where S–P–S and S–D–S refer to the solvated paramagnetic and diamagnetic forms, respectively. This may be treated as a three-site problem[20] with bulk solvent as site 1, S–D–S* as site 2, and S–P–S as site 3. The τ_{31}, τ_{13} reaction would be the normal exchange path. If it is assumed that $\tau_{21}^{-1} \gg \tau_{23}^{-1}$, *i.e.*, that desolvation of the diamagnetic species is faster than its conversion to the paramagnetic form, and that the chemical shift in the diamagnetic form, $\Delta\omega_2$, is $\ll\Delta\omega_3$, then

$$(T_{2P}P_M)^{-1} = \frac{\left(\frac{1}{\tau_{32}} + \frac{1}{\tau_{31}}\right)\left[\frac{1}{T_{23}^2} + \frac{1}{T_{23}}\left(\frac{1}{\tau_{32}} + \frac{1}{\tau_{31}}\right) + \Delta\omega_3^2\right]}{\left(\frac{1}{T_{23}} + \frac{1}{\tau_{32}} + \frac{1}{\tau_{31}}\right)^2 + \Delta\omega_3^2}$$

It can be seen by comparison to eq 4 that the effective exchange lifetime $\tau_M^{-1} = \tau_{32}^{-1} + \tau_{31}^{-1}$. Therefore the solvent exchange rate will be controlled by whichever process is faster, either direct exchange (τ_{31}^{-1}) or the S–P–S to S–D–S conversion (τ_{32}^{-1}). Unfortunately no rate constants are available for the latter process; however Wilkins, *et al.*,[21] have given a lower limit of 10^5 sec^{-1} for this interconversion in $Ni(trien)^{2+}$ and $Ni(2,3,2\text{-tet})^{2+}$ in aqueous solution. It has also been found that tetrahedral–planar interconversions of nickel(II) complexes have rate constants in the range 10^5–10^6 sec^{-1}.[22,23] Although the latter process is not really comparable to that observed here, it appears that structural and spin state changes have rate constants of this order of magnitude.

Other reaction paths are also possible such as

$$\text{S–P–S} \rightleftarrows \text{SP} + \text{S} \rightleftarrows \text{D} + 2\text{S}$$

or

$$\text{S–P–S} \rightleftarrows \text{SD} + \text{S} \rightleftarrows \text{D} + 2\text{S}$$

In these the solvent exchange rate will be controlled by the first reaction and S–P or S–D could be intermediates for the solvent exchange and spin state change. In the second reaction the solvent exchange and spin state change would proceed at the same rate and the solvent exchange rate might be expected to be unusual compared to a purely paramagnetic system. In the absence of rate data for the diamagnetic–paramagnetic change it is not possible to decide between these various possibilities.

(20) N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, **8**, 1824 (1969).
(21) R. G. Wilkins, R. Yelin, D. W. Margerum, and D. C. Weatherburn, *J. Amer. Chem. Soc.*, **91**, 4326 (1969).
(22) L. H. Pignolet, W. DeW. Horrocks, and R. H. Holm, *ibid.*, **92**, 1855 (1970).
(23) G. N. LaMar and E. O. Sherman, *ibid.*, **92**, 2691 (1970).

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Kinetic Study of the Complexing of Nickel(II) by Imidazole, Histidine, and Histidine Methyl Ester

BY J. E. LETTER, JR., AND R. B. JORDAN*

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The rate constants for complexation of nickel(II) by imidazole, histidine, and histidine methyl ester have been measured at 23.7° in the pH range 5.6–6.9 and ionic strength 0.1 M (KNO_3). For imidazole the protonated ($k = 400\ M^{-1}\ sec^{-1}$) and neutral ($k = 3.2 \times 10^3\ M^{-1}\ sec^{-1}$) forms of the ligand are found to react. Histidine is observed to react only through the neutral form ($k = 2.2 \times 10^3\ M^{-1}\ sec^{-1}$), in which one proton is removed from the imidazole group. Reaction is observed for histidine methyl ester both as the monocation ($k = 600\ M^{-1}\ sec^{-1}$) with the imidazole proton removed and as the neutral molecule ($k = 2.6 \times 10^3\ M^{-1}\ sec^{-1}$) in which both the amino and imidazole protons are removed. The results are consistent with a mechanism in which the imidazole part of the histidine derivatives complexes first with the rate constants showing the expected variation with ligand charge. A second slower reaction is observed in the two histidine systems. This is attributed to the formation of some dinickel species by complexing at the pyrrole nitrogen of the coordinated imidazole part of the histidine ligand.

