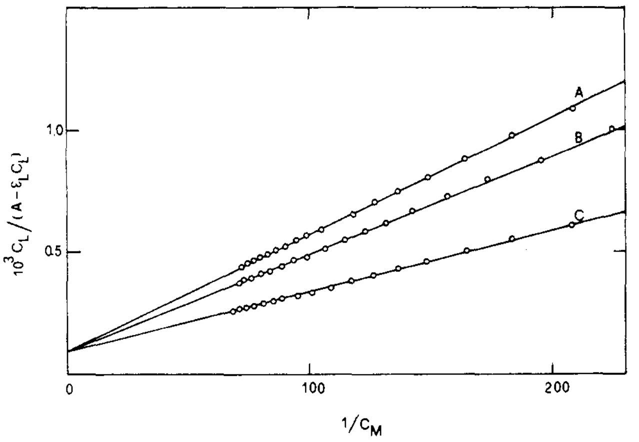

Figure 1. Plots of $c_L/(A - \epsilon_L c_L)$ as a function of $1/c_M$, from which the apparent equilibrium constants for the system In(III)–PAN are obtained (25 °C, I = 0.2 M ($NaClO_4$), x_{CH_3OH} = 0.31): (A) $[H^+]$ = 0.05 M; (B) $[H^+]$ = 0.045 M; (C) $[H^+]$ = 0.03 M.

rameters have been evaluated by using a method described earlier.[4,5] An apparent quantity, K_{app}, defines the equilibrium between complex and reactants, namely

$$K_{app} = \frac{\sum[\text{complex}]}{[\text{free metal}][\text{free ligand}]} = \frac{\sum[\text{complex}]}{[M][HL]\alpha\beta} \qquad (1)$$

where $\sum[\text{complex}] = [MH_2L^{4+}] + [MHL^{3+}] + [ML^{2+}]$, $\alpha = 1 + [H]/K_{A1}$, and $\beta = 1 + K_{OH1}/[H^+] + K_D c_M/[H^+]^2$. Values of K_{A1}, the first acid dissociation constant of HL, have been determined experimentally. The second dissociation constant, K_{A2}, has a pK of 12.2;[7] therefore, $[L^-]$ is negligible in comparison with the concentration of the other ligand species. For the first hydrolysis constant of In(III), K_{OH1}, we have used the value of 4.0 × 10^{-5} M suggested by Baes and Mesmer.[2] The last term in the expression β accounts for the formation of polynuclear species whose concentration may be nonnegligible at our lowest acidities and highest metal ion concentrations. We assumed the dimer to be predominant among the polynuclear species according to

$$2In^{3+} \rightleftharpoons In_2(OH)_4^{4+} + 2H^+ \qquad (2)$$

The equilibrium constant for this reaction, K_D, was taken[3,8,9] to be 6.2 × 10^{-6} M.

Spectrophotometric titrations were performed by adding to known amounts of the ligand of concentration c_L increasing amounts of indium(III) perchlorate under the condition $c_M \gg c_L$. The range of $[H^+]$ investigated was between 0.004 and 0.05 M, and the solvent composition was x_{CH_3OH} = 0.063, 0.14, and 0.31. The data have been processed as described elsewhere;[5] typical plots are shown in Figure 1. Values of K_{app} have been obtained from the ratios of intercept to slope of the straight lines of Figure 1.

The quantity $K_{app}\alpha\beta[H^+]$ has been found to be independent of $[H^+]$. This indicates that the unprotonated ML^{2+} is the predominant complex species. On this basis, the spectrophotometric data have been treated in order to obtain simultaneously K and K_{A1}, where $K = [ML][H^+]/[HL][M]$. Equation 2 can be rearranged to give

$$\frac{1}{K_{app}\beta[H^+]} = \frac{1}{K} + \frac{[H^+]}{K_{A1}K} \qquad (3)$$

A plot of the left-hand side of this equation vs. $[H^+]$ gives a straight line with intercept $1/K$ and slope $1/K_{A1}K$ (Figure 2, open circles). The equilibrium parameters are reported in Table I.

