blue plates (1.8 g, 85%). *Anal.* Calcd for $C_8H_{33}NB_{17}Co$. C, 24.90; H, 8.56; N, 3.63; B, 47.61; Co, 15.30. Found: C, 24.70; H, 8.58; N, 3.82; B, 47.61; Co, 15.09.

**Polyhedral Contraction of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]$. Preparation of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_7C_2H_{11})]$, (V).** $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]$ (1.0 g, 4.0 mmol) was dissolved in absolute ethanol (200 ml), ferric chloride (5.0 g, 31 mmol) was then added, and the mixture was heated to reflux for 45 min with stirring. After this time the reaction mixture was quenched with water (1000 ml), and the products were extracted into dichloromethane (3 × 300 ml). The combined extracts were dried over $MgSO_4$, filtered, and stripped onto silica gel (*ca.* 40 ml). This material was mounted on a silica gel column (400 ml), and the products were eluted with hexane–dichloromethane. The first band to elute was yellow and was purified in the manner described for IA above. This complex was identified as IA or $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}6,7\text{-}B_7C_2H_9)]$ by $^1H$ nmr, $^{11}B$ nmr, and mass spectral measurements (20 mg, 2%). The second band to elute was red and, on evaporation of the solvent, afforded the red crystalline product (380 mg, 40%) which was recrystallized from dichloromethane–hexane, mp 123°. *Anal.* Calcd for $C_7H_{16}B_7Co$: C, 35.81; H, 6.82; B, 32.23; Co, 25.15. Found: C, 35.84; H, 7.06; B, 32.07; Co, 24.86.

**Pyrolysis of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_7C_2H_{11})]$. Formation of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9)]$.** A sample of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_7C_2H_{11})]$ (V) (100 mg, 0.43 mmol) was added to cyclooctane (20 ml) and the mixture heated to reflux for 24 hr. After this time the bulk of the solvent was evaporated at reduced pressure, and the residual reaction products were separated using preparative thick layer chromatography with hexane–dichloromethane eluent. The first band to elute was yellow and contained $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9)]$ (84 mg, 85%) which was identified by $^1H$ nmr, $^{11}B$ nmr, and mass spectral measurements. Traces of a red material with an $R_f$ value equal to that of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)]$ were also observed.

The above reaction was repeated using $[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_7C_2H_{11})]$ (101 mg, 0.43 mmol) and cyclooctane (5 ml) which were placed in a tube with a break-seal. The tube was evacuated and sealed off on the vacuum line, then heated to 150° for 24 hr. After this time the tube was vented into the vacuum line, and the volume of noncondensable (−190°) gas formed was measured using a Sprengel pump (0.42 mmol, 98%). The residual material in the tube was treated in the manner described in the previous paragraph and afforded $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9)]$ (80 mg, 80%) and $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)]$ (6 mg, 6%).

**Polyhedral Contraction of $[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]^-$. Preparation of $[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)]$ (VI).** A solution of $[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})\text{-}Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]$ (1.0 g, 2.6 mmol) and $FeCl_3$ (5.0 g, 31 mmol) in ethanol (100 ml) was heated to reflux for 3.5 hr. After this time the reaction mixture was poured into water (500 ml) and the resulting aqueous phase extracted with dichloromethane (2 × 200 ml). The dichloromethane was then evaporated under reduced pressure, and the resulting oil was redissolved in a little acetone–ethanol. A dilute aqueous solution of tetramethylammonium chloride was added and the mixture once again extracted with dichloromethane. The dichloromethane extract was stripped onto silica gel (*ca.* 40 ml) which was then mounted on a silica gel column (300 ml). Elution with dichloromethane developed a red band which was collected and stripped to dryness. The residue was redissolved in acetone and treated with a solution of tetramethylammonium chloride in aqueous ethanol. Evaporation of the acetone under reduced pressure precipitated the red product (110 mg, 11%) which was recrystallized from dichloromethane–chloroform. *Anal.* Calcd for $C_8H_{32}NB_{16}Co$: C, 25.68; H, 8.56; N, 3.75; B, 46.23; Co, 15.78. Found: C, 25.56; H, 8.41; N, 4.04; B, 46.52; Co, 15.58.

**Thermal Rearrangement of $[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)]^-$ (VI). Preparation of $([CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})\text{-}Co(\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9)]$ (VII).** A solution of $[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)]$ (100 mg, 0.29 mmol) in anisole (20 ml) was heated to reflux for 50 hr. After this time the bulk of the solvent was evaporated under reduced pressure and the residue purified using preparative thick layer chromatography with dichloromethane eluent. Only one major band separated, and this was extracted into dichloromethane–acetonitrile which was then evaporated under reduced pressure. The residue was redissolved in acetone and treated with a solution of tetramethylammonium chloride in aqueous ethanol. Evaporation of the acetone precipitated the fawn product (90 mg, 90%) which was recrystallized from dichloromethane–chloroform. *Anal.* Calcd for $C_8H_{32}NB_{16}$-Co: C, 25.68; H, 8.56; N, 3.75; B, 46.23; Co, 15.78. Found: C, 25.48; H, 8.55; N, 3.97; B, 45.93; Co, 15.49.

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# Ligand Protonation and Rates of Ligation with Nickel(II)

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**Abstract:** The rate constants have been determined for the reaction of a number of ligands and their protonated forms with $Ni(H_2O)_6^{2+}$ and $NiNTA(H_2O)_2^-$. These include imidazole and derivatives, bipyridine, phenanthroline and derivatives, cysteine and penicillamine, chelidamic acids, and pyridine-2-aldoxime. Varying effects of proton attachment to a ligand on its reactivity have been found. The lowered reactivity of hydroxy derivatives of pyridine and phenanthroline is ascribed to the predominance of the pyridone tautomer in solution and the results are assessed on this basis.

The complexing of nickel continues to be studied as representative of the behavior of labile octahedral complexes, and the general results so far obtained have been summarized.[1,2] We previously studied the kinetics of formation of mono complexes of nickel(II) with a variety of ligands including amino acids, peptides, and polyamino- and pyridinecarboxylates.[3] We drew attention to the unreactivity of the zwitterion