Introduction

The histidine molecule is a potentially tridendate ligand in aqueous solution, having three different possible bonding sites, *i.e.*, an amino nitrogen, an imidazole nitrogen, and a carboxyl oxygen. Almost every combination of bonding sites has been proposed for the copper(II)–histidine system, but the calorimetric work of Meyer and Bauman[1] indicates binding through the amino and imidazole nitrogens. This is also consistent with the spectrophotometric and CD work of Martin, *et al.*[2] A temperature-jump study[3] of the copper–histidine system showed that only monoprotonated histidine was reactive in the pH range 2.5–4.0 but the complexing sequence could not be determined.

The thermodynamic parameters for the nickel(II)–histidine system have been measured recently by Williams.[4] The recent and previous work generally agree that histidine forms tridentate nickel(II) complexes and the X-ray structure[5] of bis(L-histidino)nickel(II) substantiates this conclusion.

In the hope of establishing the sequence of binding steps in the nickel(II)–histidine system we have studied the kinetics of the reaction of nickel(II) with histidine, histidine methyl ester, and imidazole. The rates of

(1) J. L. Meyer and J. E. Bauman, Jr., *J. Amer. Chem. Soc.*, **92**, 4210 (1970).
(2) E. W. Wilson, M. H. Kasperian, and R. B. Martin, *ibid.*, **92**, 5365 (1970).
(3) W. B. Makinen, A. F. Pearlmutter, and J. E. Stuehr, *ibid.*, **91**, 4083 (1969).
(4) D. R. Williams, *J. Chem. Soc.*, 1550 (1970).
(5) K. A. Fraser, H. A. Long, R. Candlin, and M. M. Harding, *Chem. Commun.*, 344 (1965).

substitution on nickel(II) are known for a large number of ligands[6] and seem to be controlled by the rate of water exchange.[6] Thus the observed rates and ligand pK_a values can be used to determine which ligand coordination site is binding.

Experimental Section

Materials.—The L-histidine (free base), supplied by Nutritiona Biochemicals Corp., was recrystallized from aqueous ethanol. The L-histidine methyl ester, imidazole, and 2,6-lutidine supplied by Eastman Organic Chemicals, KNO_3 from Fisher Chemicals, and bromothymol blue from British Drug Houses were used as obtained. The solutions of nickel(II) were prepared from $Ni(NO_3)_2 \cdot 6H_2O$ (May and Baker) and standardized by EDTA–$MgSO_4$ titration[7] using eriochrome black T as the indicator.

Kinetic Measurements.—An Aminco-Morrow stopped-flow system was used in conjunction with a standard water circulation temperature control system. The temperature of solutions in the drive syringes of the apparatus was checked periodically using a copper–constantan thermocouple.

All reactions were carried out with a large ratio of nickel(II) to ligand concentrations. Indicator was added to the ligand solution and the change in transmittance was monitored at 620 nm. All of the solutions were buffered with 2,6-lutidine with nickel(II) and ligand solutions at essentially the same pH before mixing. The pH recorded for each run is the average of the values before and after mixing. The pH was measured with a Beckman Expandomatic pH meter with a 2 pH unit full-scale expansion.

The transmittance changes were recorded photographically, and the half-time for the reaction was determined from the usual semilogarithmic plots. For each set of concentration conditions 6–16 runs were made and the average half-time was used to obtain the rate constants given in Table I.

TABLE I
KINETIC RESULTS FOR THE FIRST REACTION
(0.10 M KNO_3, 23.7°)[a]

