the minor orientation here has only about half the occupancy as did the minor orientation in the $Re_2Cl_8^{2-}$ case. Thus, the values for the Re–C bond length and the Re–Re′–C angle found in the major orientation are taken to be the "best" values, just as for the Re–Re′ bond distance.

It should be noted that no occupation of the third possible orientation of $Re_2Me_8^{2-}$ is observed. This is readily understood because in this case the Li^+ ions would have to be over basal edges of the $Re_2Me_8^{2-}$ parallelepiped, or else be disordered too. There is no indication of any electron density at the positions appropriate to such a minor set of Li^+ ions.

Interpretation of the Eclipsed Configuration in $M_2X_8{}^{n-}$ Species. In the earliest publications[2,3] describing the evidence for, and the nature of, the quadruple bond, the eclipsed configuration of $Re_2Cl_8^{2-}$ was invoked as evidence for the δ component of the bonding. It was proposed that nonbonded repulsions (Cl···Cl) would favor a staggered configuration and that only a δ component to the metal–metal bond could oppose this tendency by favoring an eclipsed configuration. This argument is in principle correct, but its forcefulness is diminished because the chlorine atom has a relatively small van der Waals radius. The same reasoning, when applied to species such as $Re_2Br_8^{2-}$ and $Re_2(CH_3)_8^{2-}$, is more cogent, since the Br and CH_3 groups have larger packing radii.

It is even more useful to examine the entire van der Waals energy curve for Cl···Cl, Br···Br and $CH_3\cdots CH_3$ in relation to this problem. In Figure 3 these curves, according to the equations of Mason and Kreevoy,[19] are shown. Also indicated on the plot are the values, or small ranges of values, for the X···X distances that have been observed experimentally in $M_2X_8{}^{n-}$ species with D_{4h} configurations. It is evident that while the Cl case may be near the minimum in the Br and, especially, the CH_3 cases, the eclipsed configuration puts the X···X distances well into the repulsive region. Thus, the occurrence of the eclipsed configuration must be taken as evidence that the δ component of the quadruple bond is strong enough to overcome significant nonbonded repulsion effects.

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Supplementary Material Available: A listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Texas A&M University; (b) Imperial College of Science and Technology.

(2) F. A. Cotton et al., *Science*, **145**, 1305 (1964).

(3) F. A. Cotton, *Inorg. Chem.*, **4**, 334 (1965); *Chem. Soc. Rev.*, **4**, 27 (1975).

(4) J. Krauss, G. Marx, and G. Schodl, *J. Organomet. Chem.*, **21**, 159 (1970).

(5) F. A. Cotton, J. M. Troup, T. R. Webb, D. H. Williamson, and G. Wilkinson, *J. Am. Chem. Soc.*, **96**, 3824 (1974).

(6) K. Mertis and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, in press.

(7) J. F. Gibson, K. Mertis, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, in press.

(8) M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *Inorg. Chem.*, **7**, 1570 (1968).

(9) The following programs were used on IBM 360 and PDP 11 computers: DATARED by Frenz for data reduction; FOURIER by Robinson and Dellaca and based on Zalkin's FORDAP; NUCLS, a full-matrix least-squares program by Ibers and Doedens based on Busing and Levy's ORFLS program; a modified version of SADIAN by Bauer for calculating atomic distances and angles; PERFACT by Frenz for analyzing structure factors and weighting schemes; ORTEP by Johnson for illustrations; the function and error program ORFFEE by Busing, Martin, and Levy as modified by Brown, Johnson, and Thiessen; LIST by Snyder for listing data.

(10) J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **8**, 7 (1969).

(11) F. A. Cotton, B. A. Frenz, B. R. Stults, and T. R. Webb, *J. Am. Chem. Soc.*, **98**, 2868 (1976).

(12) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1971).

(13) D. T. Cromer and J. T. Waber, "International Tables for Crystallography", Vol. IV, 1974.

(14) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(15) A copy of this table (6 pages) may be ordered following directions given on any current masthead page.

(16) K. Mertis and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 607 (1975).

(17) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3d ed, Wiley-Interscience, New York, N.Y., 1972, p 978.

(18) F. A. Cotton and L. W. Shive, *Inorg. Chem.*, **14**, 2027 (1975).

(19) E. A. Mason and M. M. Kreevoy, *J. Am. Chem. Soc.*, **79**, 4851 (1957); *Ibid.*, **77**, 5808 (1955).

Rate Controlling Proton Transfer in the Complexing of Copper(II) and Nickel(II) by 2-Aminomethylpyridine

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Abstract: The kinetics of complexation of 2-aminomethylpyridine (amp) with Cu(II) and Ni(II) in aqueous solution has been studied as a function of pH and total buffer concentration at 25 °C in 0.5 M $NaClO_4$. In both systems the reaction was found to be catalyzed by the basic component of the buffer. This observation demonstrates that the complexation reaction is controlled (at least in part) by proton loss from the protonated intermediate $M\text{-ampH}^+$ where M = Cu(II) and Ni(II).