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Table I. Kinetic Data for the Formation of Nickel(II) Mono Complexes at 25° and Ionic Strength 0.30 $M$

| Reacting form of ligand | Ligand abbrev | p$K^a$ | $k$, $M^{-1}$ sec$^{-1}$ | Lit. value |
|---|---|---|---|---|
| With $Ni^{2+}$ | | | | |
| Imidazole | imid | 7.1 | $6.4 (\pm 0.5) \times 10^3$ | $3.2 \times 10^{3}$ [c]; $5.0 \times 10^{3}$ [b] |
| $imidH^+$ | | | $2.0 (\pm 2.0) \times 10^2$ | $4.0 \times 10^{2}$ [c] |
| 4(5)-Imidazoleacetate | imac | 3.2, 7.4 | $7.3 (\pm 0.7) \times 10^3$ | |
| imacH | | | $2.0 (\pm 2.0) \times 10^2$ | |
| Histamine | $hisNH_2$ | 6.1, 9.8[d] | $6.0 (\pm 0.5) \times 10^5$ | |
| $hisNH_3^+$ | | | $2.0 (\pm 0.5) \times 10^2$ | |
| L-Histidine | his | 6.1, 9.2 | $3.8 (\pm 0.4) \times 10^5$ | |
| hisH | | | $1.2 (\pm 0.2) \times 10^3$ | $2.2 \times 10^{3}$ [c] |
| $hisH_2^+$ | | | ~0 | ~0[c] |
| L-$^-SCH_2CH(NH_2)COO^-$ | cys | 8.3, 10.5[e] | | $2.0 \times 10^{5}$ [f] |
| $cysH^-$ [g] | | | $4.0 (\pm 0.4) \times 10^4$ | $1.5 \times 10^{4}$ [f] |
| $cysH_2$ | | | $3.5 (\pm 1.0) \times 10^2$ | |
| DL-$HSC(CH_3)_2CH(NH_2)COO^-$ | $penH^-$ [g] | 8.0, 10.7[e] | $2.2 (\pm 0.3) \times 10^4$ | |
| $penH_2$ | | | $3.5 (\pm 1.0) \times 10^2$ | |
| 2,2′-Bipyridine | bipy | 4.4 | $2.0 (\pm 0.1) \times 10^3$ | $1.5 \times 10^{3}$ [h,k] |
| $bipyH^+$ | | | $25 \pm 3$ | |
| 1,10-Phenanthroline | phen | 5.0 | $3.5 (\pm 0.2) \times 10^3$ | $3.0 \times 10^{3}$, [h,k] $4.2 \times 10^{3}$ [i] |
| $phenH^+$ | | | $3.0 \pm 1.0$ | 3.0[i] |
| 2,2′,2″-Terpyridine | terpy | 3.3, 4.7 | $2.1 (\pm 0.2) \times 10^3$ | $1.4 \times 10^{3}$ [h,k] |
| $terpyH^+$ | | | $90 \pm 10$ | |
| $terpyH_2^{2+}$ | | | $0.5 \pm 0.5$ | |
| Phenanthroline-2-carboxylate | phencarb | 4.0[j] | $2.5 (\pm 0.3) \times 10^4$ [k] | |
| phencarbH | | | $70 \pm 15$ | |
| 4-$O^-$,7-hydroxyphenanthroline (IV, X = $O^-$) | diOHphen | 7.3, 11.5 | ~20[l] | |
| 4,7-Dihydroxyphenanthroline (IV, X = OH) | | | $0.5 \pm 0.5$ | |
| 4-OH-pyridine-2,6-dicarboxylate | $chelH^{2-}$ | 3.1, 10.9[m] | $1.7 (\pm 0.3) \times 10^2$ [n] | |
| $chelH_2^-$ | | | $60 \pm 20$ | |
| Pyridine-2-aldoxime | pald | 3.5 | $1.3 (\pm 0.2) \times 10^3$ [n] | |
| $paldH^+$ | | | $2.0 (\pm 2.0) \times 10^2$ | |
| With $NiNTA^-$ | | | | |
| bipy | | | $2.4 (\pm 0.1) \times 10^3$ [n] | |
| $bipyH^+$ | | | $1.0 (\pm 0.1) \times 10^2$ | |
| phen | | | $3.6 (\pm 0.2) \times 10^3$ [n] | |
| $phenH^+$ | | | ~0 | |
| en | | 7.5, 10.5 | $7.0 \times 10^3$ | |
| $enH^+$ | | | $3.5 \times 10^3$ | |
| $enH_2^{2+}$ | | | ~0 | |

[a] Values taken from L. G. Sillen and A. E. Martell, Ed., *Chem. Soc., Spec. Publ.*, No. 17, (1964). except where noted. Conditions chosen close to those of kinetic experiments. [b] G. G. Hammes and J. I. Steinfeld, *J. Amer. Chem. Soc.*, **84**, 4639 (1962). [c] J. E. Letter, Jr., and R. B. Jordan, *Inorg. Chem.*, **10**, 2692 (1971), but see Discussion. [d] W. J. Eilbeck F. Holmes, and T. W. Thomas, *J. Chem. Soc. A*, 113 (1969). [e] D. D. Perrin and I. G. Sayce, *ibid.*, 53 (1968). [f] G. Davies, K. Kustin, and R. F. Pasternack, *Trans. Faraday Soc.*, **64**, 1006 (1968). [g] Mixture of SH and $NH_3^+$ forms. [h] R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **4**, 929 (1965); **5**, 622 (1966). [i] M. L. Sanduja and W. M. Smith, *Can. J. Chem.*, **47**, 3774 (1969). [j] This work, spectral determination. [k] Directly obtained at neutral pH. [l] This value approximate since p$K$'s used in its estimation refer to 50% v/v dioxane/$H_2O$ and the values will probably be 0.2–0.3 unit higher in $H_2O$ (B. R. James and R. J. P. Williams, *J. Chem. Soc.*, 2007 (1961)). [m] G. Anderegg, *Helv. Chim Acta*, **46**, 1011 (1963). [n] From pH profile and direct determination.

form of the ligand and ascribed the reactivity of the monoprotonated forms of pyridine-2-carboxylate and pyridine-2,6-dicarboxylate to the presence of small amounts of the nonzwitterionic form with the proton associated with the carboxylate group.

The present paper describes the complexing of nickel(II) with an additional 13 ligands, over a range of pH. These ligands and their abbreviations are shown in Table I. They were chosen to show a variety of behavior on protonation so as to amplify and extend previous conclusions, show up possible new effects, and in certain cases use the results to shed light on the structure of the protonated form. The bulk of the study was with $Ni^{2+}$ ion, but the kinetics of reaction of the nickel(II) complex of nitrilotriacetate (presumed Ni(NTA)$(H_2O)_2^-$) with a number of ligands were also included, so as to assess the effect of presenting a charge on the metal opposite to that of the protonated form.

## Experimental Section

**Materials.** Most of the ligands used were highest quality commercial products and were used without treatment. Chelidamic acid, 4,7-dihydroxyphenanthroline, and pyridine-2-aldoxime were purified by recrystallization.[4] Phenanthroline-2-carboxylate was prepared according to the method of Corey, *et al.*,[5,6] and had mp 207° (lit.[5] 209–211°).