10^3[L], M	10^2[Ni^{2+}], M	pH	$10^{-2}k_{obsd}$, M^{-1} sec^{-1}	10^3[L], M	10^2[Ni^{2+}], M	pH	$10^{-2}k_{obsd}$, M^{-1} sec^{-1}
			Imidazole Ligand				
1.53	1.70	6.80	13.8	1.50	1.70	5.90	5.99
1.59	1.70	6.62	10.5	1.50	1.70	5.90	5.48
1.60	1.70	6.28	7.58				
			Histidine Ligand				
1.57	1.70	6.89	19.0	1.67	1.57	6.45	15.6
1.92	1.70	6.83	18.2	1.67	1.26	6.40	13.4
1.67	1.26	6.61	16.3	1.59	1.29	6.18	10.4
0.80	1.57	6.58	14.0	1.59	1.29	5.55	10.1
			Histidine Methyl Ester Ligand				
1.27	1.02	6.91	11.0	1.61	1.70	6.47	7.20
1.72	1.70	6.87	10.9	1.64	1.70	6.19	5.28
1.72	1.70	6.70	9.73	1.49	1.70	5.66	4.17

[a] The total buffer concentration was 0.015 M in all cases.

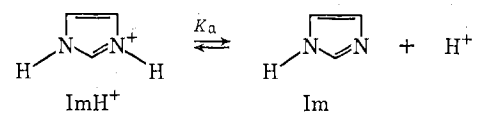
Blank experiments in which only nickel(II), buffer (2,6-lutidine), and indicator were present showed no change in transmittance on mixing. However, if the nickel(II) was replaced by histidine, a small change in transmittance with a half-time of ~2 sec was observed. This uncharacterized reaction was too slow and involved too small a transmittance change to interfere with the main reaction being studied.

Results and Treatment of Data

All of the kinetic runs were carried out with the nickel(II) to ligand concentration ratio greater than 10. Therefore the observed rate constant is given by

$$k_{obsd} = \frac{0.693}{t_{1/2}[Ni^{2+}]} \quad (1)$$

Imidazole.—The kinetic plots were linear to >90% reaction in all cases for this system. The variation of k_{obsd} with hydrogen ion concentration (Table I) is consistent with the reaction scheme



$$ImH^+ + Ni^{2+} \xrightarrow{k_1} NiIm^{2+} + H^+$$

$$Im + Ni^{2+} \xrightarrow{k_2} NiIm^{2+} \quad (2)$$

If the first reaction is considered as a rapid preequilibrium, then it can be shown that

$$k_{obsd} = \frac{k_1[H^+] + k_2K_a}{K_a + [H^+]} \quad (3)$$

or

$$k_{obsd}\left(\frac{K_a + [H^+]}{[H^+]}\right) = k_1 + \frac{k_2K_a}{[H^+]} \quad (4)$$

The plot of $k_{obsd}(K_a + [H^+])[H^+]^{-1}$ against $[H^+]^{-1}$ is shown in Figure 1. The intercept gives $k_1 = 4.0 \times 10^2\ M^{-1}$ sec^{-1} and the slope gives $k_2 = 3.23 \times 10^3\ M^{-1}$ sec^{-1}, when K_a is taken as $7.78 \times 10^{-4}\ M$.[8-10]

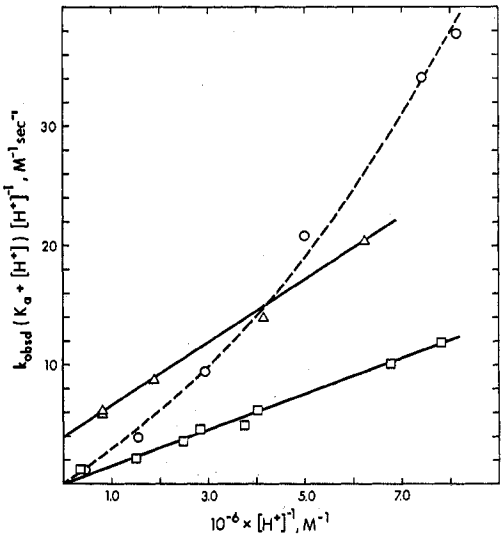


Figure 1.—Variation of $k_{obsd}(K_a + [H^+])[H^+]^{-1}$ with $[H^+]^{-1}$ at 23.7°: for imidazole (Δ), vertical scale $\times 10^{-2}$, $K_a = 7.78 \times 10^{-8}\ M$; for histidine (□), vertical scale $\times 10^{-3}$, $K_a = 6.77, \times 10^{-7}\ M$; for histidine methyl ester (○), vertical scale $\times 10^{-3}$ $K_a = 4.08 \times 10^{-6}\ M$.