Kinetic Results. At two values of $[H^+]$, namely 0.010 and 0.025 M, we found it possible to calculate K_{app} from the ratio between the slope and intercept of the plot of k_{obsd} as a function of c_M in the range between 10^{-3} and 10^{-2} M. The results are also shown in Figure 2 (squares). The agreement between the two methods is seen to be satisfactory. At lower acidity, namely $[H^+]$ = 3.56 × 10^{-3} M, the plot shows an upward curvature, indicating that under these conditions the reaction order with respect to the metal ion tends to values higher than unity. A possible explanation might be that the dimer formed in reaction 2 can also react with PAN. In order to avoid this complication, we decided to base all our calculations only on experiments with $[H^+] \geq 0.01$ M. On the other hand, at $[H^+] \geq 0.03$ M, the contribution of the back-reaction becomes predominant, so that K_{app} cannot be determined kinetically.

The plots of k_{obsd} as a function of $[H^+]$ exhibited a sharp minimum. This behavior is characteristic for systems where

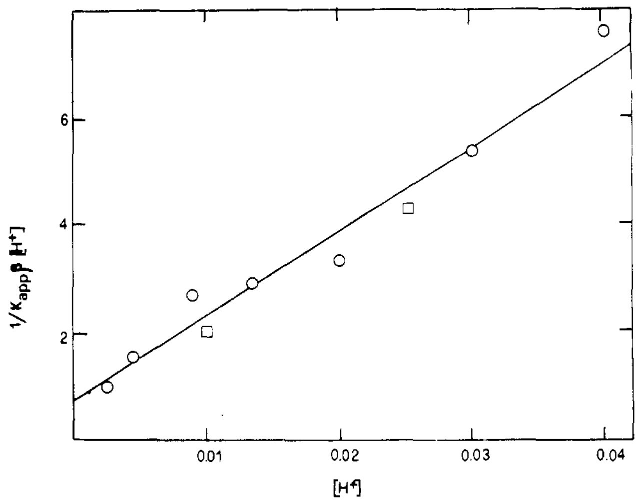

Figure 2. Plot of $1/K_{app}\beta[H^+]$ vs. $[H^+]$ from which both the formation constant of the complex In(III)–PAN and the dissociation constant of the ligand are obtained (25 °C, I = 0.2 ($NaClO_4$), x_{CH_3OH} = 0.063): (○) static experiments; (□) kinetic experiments.

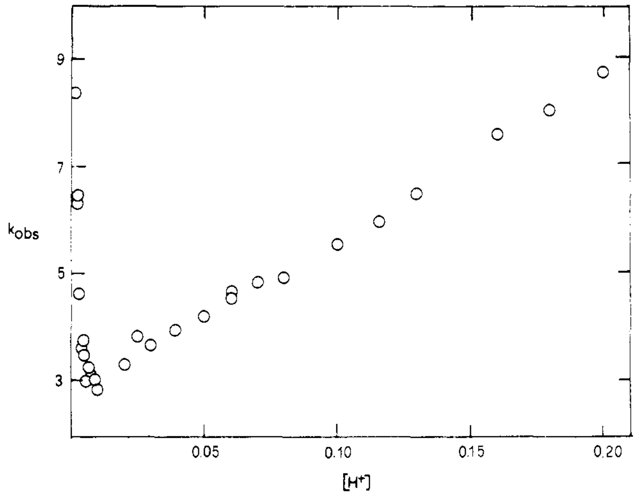

Figure 3. Dependence of the pseudo-first-order rate constant, k_{obsd}, on $[H^+]$ for the system In(III)–PAN (25 °C, I = 0.2 M ($NaClO_4$), x_{CH_3OH} = 0.063, c_M = 4 × 10^{-3} M).

Table I. Equilibrium Constants for the System In(III)–PAN at 25 °C[c]

x_{CH_3OH}	pK_{A1}	pK_{OH1}	pK_D	K
0	2.9[a]	4.4[b]	5.2[b]	
0.063	2.3			1.3
0.14	2.3			1.5
0.31	1.8			3.1

[a] Reference 7. [b] References 8 and 9. [c] Definitions: K_{A1}, first acid dissociation constant of PAN; K_{OH1}, first acid dissociation constant of In^{3+}; $K_D = [In(OH)_2^{4+}][H^+]^2/[In^{3+}]$; $K = [InL^{2+}][H^+]/[In^{3+}][HL]$.