**Kinetic Experiments.** All the reactions were followed in a stopped-flow apparatus using the general approach outlined previously.[3] The reaction of $Ni^{2+}$ with a number of ligands was followed directly: cys (400 nm), pen (400 nm), bipy (310 nm), terpy (305 nm), phen (315 nm), phencarb (280 nm), diOHphen (280 nm), chel (280 nm), and pald (300 nm), as was the reaction of $NiNTA^-$ with bipy (305 nm), phen (280, 295 nm), and en (250 nm). In these cases, 5 ×

(4) E. Blasius and B. Bronzio, *Z. Anal. Chem.*, **192**, 364 (1963), chel; A. A. Schilt, G. F. Smith, and A. Heimbuch, *Anal. Chem.*, **28**, 809 (1956), phencarb; and G. Lenart, *Ber.*, **47**, 808 (1914), pald.

(5) E. J. Corey, A. L. Borror, and T. Foglia, *J. Org. Chem.*, 30, 288 (1965).

(6) K. G. Claus and J. V. Rund, *Inorg. Chem.*, **8**, 59 (1969).

**Table II.** Kinetic Data

| Ligand | $[Ni^{2+}]$, $M$ | pH | $10^{-3}$ $k_{obsd}$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|
| imid | 0.01 | 6.9 | 2.5 |
| | 0.01 | 6.7 | 1.8 |
| | 0.01 | 6.5 | 1.7 |
| | 0.05 | 6.5 | 1.4 |
| | 0.10 | 6.5 | 1.4 |
| | 0.01 | 6.4 | 1.5 |
| | 0.10 | 5.9 | 0.5 |
| imac | 0.01 | 7.0 | 2.5 |
| | 0.01 | 6.8 | 1.3 |
| | 0.01 | 6.8 | 1.7 |
| | 0.01 | 6.6 | 0.93 |
| | 0.01 | 6.3 | 0.65 |
| | 0.10 | 6.0 | 0.53 |
| $hisNH_2$ | 0.10 | 6.9 | 0.85 |
| | 0.025 | 6.6 | 0.36 |
| | 0.05 | 6.6 | 0.50 |
| | 0.10 | 6.6 | 0.45 |
| | 0.10 | 6.2 | 0.20 |
| | 0.10 | 5.9 | 0.09 |
| his | 0.01 | 6.9 | 2.6 |
| | 0.01 | 6.5 | 1.3 |
| | 0.01 | 5.9 | 0.51 |
| | 0.10 | 5.9 | 0.56 |
| chel | 0.005 | 5.2 | 0.17 |
| | 0.005 | 4.5 | 0.18 |
| | 0.005 | 3.7 | 0.16 |
| | 0.025 | 3.0 | 0.096 |
| | 0.05 | 3.0 | 0.092 |
| | 0.05 | 2.9 | 0.10 |
| | 0.05 | 2.7 | 0.090 |
| cys | 0.01 | 7.0 | 2.6 |
| | 0.01 | 6.7 | 1.5 |
| | 0.01 | 6.3 | 0.8 |
| | 0.01 | 6.0 | 0.48[a] |
| | 0.05 | 6.0 | 0.30 |
| | 0.10 | 6.0 | 0.23 |
| pen | 0.025 | 6.9 | 1.9 |
| | 0.05 | 6.45 | 0.9 |
| | 0.10 | 6.05 | 0.7[b] |
| | | | $k_{obsd}$ |
| bipy | 0.01 | 3.1 | 115 |
| | 0.01 | 2.75 | 66 |
| | 0.01 | 2.0 | 31 |
| | 0.10 | 2.0 | 31 |
| | 0.07 | 0.1 $M$[c] | 7.8 |
| | 0.02 | 0.1 $M$[c] | 6.5 |
| | 0.25 | 1.0 $M$[c] | 1.8 |
| terpy | 0.01 | 4.1 | 435 |
| | 0.01 | 3.7 | 200 |
| | 0.01 | 3.05 | 54 |
| | 0.10 | 2.0 | 4.5 |
| | 0.10 | 1.6 | 1.6 |
| | 0.10 | 1.1 | 0.45 |
| phen | 0.01 | 3.0 | 40 |
| | 0.01 | 2.7 | 20 |
| | 0.01 | 2.0 | 5.6 |
| | 0.10 | 2.0 | 6.9 |
| | 0.10 | 1.6 | 4.7 |
| | 0.10 | 0.1 $M$[c] | 2.4 |
| | 0.25 | 1.0 $M$[c] | 0.3 |

| Ligand | $[Ni^{2+}]$, $M$ | pH | $10^{-3}$ $k_{obsd}$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|
| diOHphen | 0.025 | 7.2 | 8.9 |
| | 0.10 | 7.1 | 9.0 |
| | 0.02 | 7.1 | 7.6 |
| | 0.05 | 7.05 | 8.2 |
| | 0.02 | 6.95 | 5.7 |
| | 0.02 | 6.6 | 4.0 |
| | 0.10 | 6.4 | 2.3 |
| | 0.10 | 6.35 | 2.5 |
| | | | $10^{-3}k_{obsd}$ |
| phencarb | 0.002 | 6.5 | 25 |
| | 0.001 | 5.8 | 25 |
| | 0.005 | 2.6 | 1.2 |
| | 0.005 | 2.05 | 0.51 |
| | 0.005 | 1.8 | 0.36 |
| | 0.005 | 1.7 | 0.25 |
| | 0.01 | 1.65 | 0.25 |
| | 0.005 | 1.4 | 0.18 |
| | 0.005 | 1.05 | 0.095 |
| | $[NiNTA^-]$, $M$ | | |
| bipy | 0.013 | 9.5 | 2.5 |
| | 0.0026 | 6.9 | 2.5 |
| | 0.0026 | 3.9 | 0.61 |
| | 0.0047 | 3.7 | 0.45 |
| | 0.0047 | 3.1 | 0.21 |
| | 0.0047 | 3.0 | 0.19 |
| phen | 0.0033 | 9.9 | 3.9 |
| | 0.00065 | 9.7 | 4.3 |
| | 0.0033 | 7.4 | 4.1 |
| | 0.0065 | 4.4 | 0.76 |
| | 0.0065 | 4.0 | 0.31 |
| | 0.0065 | 3.7 | 0.15 |
| | 0.0065 | 2.8 | 0.017 |
| en | 0.001[d] | 11.4 | 8.0 |
| | 0.01[e] | 10.4 | 5.0 |
| | 0.001[d] | 9.9 | 3.5 |
| | 0.001[d] | 8.7 | 3.4 |
| | 0.001[d] | 7.4 | 2.0 |
| pald | 0.05 | 2.4 | 0.070 |
| | 0.005 | 5.2 | 1.7 |
| | 0.005 | 4.3 | 1.3 |
| | 0.005 | 4.0 | 1.0 |
| | 0.005 | 4.0 | 1.2 |
| | 0.005 | 3.5 | 0.70 |

Dissociation of $Ni(imid)^{2+}$

| $[H^+]$, $M$ | [I], $M$ | $k_{obsd}$, sec$^{-1}$ |
|---|---|---|
| 0.001 | 0.3 | 4.1 |
| 0.010 | 0.3 | 4.4 |
| 0.010 | 2.0 | 3.0 |
| 0.05 | 2.0 | 4.5 |
| 0.10 | 2.0 | 6.6 |
| 0.25 | 2.0 | 11 |
| 0.50 | 2.0 | 33 |
| 1.00 | 2.0 | 57 |

[a] This value used in plot. [b] Same value with lower $[Ni^{2+}]$. [c] Concentration of $HClO_4$. [d] Ligand in excess $6 \times 10^{-3}$ $M$ and acts as buffer. [e] [Ligand] = $10^{-3}$ $M$.