Histidine.—The kinetic plots of the logarithm of the absorbance difference *vs.* time show that two reactions

(6) (a) R. G. Wilkins, *Accounts Chem. Res.*, **3**, 408 (1970), and references cited therein; (b) K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, **13**, 107 (1970).

(7) G. Scharzenbach and H. Flaschka, "Complexometric Titrations," Methuen, London, 1969.

(8) J. E. Bauman, Jr., and J. C. Wang, *Inorg. Chem.*, **3**, 368 (1964).

(9) No temperature correction has been applied to the K_a values to adjust from 25 to 23.7°. The change would generally be <5% since $\Delta H°$ is ~9 kcal mol^{-1} for all the K_a's used.

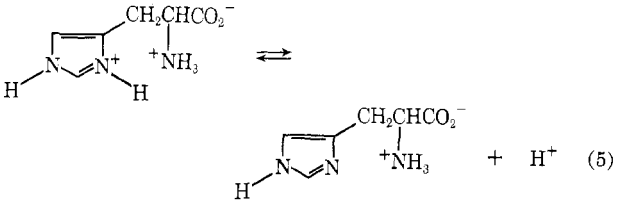
(10) A referee has pointed out that the last term in eq 4 could result also from the reaction NiOH + ImH^+, in which case the term would be $k_2'K_M/[H^+]$, where K_M is the hydrolysis constant for $Ni(OH_2)_6^{2+}$ ($pK_M \approx 10.6$). If this were the case, then $k_2' \approx 1 \times 10^7$ for imidazole, with analogous values of 7×10^7 and 9×10^7 for histidine and methylhistidine, respectively. It has generally been found[8] in many other systems that approximately constant k_2 values are obtained if a scheme similar to eq 2 is applied, but, for example, if NiOH were reacting with glycine, $k_2' \approx 10^4$, much different from the above values. Finally, the rate constant of 10^7 would be impossible for NiOH, since its rate of proton transfer to water is $<10^3$ (T. J. Swift and T. A. Stephenson, *Inorg. Chem.*, **5**, 1100 (1966)) and should not be greater to a poor base such as ImH^+.

are occurring in this system. The half-times for the two steps are sufficiently different that they can be obtained independently and eq 1 was used to obtain k_{obsd} for each reaction. The experimental results are given in Tables I and II for the first and second reactions, respectively.

TABLE II
KINETIC RESULTS FOR THE SECOND REACTION
(0.10 M KNO_4, 23.7°)

10^3[L], M	10^3[Ni^{2+}], M	[Buffer], M	pH	$10^{-2}k_{obsd}$, M^{-1} sec^{-1}
		Histidine Ligand		
1.19	1.02	0.015	6.87	1.62
1.19	1.70	0.015	6.84	1.50
1.03	1.70	0.015	6.84	1.45
1.92	1.70	0.012	6.83	1.64
1.13	1.70	0.010	6.84	1.42
1.67	1.26	0.012	6.61	1.34
1.67	1.26	0.012	6.40	1.17
1.59	1.26	0.012	6.18	1.13
		Histidine Methyl Ester Ligand		
1.27	1.70	0.012	6.90	1.03
1.27	1.02	0.012	6.91	1.19
1.72	1.70	0.015	6.87	0.87
1.72	1.70	0.015	6.70	1.04
1.61	1.70	0.015	6.47	0.90
1.64	1.70	0.015	6.19	1.06
1.49	1.70	0.015	5.66	0.73

The results for the faster reaction are consistent with a rate law given by eq 3. The preequilibrium is assigned to the reaction



(5)

for which K_a is taken to be 6.77×10^{-7} M.[1,9] The appropriate plot of $k_{obsd}(K_a + [H^+])[H^+]^{-1}$ against $[H^+]^{-1}$ is shown in Figure 1. The intercept of this plot is not detectably different from zero while the slope gives $k_2 = 2.9 \times 10^3$ M^{-1} sec^{-1}.