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Table II. Rate Constants for the System Indium(III)–PAN at 25 °C and I = 0.5 M ($NaClO_4$)

x_{CH_3OH}	D^a	k_{-1}, $M^{-1}\ s^{-1}$	k_{-2}, s^{-1}	k_1, $M^{-1}\ s^{-1}$	$10^{-3}k_1'$, $M^{-1}\ s^{-1}$	$10^{-4}k_2$, $M^{-1}\ s^{-1}$
0	78.5	$\sim 47^b$	$\sim 3.2^b$	$\leqslant\sim 55^b$	$\sim 5^b$	$\sim 8^b$
0.028	76.5	41.0 ± 2.1	2.49 ± 0.23	$\leqslant 53$	$\leqslant 6.2$	8.1
0.063	74.0	30.0 ± 0.6	2.68 ± 0.06	$\leqslant 39$	$\leqslant 4.6$	8.7
0.14	68.5	15.6 ± 2.5	1.63 ± 0.26	$\leqslant 24$	$\leqslant 3.0$	6.1
0.31	59.0	7.35 ± 0.60	0.782 ± 0.064	$\leqslant 23$	$\leqslant 8.6$	6.1

[a] Dielectric constant of the solvent (Landolt-Br̈nstein, "Physikalische und Chemische Tabellen"; Springer-Verlag: Berlin, Part 6, Elektrische Eigenschaften I, p 750). [b] Extrapolated.

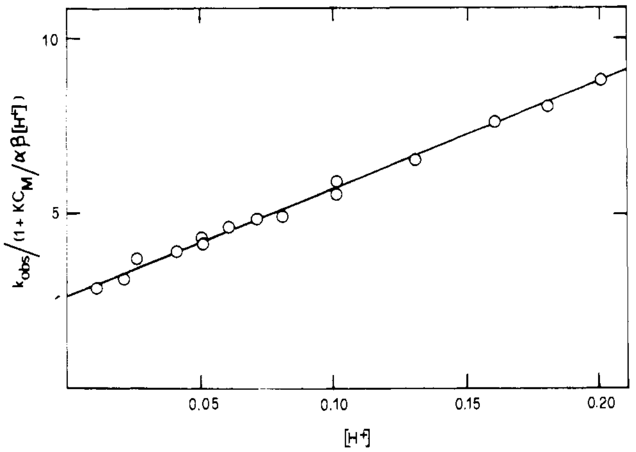


Figure 4. Plot of $k_{obsd}/(Kc_M/\alpha\beta[H^+] + 1)$ vs. $[H^+]$ allowing the determination of the rate parameters *a* and *b* for the system In(III)–PAN (25 °C, I = 0.2 M ($NaClO_4$), x_{CH_3OH} = 0.063).

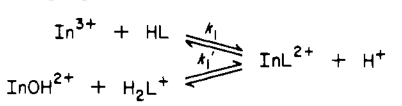
reactants that differ in their degree of hydrolysis or protonation undergo complexation, whereas proton-assisted decomposition of the complex is operative in at least one of the reverse paths. A typical example is shown in Figure 3.

In order to estimate the contributions of all possible reaction paths to the observed rate, we used eq 4 adapting an expression

$$\frac{k_{obsd}}{Kc_M/(\alpha\beta[H^+]) + 1} = a + b[H^+] + c[H^+]^2 + d[H^+]^{-1} \qquad (4)$$

derived earlier[5] to the fact that, except at our lowest values of $[H^+]$, we have $Kc_M/\alpha\beta[H^+] < 1$, and the back-reactions predominate. A plot of the left-hand side of eq 4 as a function of $[H^+]$ is linear. The contributions of the last two terms on the right-hand side of this equation are thus negligible, which means that, in the $[H^+]$ range investigated, reactions between In^{3+} and H_2L on the one hand, and reactions between $In(OH)_2{}^+$ and HL (or $InOH^{2+}$ and L^-) on the other, make negligible contributions.

We therefore propose the reaction scheme



(5)