$10^{-5}$ $M$ ligand ($10^{-3}$ $M$ cys, pen, or en) was allowed to react with a large excess of $Ni^{2+}$, $10^{-3}$–$10^{-1}$ $M$, and the total ionic strength of 0.3 $M$ was made up with $NaClO_4$. In all the other systems, the reaction was monitored by a small pH change attending the reaction, registered with bromothymol blue indicator, $pK \sim 6.8$, $\lambda$ 620 nm. Enough lutidine buffer was added to control the pH change to *ca.* 0.1 unit. The rates were independent of the concentration of buffer at the constant ionic strength of 0.3 $M$ provided now by $NaNO_3$. In these reactions followed by indicator, $10^{-4}$–$10^{-3}$ $M$ ligand solutions were allowed to react with excess $Ni^{2+}$ ion. No buffers were required for the reactions at low pH. The dissociation of $Ni(imid)^{2+}$ in $HClO_4$–$NaClO_4$ was followed directly at 230 nm ($I$ = 0.3 $M$ and 2.0 $M$). Excellent first-order plots ($k_1$) were obtained, from which the second-order rate constants, $k_{obsd} = k_1[Ni(II)]^{-1}$, were computed. These were the mean of a number of determinations. Except for cysteine, the values of $k_{obsd}$ were independent of [Ni(II)], usually over a 5–10-fold change. In all cases the mono complex was completely formed in the kinetic experiments. This was shown by calculations using known thermodynamic data where available, and by spectral examination of the product, and/or from a linear dependence of $k_1$

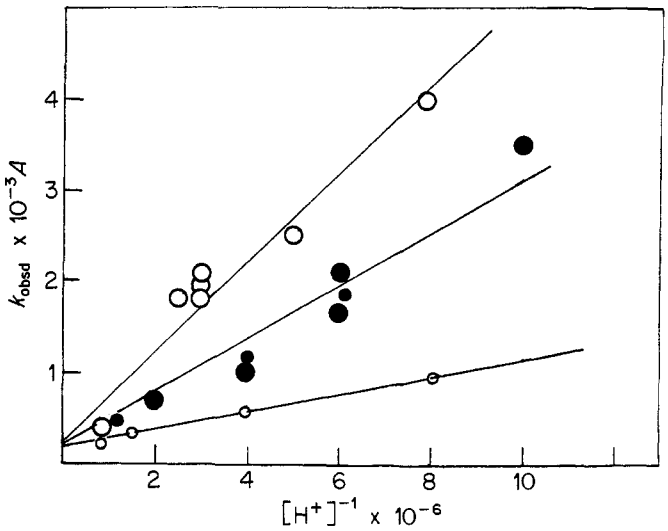



Figure 1. $k_{obsd} \times 10^{-3}A$ as a function of $[H^+]^{-1} \times 10^{-6}$ for the reaction of $Ni^{2+}$ with imidazole (○), imidazoleacetate (●), and histamine (◦). $A = (K_1 + [H^+])/[H^+]$ except for histamine where $A = (K_2 + [H^+])/K_2$.

on [Ni(II)] with zero intercept. All experiments were carried out at 25° and an ionic strength of 0.3 *M*. Typical plots are contained in Figure 1, and the results are collected in Tables I and II.

## Results and Discussion

Consider a monobasic ligand L which is rapidly protonated in the pH region of investigation to $LH^+$ and assume that both forms react with $Ni^{2+}$ ion.[7]

$$LH^+ \rightleftharpoons L + H^+ \qquad K_1 = [L][H^+]/[LH^+]$$

$$L + Ni^{2+} \longrightarrow NiL^{2+} \qquad k_1$$

$$LH^+ + Ni^{2+} \longrightarrow NiL^{2+} + H^+ \qquad k_2$$

It can be easily shown that

$$k_{obsd}\frac{K_1 + [H^+]}{[H^+]} = k_2 + \frac{k_1K_1}{[H^+]} \qquad (1)$$

The appropriate plots[6] yield values from the intercept and slope/$K_1$ for $k_2$ and $k_1$, rate constants for the protonated ($k_2$) and unprotonated ($k_1$), forms, respectively. With a dibasic ligand L the situation is slightly more complicated. In addition to the equilibria or reactions above, we have

$$LH_2^{2+} \rightleftharpoons LH^+ + H^+ \qquad K_2$$

$$LH_2^{2+} + Ni^{2+} \longrightarrow NiL^{2+} + 2H^+ \qquad k_3$$

$$\frac{d[NiL^{2+}]/dt}{[Ni^{2+}]([L] + [LH^+] + [LH_2^{2+}])} = k_{obsd} = \frac{k_1K_1K_2 + k_2K_2[H^+] + k_3[H^+]^2}{K_1K_2 + K_2[H^+] + [H^+]^2} \qquad (2)$$

At low pH, the reaction *via* the free base L may be insignificant, and also $K_1K_2$ is negligible compared with $K_2[H^+]$ and $[H^+]^2$, in which case 3 obtains.

$$k_{obsd}\frac{K_2 + [H^+]}{[H^+]} = k_3 + \frac{k_2K_2}{[H^+]} \qquad (3)$$

If on the other hand, the contribution of the $LH_2^{2+}$ form is ignored, (4) holds, and if $[H^+] > K_1$, (5) is obtained.