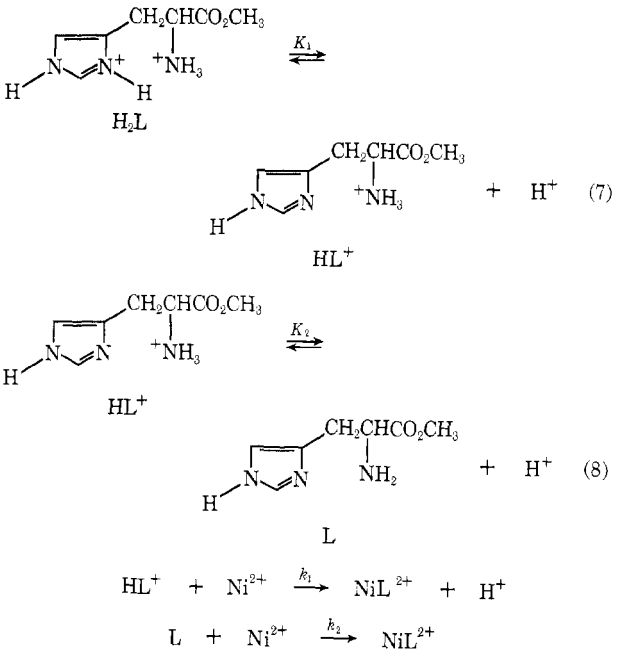
The absorbance change associated with the second reaction is much smaller than that for the first reaction, and the precision of the results is correspondingly poorer. The results in Table II indicate a first-order dependence on nickel(II), some dependence on hydrogen ion, and no dependence on buffer concentration. Therefore

$$k_{obsd} = \frac{0.693}{t_{1/2}[Ni^{2+}]} = k_1' + \frac{k_2'}{[H^+]} \quad (6)$$

with $k_1' = 97 \pm 10$ M^{-1} sec^{-1} and $k_2' = (8.6 \pm 4) \times 10^{-6}$ sec^{-1}. The latter value especially is highly uncertain due to the lack of precision in the k_{obsd} values.

Histidine Methyl Ester.—The results for this system are qualitatively similar to those for histidine in that two reactions were observed. The k_{obsd} values for the first and second reactions are given in Tables I and II, respectively.

The data for the first reaction give a nonlinear plot of $k_{obsd}(K_a + [H^+])[H^+]^{-1}$ against $[H^+]^{-1}$ as shown in Figure 1 with $K_a = 4.08 \times 10^{-6}$ M.[1,9] Variation of K_a by as much as a factor of 10 did not produce a linear plot. The direction of the deviation from linearity is consistent with complexation by both the monocation (HL^+) and the neutral molecule (L)



(7)

(8)

$$HL^+ + Ni^{2+} \xrightarrow{k_1} NiL^{2+} + H^+$$

$$L + Ni^{2+} \xrightarrow{k_2} NiL^{2+}$$

It is assumed, based on the results with histidine, that H_2L^{2+} does not react with nickel(II). If the proton dissociation reactions are rapid compared to the rate of complexation, then

$$k_{obsd} = \frac{k_1K_1[H^+] + k_2K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2} \quad (9)$$

A plot of the appropriate function, shown in Figure 2,

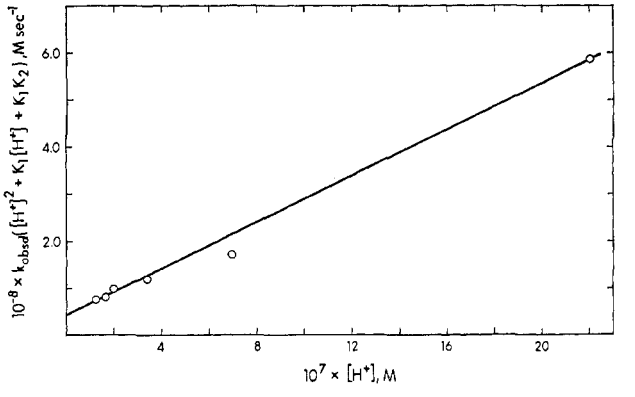


Figure 2.—Variation of $k_{obsd}([H^+]^2 + K_1[H^+] + K_1K_2)$ with $[H^+]$ for histidine methyl ester at 23.7°; $K_1 = 4.08 \times 10^{-8}$ M, $K_2 = 4.26 \times 10^{-8}$ M.

gives $k_1K_1 = 2.45 \times 10^{-3}$ sec^{-1} from the slope and $k_2K_1K_2 = 4.5 \times 10^{-10}$ M sec^{-1} from the intercept. These results combined with the known values[1] of $K_1 = 4.08 \times 10^{-8}$ M and $K_2 = 4.26 \times 10^{-8}$ M give $k_1 = 0.60 \times 10^3$ M^{-1} sec^{-1} and $k_2 = 2.6 \times 10^3$ M^{-1} sec^{-1}.