$$InOH^{2+} + HL \overset{k_2}{\rightleftharpoons} InL^{2+} + H_2O \qquad (6)$$

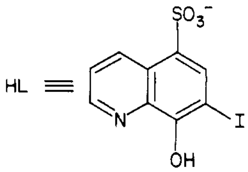
where the protolytic equilibria are again assumed to be rapid. The meaning of *a* in eq 4 is then k_{-2}, and that of *b* is k_{-1}. In this scheme we have omitted two reactions that have the same $[H^+]$ dependence as reaction 6. One is the reaction between $In(OH)_2{}^+$ and H_2L^+. Since no experimental evidence has been obtained even for the reaction between $In(OH)_2{}^+$ and the *neutral* species HL, this reaction can be assumed to make a negligible contribution. The second proton-ambiguous reaction is that between In^{3+} and L^-. Because of the extremely low concentration of L^- (pK_{A2} = 12.2[7]), this reaction would have to proceed with a rate constant higher than diffusion controlled to make itself felt in the overall reaction rate. For the forward rate constants of the two proton-ambiguous reactions (5) we can calculate only upper limits, namely, the value of k_1 if k_1' were zero and that of k_1' if k_1 were zero. We thus get $k_1 \ll k_{-1}K$ and $k_1' \ll k_{-1}KK_{A1}/K_{OH1}$. Reaction 6 is unambiguous, with $k_2 = k_{-2}K/K_{OH1}$. The equilibrium constants used in our calculations are shown in Table I, and the rate constants obtained are shown in Table II. The values of k_1' and k_2 are only very approximate—especially at high values of x_{CH_3OH}—because we did not determine K_{OH1} in the presence of methanol.

Discussion

Influence of Methanol. The change of K with solvent composition can be rationalized in terms of the influence of the dielectric constant on the electrostatic interaction energy between ions. Clearly, however, other factors are also at work: the value of k_{-1} decreases more strongly with decreasing dielectric constant than calculated on this basis, and k_1, k_2, and K_{A1} should not change at all, which is contrary to our findings. Furthermore, an equilibrium constant similar to ours has recently[10] been found to change with changing methanol concentration in the direction expected from the electrostatic theory but to change in the opposite direction with a change in the concentration of dimethyl sulfoxide, dimethylformamide, and methyl cyanide. We suggest that the influence of methanol on our constants should be connected with the influence of this substance on the structure of water.[11]

In order to be able to compare our results with previous data on similar systems, we are chiefly interested in the values in pure water. The necessary extrapolations, though not far, are somewhat arbitrary; this does not, however, affect our conclusions.

Equilibrium Constants. The absence of monoprotonated complex is in contrast with the system In(III)–ferron,[5] where MHL is present in amounts comparable to those of ML:



It is at first sight surprising that ferron, the stronger acid, should retain its last proton, whereas our extremely weak HL should not. However, in analogy with the very similar (phenylazo)resorcinols, our HL can be assumed to form a strong hydrogen bond between the naphtholic proton and one of the two nitrogen atoms of the azo group.[12,13] It is this hydrogen bond that causes the low value of K_{A2}. It is therefore reasonable to assume that, once the hydrogen bond is broken by the presence of the metal ion, the remaining OH should have a pK lower than that of naphthol, and the complex MHL should tend to lose its proton.

The strength of the complex in the two systems should be compared by comparing the chelation equilibrium constants $K_{chel} = K/K_{A1} = [ML]/[L][M]$. For ferron, we calculate from our previous data[5] that this constant equals $2.4 \times 10^9\ M^{-1}$, whereas in our present system, it equals $1.9 \times 10^{12}\ M^{-1}$. As expected, the weaker acid forms the stronger complex.

Rate Constants. The hydrolyzed species $InOH^{2+}$ again shows enhanced reactivity. This behavior is in line with that of other tervalent metal cations[14] (with the exception of V(III)[15] and

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Inorg. Chem. **1985**, *24*, 3831–3835

Table III. Comparison of Rate Constants for Substitution at In^{3+} (k_1) and at $InOH^{2+}$ (k_2)

ligand	I, M	k_1, $M^{-1}\ s^{-1}$	k_2, $M^{-1}\ s^{-1}$
PAN^0	0.2	$\leqslant\sim 55^a$	$8 \times 10^{4\,a}$
$Hferron^{+\,b}$	0.2	1.1×10^3	
$Ferron^{0\,b}$		9.7×10^4	1.2×10^7
murexide(1−)^c	0.1	6.0×10^5	
$SOX^{-\,d}$	0.1	2.8×10^5	
$SO_4^{2-\,e}$	0	2.6×10^5	2.5×10^7
$InOH^{2+\,f}$	0.5		4.1×10^5
H_2O^g		2×10^4	

[a] This work, extrapolated. [b] Reference 5. [c] Kaway, Y.; Imamura, T.; Fujimoto, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3142–3145. Ohtani, Y.; Yagihashi, S.f Fujimoto, M. *Ibid.* **1977**, *50*, 1345–1346. [d] Semixylenol orange: Kaway, Y.; Takahashi, T.; Hayashi, K.; Imamura, T.; Nakayama, H.; Fujimoto, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1417–1423. [e] Miceli, J.; Stuehr, J. *J. Am. Chem. Soc.* **1968**, *90*, 6967–6972. [f] Reference 7. [g] k_1 in s^{-1}: Glass, G. E.; Schwabacher, W. B.; Tobias, R. S. *Inorg. Chem.* **1968**, *7*, 2471–2478.