$$k_{obsd}\frac{[H^+]^2 + K_2[H^+] + K_1K_2}{K_2[H^+]} = k_2 + \frac{k_1K_1}{[H^+]} \qquad (4)$$

$$k_{obsd}\frac{[H^+] + K_2}{K_2} = k_2 + \frac{k_1K_1}{[H^+]} \qquad (5)$$

The form of equation used will be governed by a consideration of the probable values of $k_1$ or $k_3$, the pH range, and in the final analysis the linearity of the appropriate plots. The rate law can be reconciled with the stepwise mechanism for chelation depicted in (6); charges have been omitted and the case of a monobasic ligand is considered for simplicity. Equilibrium be-

$$\begin{array}{ccccc} M + L\text{-}LH & \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} & M\text{-}L\text{-}LH & & \\ K_1 \downarrow \uparrow + H & & k_{23} \downarrow \uparrow k_{32}\ H & & \\ M + L\text{-}L & \underset{k_{34}}{\overset{k_{43}}{\rightleftharpoons}} & M\text{-}L\text{-}L & \xrightarrow{k_{35}} & M\langle L \\ & & & & L \end{array} \qquad (6)$$

tween the protonated and basic forms of the ligand and of the complexes M-L-LH and M-L-L is considered established rapidly compared with the other processes, *e.g.*, $k_{21}$ or $k_{35}$, which is likely with M = Ni. Ring closure *via* M-L-L is considered more important than *via* M-L-LH, which is certainly the case when L is N< and most likely even when L = O–. Assuming stationary state concentrations for nonchelated complexes

$$\text{rate} = k_{obsd}[M]([L\text{-}L] + [L\text{-}LH]) = \frac{k_{12}k_{23}k_{35}[M][L\text{-}LH] + (k_{21} + k_{23})k_{35}k_{43}[M][L\text{-}L]}{k_{21}k_{32}[H^+] + (k_{35} + k_{34})(k_{23} + k_{21})}$$

Since $[L\text{-}L]/([L\text{-}L] + [L\text{-}LH]) = K_1/(K_1 + [H^+])$ and $[L\text{-}LH]/([L\text{-}L] + [L\text{-}LH]) = [H^+]/(K_1 + [H^+])$

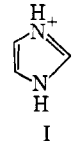
$$\frac{k_{obsd}(K_1 + [H^+])}{[H^+]} = \frac{k_{12}k_{23}k_{35} + k_{23}k_{35}k_{43}K_1[H^+]^{-1}}{k_{21}k_{32}[H^+] + k_{23}(k_{35} + k_{34})} \qquad (7)$$

If $k_{21}k_{32}[H^+] < k_{23}(k_{35} + k_{34})$, which is usually the case (see, however, the discussion of bipy and phen below)

$$k_{obsd}\frac{(K_1 + [H^+])}{[H^+]} = \frac{k_{12}k_{35}}{k_{35} + k_{34}} + \frac{k_{35}k_{43}}{k_{35} + k_{34}}\frac{K_1}{[H^+]} \qquad (8)$$

which is of required form (1) where $k_2 = k_{12}k_{35}/(k_{35} + k_{34})$ and $k_1 = k_{35}k_{43}/(k_{35} + k_{34})$. Whether $k_1$ and $k_2$ are single or composite values will therefore depend on whether $k_{35} > k_{34}$ or $k_{34} > k_{35}$, respectively, a situation which has been frequently discussed in the literature for unprotonated chelating ligands.[1]

**Imidazole.** In principle the protonated form of imidazole (I) could react with $Ni^{2+}$ since it still contains a



I

nonbonded electron pair. It is uncertain from our results whether the appropriate plot (Figure 1) goes through or above the origin. The intercept ($k_{imidH}$-)

(7) The notation of $k_1$ and $k_2$ is reversed from that in ref 3 to ensure continuity with $k_3$.

is unlikely, however, to exceed $2 \times 10^2\ M^{-1}\ sec^{-1}$ and may very well be less. The value for $k_{imid}$ is in reasonable agreement with some early temperature jump data,[8] but much higher than from some recent flow data, at 23.7° and 0.10 $M$ $KNO_3$.[9] Their[9] plot, equivalent to ours (Figure 1), gives a definite intercept ($k_{imidH^+} = 4.0 \times 10^2$) and from the slope, $k_{imid} = 3.2 \times 10^3\ M^{-1}\ sec^{-1}$. However, considerations of the formation constant of Ni(imid)$^+$, $1.9 \times 10^3\ M^{-1}$, and the p$K_a$ of imidH$^+$, show that formation of Ni(imid)$^{2+}$ was incomplete, most serious at their lower pH's (5.90 and 6.28) since they used a lower [Ni$^{2+}$], $1.7 \times 10^{-2}\ M$, than is necessary to drive the reaction to completion. Thus, their first-order rate constant (their $k_{obsd}$[Ni$^{2+}$]) governs an approach to equilibrium and is composite ($= k_f$[Ni$^{2+}$] + $k_r$, where $k_f$ and $k_r$ are the forward and reverse rate constants). We can use the value $k_r = 2.7\ sec^{-1}$ (ref 8, see also below) and calculate true values of $k_f$ from Letter and Jordon data.[9] These new points (Figure 1) decrease the intercept and slightly increase the slope and give $k_{imidH^+} \approx 2 \times 10^2$ and $k_{imid} = 3.5 \times 10^3$. We are still puzzled why the value for the base reactivity is so much less than ours (ionic strength and slight temperature differences will only be a small factor). Considerations below indicate that the reactivity of the protonated form of imidazole must be very small.

We have studied the dissociation of Ni(imid)$^{2+}$ at 25° and $I = 2.0\ M$ over the range $10^{-3}$–$1.0\ M$ $HClO_4$ and find $k_r = 3.0 + 55$[H$^+$]. At $I = 0.3\ M$ the pH-independent value of $k_r$ is $4.1\ sec^{-1}$. In conjunction with the $k_f$ value in the same conditions ($6.4 \times 10^3$) a formation constant of $1.5 \times 10^3\ M^{-1}$ is obtained in good agreement with the literature value of $1.9 \times 10^3\ M^{-1}$.

For the reaction

$$Ni^{2+} + \text{imid } H^+ \rightleftharpoons Ni(\text{imid})^{2+} + H^+ \quad k_f', k_r', K'$$

the value of $k_f' = K'k_r' = 10^{-4} \times 55 = 5 \times 10^{-3}$. Obviously this would appear as an intercept of approximately zero in Figure 1. The value of $k_f'$ may represent the rate constant for reaction of I and the tautomer of I containing the $NH_2^+$ grouping, which is in much smaller concentration.