The rate constants for the slower reaction in this histidine methyl ester system are given in Table II. The values do not show any significant trend with pH and have an average of 97 M^{-1} sec^{-1}. As in the case of histidine the precision on these results is low because of the small absorbance change associated with the reaction.

Discussion

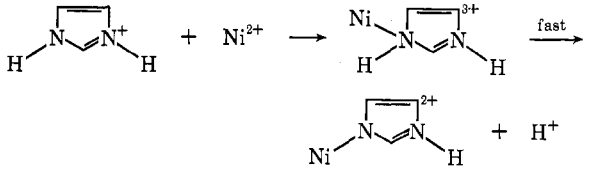
The rate constants obtained in this work and from some previous studies are collected in Table III.

TABLE III
SUMMARY OF COMPLEX FORMATION RATE CONSTANTS FOR NICKEL(II)

Ligand	Species	Rate constant, M^{-1} sec^{-1}	Ref
Imidazole	H_2L^+	4.0×10^2	*a*
	HL	3.2×10^3	*a*
Histidine	HL	2.2×10^3	*a*
Histidine	HL^+	6.0×10^2	*a*
methyl ester	L	2.6×10^3	*a*
Ethylenediamine	HL^+	5.9×10^2	*b*
	L	1×10^5	*c*

[a] This work; values at 23.7° and μ = 0.10 *M*. [b] J. C. Cassat and R. G. Wilkins, *J. Amer. Chem. Soc.*, **90**, 6045 (1968); value at 25° and μ = 0.30 *M*. [c] A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 4700 (1959); value at 25° and variable ionic strength.

The complexing of nickel(II) by imidazole is unusual in that the protonated as well as the unprotonated form of the ligand reacts. For most ammine and pyridine type ligands protonation removes the only nonbonded electron pair on the ligand and the protonated form is not reactive. However, for imidazole one electron pair is essentially nonbonding even in the protonated form and can be used for complexation as shown by the reaction

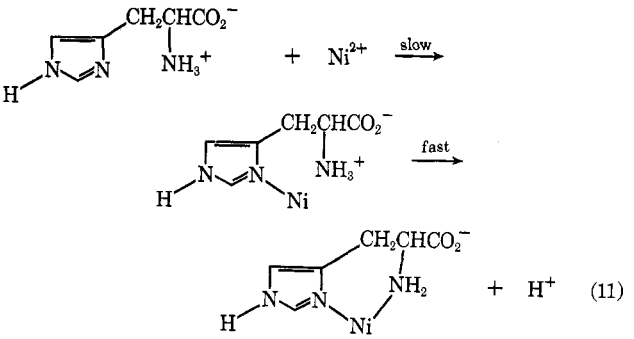


(10)

The pH-independent term was not found in the previous work of Hammes and Steinfeld[11] because the pH dependence of the rate was not studied. Complexing by HIm^+ has been proposed previously by Dunford, *et al.*,[12] to explain the kinetics of imidazole complexing with ferriprotoporphyrin IX. This proposal in the latter case was somewhat equivocal because of possible hydrolysis of the iron(III) species but was supported by relative rates and solvent-exchange studies.[13] The result reported here supports the arguments of Dunford, *et al.*, that HIm^+ is complexing to ferriprotoporphyrin IX.

Two reactions have been observed in the histidine and histidine methyl ester systems. The pH dependence of the rate of the first reaction is consistent with complexing of the species with a proton removed from the imidazole part of both histidine and histidine methyl ester. With this interpretation "normal"[6] complexing rates for nickel(II) of about 10^3 M^{-1} sec^{-1} are obtained. The reaction sequence is then represented by eq 11. The work of Williams[4] indicates the carboxyl group will also chelate in histidine. This is not the case with the ester however.