Ti(III))[14] and is usually ascribed to the labilization of the water molecules in the inner coordination sphere as a result of the hydrolysis. As has already been pointed out,[15] the enhanced reactivity of the hydrolyzed species cannot be adduced as a criterion for the mechanism by which the *aquo* ion reacts.

In Table III we have collected the known forward rate constants for complex formation by In^{3+} and $InOH^{2+}$. The data cover a fairly wide range, which points in the direction of an associative mechanism.[5] Nevertheless, the difference between the present results and those pertaining to all other ligands is quite striking and must have a specific reason. We suggest that an internal hydrogen-bond mechanism[16] should be operative in this system.

Proton transfer to OH^- and general bases from internally hydrogen-bonded acids is known to proceed as well below the "normal", diffusion-controlled rate.[13,17,18] This feature is parallelled by an unusually slow rate of complex formation by substitution-labile cations such as[16] Ni^{2+}, Co^{2+}, and[19] Mg^{2+}, though the accelerating effect is absent for the more substitution-inert cations such as Al^{3+}. Among the possible mechanisms by which the internal hydrogen bond might slow down an otherwise rapid reaction, we can rule out rate-determining bond opening because in that case the plot of $1/\tau$ vs. c_M would not be a straight line. There remains the possibility that the hydrogen bond should be broken in a concerted attack by the cation; alternatively, the hydrogen-bonded form might be completely inactive and the cation react only with the nonbonded form present in small concentrations. The former explanation has been brought forward for the reaction between Ni^{2+} and substituted (phenylazo)resorcinols. It is interesting that $NiOH^+$ (which, in general, does not react significantly more rapidly than Ni^{2+} itself) forms the complex with these substances at a rate that is normal for Ni^{2+}. It was suggested that in this case the $NiOH^+$ acts as a strong base. On the other hand, $InOH^{2+}$ is much less basic and it is not surprising that its rate should be slowed down to the same extent as that of In^{3+}.

Acknowledgment. We are indebted to the Italian CNR and the Kultusministerium Niedersachsen, West Germany, for financial support and to Prof. H. J. G. Hayman for programming the computer.

Registry No. PAN, 85-85-8; In, 7440-74-6.

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(21) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Mechanism of Acid-Catalyzed Decomposition of the (ΔΔ,ΛΛ)-(μ-Hydroxo)(μ-peroxo)bis[bis(ethylenediamine)cobalt(III)] Ion

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The change in the absorption spectrum accompanied by the decomposition of the title ion to cobalt(II) ions and dioxygen in perchloric acid solution, $[H^+] = 0.01–1.5$ M, takes place in two stages. The initial stage is completed within the stopped-flow mixing time (<5 ms) and corresponds to protonation equilibrium (protonation constant $\sim 10\ M^{-1}$, M = mol dm^{-3}, at 5–45 °C and $I = 1.0–3.0$ M). The protonated species exhibits an absorption maximum at ca. 520 nm. The second slow stage enables kinetic studies in 0.01–0.20 M $HClO_4$ to be made, the observed rate constants being 0.02–0.3 s^{-1} at 35 °C and $I = 1.0$ M. The decomposition seems to proceed exclusively from the protonated species through the cleavage of the hydroxide bridge to give a singly bridged μ-peroxo binuclear cobalt(III) complex $[(en)_2(H_2O)Co^{III}(\mu\text{-}O_2^{(2-)})Co^{III}(H_2O)(en)_2]^{4+}$, which subsequently undergoes deoxygenation.

The (μ-peroxo)(μ-hydroxo)bis[bis(ethylenediamine)cobalt(III)] ion, $[(en)_2Co^{III}(\mu\text{-}OH)(\mu\text{-}O_2^{(2-)})Co^{III}(en)_2]^{3+}$ (**1**), undergoes proton-assisted decomposition into dioxygen and cobalt(II) species in the pH region from 1 to 3.5.[2,3] No $[H^+]$ dependence was observed for the decomposition of the singly bridged μ-peroxo dicobalt(III) complexes such as $[(en)_2NH_3Co^{III}(\mu\text{-}O_2^{(2-)})\text{-}Co^{III}NH_3(en)_2]^{4+}$ over a wide pH range from 1.1 to 10.[4-8]

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