**Imidazole Derivatives.** Letter and Jordan[9] studied the complexing of Ni$^{2+}$ by histidine and obtained rate constants for the reaction of the mono- and diprotonated forms (Table I). A similar plot of our data gave curvature, however, indicating that with our conditions the nonprotonated form was contributing to the rate. The appropriate plot (5) gave values for the monoprotonated zwitterionic species and nonprotonated (single negatively charged) forms on the reasonable assumption that the diprotonated did not react[9] (Table I). The high rate constant for histamine and histidine recall a similar estimated value for ethylenediamine ($4 \times 10^4\ M^{-1}\ sec^{-1}$ at 0°)[10] and so for all these diamines an internal conjugate base mechanism[11] may be operative. The value for imidazoleacetate (imac) is quite close to that for β-alanine ($1.0 \times 10^4\ M^{-1}\ sec^{-1}$),[12] and for both some steric control may be operative.[12] In both cases six-membered chelate rings are formed. The plots for imac are poor with much larger scatter than is usual.

hisH and hisNH$_3^+$ in which the proton is associated with a terminal $NH_2$ group have reactivities similar (allowing for charge differences) to that of $NH_2CH_2$-$CH_2NH_3^+$ ($6 \times 10^2\ M^{-1}\ sec^{-1}$)[3] showing that coordination to the imidazole residue is an effective (and necessary) first step in the chelation process. However, imacH in which the proton is attached to the imidazole appears to have little reactivity and resembles the normal behavior of the zwitterion forms of aminocarboxylates.[3]

A slow reaction following chelation of histidine has been reported.[9] We also observed this but found the two rates more pronounced with histamine. Since we checked that the fast reaction was second order and was accompanied by the release of the correct amount of protons for chelation, the slower reaction is less germane to the present topic. However, the rate of the slow reaction was independent of [Ni$^{2+}$] and little dependent on pH, 6.5–7.0 ($k \sim 2.0\ sec^{-1}$). It is ascribed to formation of small amounts of the hydroxy complex Ni(his)$(OH_2)_3OH^+$.

**Sulfur-Containing Amino Acids.** Nickel complexing with cysteine (cys) and penicillamine (pen) was studied in a pH range 6–7. Here the dominant ligand species is the diprotonated form, and only contributions to the rate from the di- and monoprotonated forms need be considered. At low concentrations of nickel (1–10 m$M$), the reaction between nickel and cysteine is first order in metal and ligand concentrations, and these conditions were used to collect the data in Table I. At higher concentrations of nickel (>10 m$M$), deviations from overall second-order behavior were observed. These deviations were considered to arise from the formation of polynuclear species, for which there is ample evidence.[13] This idea was strongly supported by the results of a study of the Ni–penicillamine system. Polynuclear complexes are not observed with the latter, probably because the methyl groups prevent bridging of nickel ions by sulfur atoms. Consistent with this, second-order kinetics were observed with this ligand over a reasonable range of metal ion concentrations.

Davies, *et al.*,[14] studied the kinetics of complexing of Ni(II) with L-cys at 20° and $I = 0.1\ M$ using the temperature jump method. They obtained rate constants for the free base, $^-SCH_2CH(NH_2)COO^-$ ($2 \times 10^5$), and the monoprotonated form ($1.5 \times 10^4\ M\ sec^{-1}$) since they worked at pH's higher than 7. Our value for the monoprotonated form ($4.0 \times 10^4\ M^{-1}\ sec^{-1}$ at 25°, $I = 0.3\ M$) is consistent with theirs. This form is a tautomeric mixture of $HSCH_2CH(NH_2)$-$COO^-$ and $^-SCH_2CH(NH_3^+)COO^-$ in about equal amounts. We would *guess* that the former might be expected to make the major contribution to the rate in view of the results for the diprotonated form cysH$_2$, $HSCH_2CH(NH_3^+)COO^-$. The ability of the SH group

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

(9) J. E. Letter, Jr., and R. B. Jordan, *Inorg. Chem.*, **10**, 2692 (1971). Further experiments have confirmed the earlier results at higher pH values, and the differences in our rate constants for the imid persist (Dr. Jordan, private communication).

(10) M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, No. **49**, 55 (1965).

(11) D. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966).

(12) K. Kustin, R. F. Pasternack, and E. M. Weinstock, *J. Amer. Chem. Soc.*, **88**, 4610 (1966).

(13) D. D. Perrin and I. G. Sayce, *J. Chem. Soc. A*, 53 (1968).

(14) G. Davies, K. Kustin, and R. F. Pasternack, *Trans. Faraday Soc.*, **64**, 1006 (1968).

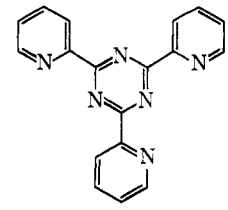
to complex with Ni(II) is shown by the value of the rate constant for $cysH_2$ ($3.5 \times 10^2$), much higher than that of $dapH_2^+$, $^+NH_3CH_2CH(NH_3^+)COO^-$ ($\sim 0$).[3] Unfortunately we cannot compare the results with $NH_2CH_2CH(NH_3^+)COO^-$ since this is not the predominant tautomer of dapH. The rate constant, $3.5 \times 10^2$ $M^{-1}$ $sec^{-1}$, is about five times smaller than the value for similar type neutral ligands and close to that of $NH_2CH_2CH_2NH_3^+$ ($6 \times 10^2$ $M^{-1}$ $sec^{-1}$) suggesting that the Ni–SH bond is rather labile with its bond rupture and subsequent ring closure rate constants comparable.

The results with pen are quite similar to those of cys and suggest that the *gem*-dimethyl groups play little role in the chelation mechanism.

**Bipyridine, Phenanthroline, and Derivatives.** The complexing of Ni(II) by unprotonated bipy, phen, and terpy was previously studied by flow methods in neutral pH.[15] The closeness of the rate constants to that of pyridine was used as support for $k_{35} \gtrsim k_{34}$ in (6). The value for phencarb from the present study, some sevenfold larger than for phen, is also consistent with the expected effect of a negative charge at the reaction site of the ligand.

The rate–pH profile for these ligands enables us to determine the rate constants for reaction of the protonated forms. We shall consider first the unsubstituted heterocyclics (Table I). All the protonated forms react more slowly than might be anticipated.[16] Equation 8 and the considerations above show that this must arise from the value of $k_{12}$, the rate constant for the formation of the first Ni–N bond, and not as a result of subsequent steps. The decreasing rate constants in the order $terpyH^+ > bipyH^+ > phenH^+ > terpyH_2^{2+}$ reflect increasing blocking action of the proton, and increased positive charge of the ligand, toward the metal ion. Both effects can lead to anomalous (low) values for $K_o$ and/or $k_o$.[16]

The preferred structure of $terpyH^+$ on the basis of uv spectra[17] shows protonation of nitrogen in a terminal ring, so that $terpyH^+$ can be considered as a bipyridine substituted in the 2 position by a charged substituent. The rate constant ($90$ $M^{-1}$ $sec^{-1}$) is only slightly less than might be anticipated on such a basis. The nearly ten times larger rate constant for reaction of $bipyH^+$ compared to $phenH^+$ suggests that these have different structures. A cis conformation for $bipyH^+$ with pyridine rings slightly twisted is preferred to a trans conformation on spectral evidence.[17] Our results indicate that this twisting is sufficient to allow approach of nickel ion to the nitrogen center much more easily than with $phenH^+$ where twisting in the cis conformation is not possible.[18] The very small rate constant for reaction of $terpyH_2^{2+}$ ($<0.5$ $M^{-1}$ $sec^{-1}$) probably arises from very unfavorable charge as well as steric hindrance considerations. The cis–cis conformation has been assigned to $terpyH_2^{2+}$ on the basis of spectral data.[17] The terminal rings containing the protons are probably twisted slightly in opposite directions and in this conformation the protons effectively block the lone free nitrogen. An interesting comparison of these results with complexing by TPTZ (II), $TPTZH^+$, and $TPTZH_2^{2+}$ can be made. The rate



II

constants for reaction with $Ni^{2+}$ at 25° are $2.0 \times 10^3$, $1.7 \times 10^3$, and $\sim 10$ $M^{-1}$ $sec^{-1}$, respectively.[19] The rate constants for the protonated forms are much higher than the corresponding terpy forms to which they are obviously related structurally. Monoprotonation has hardly any effect on the rate. Diprotonation locks three of the rings in cis–cis conformation and this (as well as the 2+ charge) reduces the rate constant for $TPTZ(H_2)^{2+}$. It is, however, more reactive than $terpyH_2^{2+}$.