No pH-independent term has been observed in the

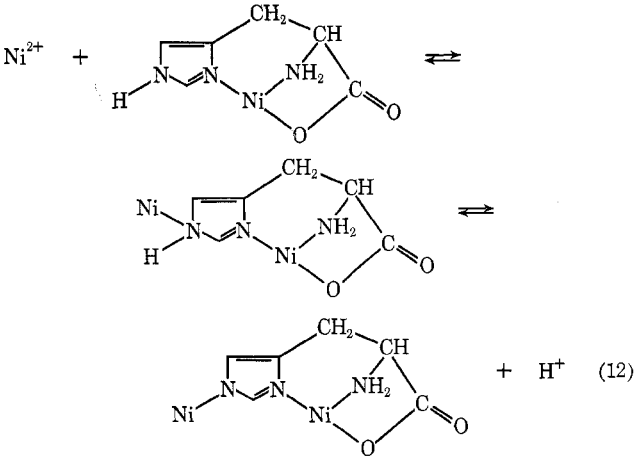


(11)

two histidine systems. This may be due to the lower basicity of the imidazole part of these systems compared to imidazole itself. This is indicated by the pK_1 values of these ligands, if it is assumed that this value can be used as a general measure of basicity of the imidazole nitrogen atoms. The latter assumption cannot be completely justified however because of possible hydrogen-bonding influences in the histidine systems.

Reaction of the species with the $-NH_3^+$ proton removed (L in eq 7) is only observed for the histidine methyl ester. This does not reflect any lack of reactivity for the corresponding histidine species but simply results from the smaller pK_2 of 7.37 for histidine methyl ester, compared to 9.21 for histidine. Thus, there is very little of the amino-deprotonated histidine species present under our experimental conditions.

The second reaction observed with histidine and histidine methyl ester is first order in nickel(II) and has nearly the same rate constant in the two systems. The rate is nearly independent of pH and the hydrogen ion change, as judged by the absorbance change of the indicator which is 5–15% of that for the first reaction. The latter observation plus the nickel(II) dependence shows that the second reaction is not a slow chelation of the amino group. The results are consistent with a system reaching equilibrium according to the reaction



(12)

The exact displacement of the individual equilibria is difficult to assess. Formation of a dinickel species such as this is possible under our experimental conditions, since nickel(II) is in large excess. Complexation at the pyrrole nitrogen, as in eq 12, has been observed previously in the solid state for bis(benzimidazolato)-cobalt(II)[14] and bis(imidazolato)zinc(II).[15] Ionization of the pyrrole proton with a pK of 9.25 has been ob-

(11) G. G. Hammes and J. I. Steinfeld, *J. Amer. Chem. Soc.*, **84**, 4639 (1962).

(12) B. B. Hasinoff, H. B. Dunford, and D. G. Horne, *Can. J. Chem.*, **47**, 3225 (1969).

(13) N. S. Angerman, B. B. Hasinoff, H. B. Dunford, and R. B. Jordan, *ibid.*, **47**, 3217 (1969).

(14) M. Goodgame and F. A. Cotton, *J. Amer. Chem. Soc.*, **84**, 1543 (1962).

(15) I. Lindquist, quoted in footnote 16a of ref 13.

served in the nickel(II) and copper(II) complexes of glycylhistidine.[16]

Failure to observe this reaction in imidazole is somewhat surprising, but it is possible that the charge donation of the nickel(II) ion makes the pyrrole nitrogen less basic and complexing does not occur, whereas in histidine the added amino group provides greater charge neutralization of the metal ion and the latter does not influence the basicity of the pyrrole nitrogen.

(16) R. B. Martin and J. T. Edsall, *J. Amer. Chem. Soc.*, **84**, 1543 (1962).

Finally it may be noted that the rate constants in Table III show a strong correlation with net ligand charge. This type of correlation has been discussed recently[6b] for other nickel(II) systems and is qualitatively consistent with Eigen's proposed ion-pair mechanism for these reactions.[6b]

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Ligand-Exchange Reactions in Platinum–Acetylene Complexes

BY C. D. COOK* AND K. Y. WAN

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Ligand-exchange reactions in complexes of the type $(P(C_6H_5)_3)_2Pt(ac)$, where ac is a phenylacetylene, have been reinvestigated, and the previously suggested mechanism has been modified.

Introduction

Substitution and addition reactions of complexes having the general formula $(P(C_6H_5)_3)_2Pt(un)$, where un is an olefin or acetylene, have been said[1] to involve the intermediate $(P(C_6H_5)_3)_2Pt$. Nmr spectroscopy, however, has failed to provide evidence for the dissociation of the acetylenic[2] or olefinic complexes and recently we[3] have proposed an alternative associative mechanism for certain reactions of $(P(C_6H_5)_3)_2PtC_2H_4$. Synthetic studies[4] on the acetylenic complexes provide further evidence for the nondissociative behavior of these complexes in solution, and in this paper we report nmr and kinetic studies on a number of complexes having the formula $(P(C_6H_5)_3)_2Pt(ac)$ where ac is a ring-substituted phenylacetylene.

Experimental Section

Preparation of Ligands. (i) **Perdeuteriotriphenylphosphine.**—A 50-g sample of bromobenzene-d_5 was prepared by the usual method.[5] It was metalated by lithium wire in ether solution,[6] after which an equivalent amount of phosphorus trichloride was added with cooling and stirring. The crude product was recrystallized from ethanol–water (mp 79–79.5°). The C–D stretch was found at 2295–2300 cm^{-1}. The nmr spectrum showed no proton signals.

(ii) **Ring-Deuterated Phenylacetylene.**—A 10-g sample of ring-deuterated acetophenone was prepared by the Friedel–Crafts method.[7] A slight molar excess of phosphorus pentachloride was added to the acetophenone and the mixture was refluxed for 20 min. The α,α-dichloroethane was dehydrochlorinated by alcoholic potassium hydroxide.[8] After separation in the usual manner the crude product was distilled at 142°. The yield of pure product (nmr) was 2 g.

(iii) **Perdeuteriophenylacetylene.**—Compound ii (1 g) in cold (0°) ether solution was treated with a slight excess of *n*-butyllithium (hexane). After 1 hr of stirring, deuterium oxide was added dropwise after which the organic layer was separated, washed, dried, and distilled. The product distilling at 142° showed a very weak nmr signal at τ 7.10 resulting from H–D exchange in the washing process.[9]

The 3- or 4-monosubstituted phenylacetylenes were prepared by standard methods.[10]

The platinum complexes were synthesized by reported methods[11] and were analytically pure.

The nmr spectra were obtained on a Varian Associates A-56/60 or HA 100 spectrometer and were calibrated by frequency modulation; low-temperature readings were corrected by means of the methanol spectrum according to the procedure developed by Varian Associates.

Kinetic measurements were made using a Cary 16 spectrophotometer with a thermostated cell chamber. Pseudo-first-order conditions were employed throughout and good linear plots of log $(A_t - A_\infty)$ *vs.* time were obtained, where A_t are the absorbances at times t covering at least 3 half-lives of the reaction. The rate coefficients obtained were reproducible to within 5%.

Results and Discussion

The nmr spectrum of bis(perdeuteriotriphenylphosphine)(ring-deuterated phenylacetylene)platinum reveals the sharp 12-line pattern resulting from ^1H–^{195}Pt (33%) and ^1H–^{31}P (100%) couplings to the acetylenic proton (Figure 1). We are able to identify and analyze the acetylenic protons of other bis(perdeuteriotriphenylphosphine(monosubstituted phenylacetylene)-platinum complexes similarly and the relevant data are recorded in Table I.

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(1) A. D. Allen and C. D. Cook, *Can. J. Chem.*, **42**, 1063 (1964); J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, **90**, 4491 (1968).

(2) E. O. Greaves, R. Bruce, and P. M. Maitlis, *Chem. Commun.*, 860 (1967).

(3) C. D. Cook and K. Y. Wan, submitted for publication.

(4) P. B. Tripathy and D. M. Roundhill, *J. Amer. Chem. Soc.*, **92**, 3825 (1970).

(5) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., London, 1956, p 535.

(6) R. G. Jones and H. Gilman, *Org. React.*, **6**, 353 (1951).

(7) H. Gilman and A. H. Blatt, Ed., "Organic Syntheses," Collect. Vol. I, 2nd ed, Wiley, New York, N. Y., 1967, p 109

(8) T. L. Jacobs, *Org. React.*, **5**, 1 (1949).

(9) R. E. Dessy, Y. Okuzumi, and A. Chen, *J. Amer. Chem. Soc.*, **84**, 2899 (1962).

(10) A. D. Allen and C. D. Cook, *Can. J. Chem.*, **41**, 1084 (1963).

(11) J. Chatt, G. A. Rowe, and A. A. Williams, *Proc. Chem. Soc., London*, 208 (1957).