Finally, some remarks about the complexing of bipy and phen in high acid concentration may be made. At $(H^+) \gtrsim 5 \times 10^{-2}$ $M$ one would anticipate a limiting value for $k_{obsd}$ equal to the value for the protonated form since it can be shown that here the contribution of the basic form is negligible. This is not observed, however, and this behavior is ascribed to the condition $k_{21}k_{32}[H^+] \gtrsim k_{23}(k_{35} + k_{34})$ in eq 7 which in the limit would lead to ($[H^+] \gg K_1$)

$$k_{obsd}[H^+] = \frac{k_{12}k_{23}k_{35}}{k_{21}k_{32}} + \frac{k_{23}k_{35}k_{43}}{k_{21}k_{32}}\frac{K_1}{[H^+]} \qquad (9)$$

The condition specified is not unreasonable at high $[H^+]$. Second protonation of bipy and phen is difficult[20] so that M–L–LH is likely to be a very strong acid and $k_{32} \approx k_{23}$. The value of $k_{21}$ will not be much less than $k_{35}$ and is larger than $k_{34}$. This complex behavior was observed for the formation and dissociation of $Ni(phen)^{2+}$ ion some years ago.[21]

The relatively high rate constant for reaction of phenanthrolinecarboxylic acid (phencarbH) and the low rate constant for the hydroxyphenanthrolines can be understood in terms of ligand structure. If the zwitterion form of phencarbH is associated with a rate constant $\sim 3$ $M^{-1}$ $sec^{-1}$, then 3% of the nonzwitterionic form (III) reacting with a rate constant $\sim 3 \times 10^3$ $M^{-1}$ $sec^{-1}$ accounts for the observed rate constant of 70 $M^{-1}$ $sec^{-1}$ for the tautomeric mixture.

Anomalous behavior of 4,7-dihydroxyphenanthroline as a complexing ligand has been observed previously

(15) R. M. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, 4, 729 (1965); **5**, 622 (1966).

(16) On the basis of the equation $k_f = K_o k_o$, where $K_o$ is the outer sphere association constant and $k_o$ is the rate constant for breakdown of the outer sphere to inner sphere complex: M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 107 (1962).

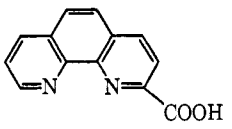
(17) K. Nakamoto, *J. Phys. Chem.*, **64**, 1420 (1960).

(18) Using known formation constants for $Ni(phen)^{2+}$ and $Ni(bipy)^{2+}$ and the $pK_a$ of the ligands, one can estimate the rate laws for dissociation as $-d[Ni(phen)^{2+}]/dt = 9 \times 10^{-6}[Ni(phen)^{2+}] + 7.5 \times 10^{-4}[Ni(phen)^{2+}][H^+]$ and $-d[Ni(bipy)^{2+}]/dt = 6.6 \times 10^{-5}[Ni(bipy)^{2+}] + 20 \times 10^{-3}[Ni(bipy)^{2+}][H^+]$. These data are in reasonable agreement with dissociative data from $^{63}Ni^{2+}$ exchange experiments at pH 1.1–1.3 and 25°: R. G. Wilkins and M. J. G. Williams, *J. Chem. Soc.*, 4514 (1957); P. E. Ellis and R. G. Wilkins, unpublished results. The dissociation of metal–bipyridine complexes is commonly more pH dependent than that of the corresponding phenantholine complex.

(19) T. S. Roche and R. G. Wilkins, unpublished results.

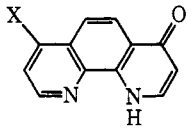
(20) The $pK_{LH_2^{2+}}$ values are $-0.52$ and $-1.55$ for L = bipy and phen, respectively: O. T. Benfey and J. W. Mills, *J. Amer. Chem. Soc.*, **93**, 922 (1971), and references therein.

(21) D. W. Margerum, R. I. Bystroff, and C. V. Banks, *ibid.*, **78**, 4211 (1956).



III

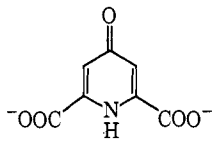
and ascribed to the dominance of the pyridone form.[22] Thus, IV is the important form of the mono (X = O⁻)



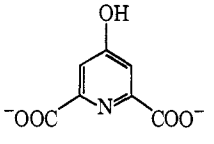
IV

or di (X = OH) protonated forms,[23] and it is anticipated that this will be as unreactive as phenH⁺. The rate constants observed (20 and ~0.5) indicate very small and decreasing contribution from the nonpyridone tautomer to the rate.

**Pyridine Derivatives.** The monoprotonated form of the chelidamate ion (chel³⁻) exists predominantly as the pyridone form (V) rather than the tautomer (VI), from

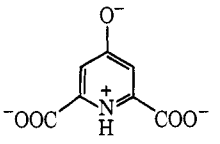


V

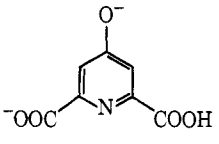


VI

consideration of p$K$ and uv spectra.[24] Form V would be expected to be quite unreactive, considering that a zwitterion canonical form (VII) would make an important contribution.[25] If a rate constant is assigned to VI similar to that for pyridine-2,6-dicarboxylate ($6.3 \times 10^4$), then the observed rate constant ($1.7 \times 10^2$) for the tautomeric mixture would be due to 0.3% VI. If a reactive form (VIII) was also present, then <0.3% VI would be necessary to explain the results.



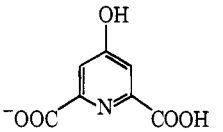
VII



VIII

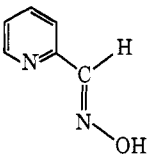
Although there have been determinations of the tautomeric ratio for a number of hydroxypyridines,[26] these do not include chelidamic acid. In 4-hydroxypyridine the ratio is $2 \times 10^3$ in favor of the pyridone form.[25,26] Substitution in the pyridine ring does not usually affect this ratio markedly[26] although it is difficult to assess the effect of two adjacent carboxylate groups. Our ratio of $\geq 4 \times 10^2$ (NH/OH form) appears a reasonable value.

ChelH₂⁻ exists as 4-hydroxypyridinium-2,6-dicarboxylate. We explained the reactivity of the monoprotonated form of pyridine-2,6-dicarboxylate (pydicH⁻) as due to ~25% of the nonzwitterion tautomer.[3] If this is the correct explanation, the reduced reactivity of chelH₂⁻ compared with pydicH⁻ could arise from a much smaller percentage (~0.2%) of the nonzwitterion form (IX). It is uncertain whether the ligand retains the form V or VI in the metal complex.[27]



IX

Pyridine-2-aldoxime exists predominantly as the enol form of syn configuration X coexisting with only



X

about 0.01% of the zwitterion N–H tautomer.[28] This behavior contrasts sharply with the hydroxypyridines. It is therefore not surprising that the rate constants for reaction of pald and paldH⁺ are of the expected order for a neutral bidentate ligand and a protonated pyridine, respectively.

**Reactions of NiNTA(H₂O)₂⁻.** NTA = $N(CH_2COO)_3^{3-}$ is a tetradentate ligand in the nickel complex since the formation constant is much higher than for $Ni(NH(CH_2COO)_2)^{2-}$.[29] There is rapid interchange of the three carboxyl groups among the octahedral coordination sites judging from pmr studies.[30,31] The two coordinated waters occupy cis positions, thus presenting no steric problems to an incoming bidentate ligand. The rate constant for reaction 10 is similar to

$$NiNTA(H_2O)_2^- + NH_3 \rightleftharpoons NiNTA(H_2O)NH_3^- + H_2O \quad (10)$$

that for replacement of $H_2O$ by $NH_3$ in $Ni(H_2O)_6^{2+}$, $4.6 \times 10^3$ and $2.8 \times 10^3$ $M^{-1}$ sec$^{-1}$ at 25° and $I$ = 0.25 $M$.[32] In agreement with this, the rate constants for reaction of NiNTA⁻ and Ni²⁺ with phen and bipy are close with, once again, the rate constant for phen the higher. The difference between bipyH⁺ and phenH⁺ (the electrostatic effect is now favorable) is accentuated, showing some 100-fold or more difference in their rate constants for reaction with NiNTA⁻. The strong resistance to the breakdown of the phenH⁺ structure is thus dramatically shown.

The reaction of NiNTA⁻ with en and enH⁺ shows very interesting features. The rate constant for the neutral ligand is only a little higher than that obtained for ammonia and indicates that no special mechanism needs to be invoked as is the case with the reaction of Ni²⁺ with en.[11] The internal conjugate base mechanism[11] relies on similar protonation constants for Ni$(H_2O)_6^{2+}$ and enH⁺, and this relation probably does not persist with $NiNTA(H_2O)_2^-$ and enH⁺. The favorable

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charge product for the reaction of $NiNTA^-$ with $enH^+$ still only produces a rate constant similar to that for the reaction with the neutral $NH_3$.

### General Conclusions

We see in this and related work of a number of investigators some ways in which a proton attached to a ligand can affect the rate of metal complexing. If it is far removed from potential reaction sites, as in $TPTZH^+$, it has little effect. Often its role may be solely one of increasing the positive charge and decreasing the outer sphere association constant as in the reaction with $Ni^{2+}$. The proton may play a much more significant role by blocking the reaction site as in $bipyH^+$ and particularly $phenH^+$. Intramolecular hydrogen bonding may be more important in the latter because of the rigidity of phen, or there may be present an even more stable structure involving hydrogen bonding *via* a water molecule bridging the phenanthroline nitrogens.[33] The latter idea has not, however, been supported by recent work.[34] The lack of reactivity of these protonated forms, as well as of the zwitterions,[3] may reside in a reduced value for $K_o$ and/or $k_o$ in the Eigen mechanism.[16] One effect of protonation which apparently does not show up in our studies is the incidence of proton loss from a protonated intermediate being rate determining. This will rarely be the case with the slower reacting nickel (except perhaps in its reaction with the enol form of β-diketones[35]) but may be quite important in the reactions with very labile ions, such as Cu(II) ions.[19,36,37] Finally, protonation may lead to a radical structural change with the production of a unreactive tautomer, as in the hydroxy derivatives of pyridine and phenanthroline, typified by chelidamic acid and 4,7-dihydroxyphenanthroline.

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# Cesium Tetrachlorocuprate. Structure, Crystal Forces, and Charge Distribution

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**Abstract:** The crystal and molecular parameters of cesium tetrachlorocuprate have been refined using an X-ray diffraction intensity data set. The crystal system is orthorhombic, space group *Pnam*, with four formula weights per unit cell; the unit cell parameters are $a = 9.7599$ (12), $b = 12.3967$ (12), and $c = 7.6091$ (9) Å. A total of 1786 independent reflections were used in least-squares refinement of the molecular parameters, leading to a final $R$ factor (on $F$) of 5.5%. The anion has crystallographically imposed $m$ symmetry and the three independent copper–chlorine bond lengths are 2.244 (4), 2.235 (4), and 2.220 (3) Å. The crystal forces acting upon the bonds within the anion were calculated, and after correction for their effects and for thermal motion the copper–chlorine bond length in an isolated anion is 2.283 Å. The charge distribution within the anion is estimated to be $[Cu^{0.60}(Cl^{-0.65})_4]^{2-}$ and this was compared with results obtained from semiempirical molecular orbital calculations. A normal coordinate analysis of the vibrational spectrum was performed, and there was good agreement between the force constant derived in this way and that derived from the structural results. Similar crystal force calculations were carried out using reported parameters for salts of the pentachlorocuprate anion, and it was concluded that there would be very little difference between the axial and equatorial copper–chlorine bond lengths in the absence of crystal forces.

The structure of cesium tetrachlorocuprate has been determined approximately using a limited X-ray diffraction data set[1] and the reported parameters have been refined by difference syntheses.[2] The anion has an unusual geometry in that coordination around the metal is intermediate between square planar and tetrahedral. The symmetry of the anion in the lattice closely approximates $D_{2d}$, and the extent of the flattening from $T_d$ symmetry can be judged from the magnitude of the two angles greater than the tetrahedral angle. In cesium tetrachlorocuprate this angle ($\alpha$) was reported to be about 124°, whereas in other salts of the anion[3] $\alpha$ is considerably larger (~130°); the possible significance of this difference is important, particularly as at least one empirical model for the bonding in this anion is expressed as a function of this angle.[4] To clarify this point, the structural parameters of cesium tetrachlorocuprate have been determined accurately using X-ray diffraction data collected using a four-circle diffractometer.

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