In spite of the added complication of a multiplicity of steps, the overall rate for complexation of multidentate ligands by bivalent metal ions in aqueous solution has, in many cases, been assumed to be governed by the rate of formation of the first bond which, in turn, triggers a rapid sequence of ring closures.[1] Reactions for which first bond formation is rate determining are commonly referred to as "normal" substitutions. In these cases, the first bond formation can be described in terms of the generally accepted Eigen mechanism of complex formation[2] which proceeds by a fast preequilibrium to yield an outer-sphere complex followed by rate limiting elimination of a water molecule from the first coordination sphere of the metal ion

$$\mathrm{M_{aq}}^{2+} + \mathrm{L_{aq}}^{m-} \underset{\text{fast}}{\overset{K_{\mathrm{os}}}{\rightleftharpoons}} \mathrm{M_{aq}}^{2+}, \mathrm{L}^{m-} \underset{\text{slow}}{\xrightarrow{k_0}} \mathrm{ML}^{(2-m)} + \mathrm{H_2O} \qquad (1)$$

Therefore, the observed rate constant for complex formation, k_f, can be expressed as

$$k_f = K_{\mathrm{os}} k_0 \qquad (2)$$

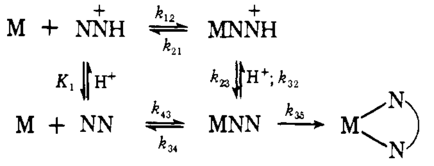
According to the Eigen mechanism the rate determining step is little affected by the incoming ligand such that the value of k_0 is expected to be very close to the value of the rate constant for solvent exchange. A complexation reaction is characterized as "normal" when reasonable agreement is found between the experimental rate constant and that predicted by eq 2.

Departure from the "normal" behavior discussed above can occur for multidentate ligands when chelate ring closure rather than the release of a coordinated water molecule becomes an important rate determining factor. Inhibition of ring closure can arise in cases where there is steric hindrance or where deprotonation of a coordinated protonated intermediate must occur before chelation.

Sterically controlled substitution was first invoked by Kustin et al.[3] to explain the smaller rate constants observed for the reaction of Co(II) and Mn(II) with β-alanine compared with the corresponding values for α-alanine. Sterically hindered ring-closure has since been used as an explanation to account for the anomalously slow formation rates of: (i) Ni(II) with malonate and other dicarboxylate ligands,[4] (ii) Co(II) and Ni(II) with *N,N,N′,N′*-tetrakis(2-hydroxyethyl)ethylenediamine), and *N,N,N′,N′*-tetrakis(2-hydroxypropyl)ethylenediamine,[5,6] and (iii) Ni(II) and Cu(II) with the enol form of acetylacetone.[7] A recent study of the kinetics of complexing of Ni(II) by picolinic acid has revealed a pathway involving initial complexing at the carboxylate group of the zwitterion form of the ligand followed by rate controlling chelate ring closure.[8]

The possibility of complexation reactions controlled by rate limiting proton loss was first suggested from observations that the rate of reaction of some of the more labile metal ions with certain protonated ligands was substantially less than that for reaction with the corresponding unprotonated species. The difference in reactivity was significantly greater than could be accounted for by effects of electrostatic repulsion on K_{os} (eq 2). Thus, Rabenstein and Kula[9] found the rate constants for the reaction of Zn(II) and Co(II) with HNTA^{2-} were three to fiv orders of magnitude smaller than the values predicted for a mechanism in which water loss from the primary coordination sphere of the metal ion is rate determining (i.e., eq 2). Similarly, abnormally low rate constants were observed for the reaction between Cu(II) and the monoprotonated forms of ethylenediamine,[10] histamine,[11] *N,N,N′,N′*-tetramethylethylenediamine,[12] 2-aminomethylpyridine,[13] nitrilotriacetic acid,[14] and the triprotonated form of triethylenetetramine.[12] The above observations of diminished rate constants, uncharacteristic of "normal" behavior, led the various authors to propose that, in each case, proton loss is the rate determining step. The slow rate constant for the reaction between Fe(III)[15] and Cu(II)[7] and the keto form of acetylacetone was attributed to metal ion catalyzed proton transfer from the weakly bound keto tautomer.

The complexing of a metal ion (M) by an N,N donor ligand such as ethylenediamine can be represented by the reaction scheme


(3)

Given that

$$\text{rate} = \frac{d[\mathrm{M}{<}^{\mathrm{N}}_{\mathrm{N}}]}{dt} = k_{\mathrm{obsd}}[\mathrm{M}]\{[\mathrm{L{-}L}] + [\mathrm{L{-}LH}]\}$$

and assuming steady state conditions for the two nonchelated intermediates, an analysis of the above scheme leads to the following expression

$$k_{\mathrm{obsd}} \frac{(K_1 + (\mathrm{H}^+))}{(\mathrm{H}^+)} = \frac{k_{12}k_{23}k_{35} + (k_{21} + k_{23})k_{35}k_{43}K_1(\mathrm{H}^+)^{-1}}{k_{21}k_{32} + (k_{21} + k_{23})(k_{35} + k_{34})} \qquad (4)$$

Before considering limiting forms of eq 4 it is worthwhile to note that it has been known for some time that the rate constants for reactions involving hydrogen ions or hydroxide ions are normally diffusion controlled (ca. 10^{10} M^{-1} s^{-1}).[16] However, the corresponding rate constants for the donation of a proton from a weak acid to water may be quite modest. For example, the rate constant for proton transfer from the trimethylammonium ion to water has a value of 10 s^{-1} at 25 °C.[16]

In previous analyses of schemes such as eq 3 or applications of eq 4,[17,18] it has been common practice to assume that proton transfer is very rapid compared to the the other reaction steps, i.e., $k_{23} \gg k_{21}$ in eq 4. However, rate controlling proton transfer requires that $k_{23} \ll k_{21}$ in which case eq 4 (assuming $k_{35} \gg k_{34}$) takes the following form

$$k_{\mathrm{obsd}} \left(\frac{K_1 + (\mathrm{H}^+)}{(\mathrm{H}^+)}\right) = \frac{k_{12}k_{23}k_{35} + k_{21}k_{35}k_{43}K_1(\mathrm{H}^+)^{-1}}{k_{21}k_{32} + k_{35}k_{21}} \qquad (5)$$

Rearranging the above by dividing numerator and denominator by $k_{35}k_{21}$ gives

$$k_{\mathrm{obsd}} \frac{(K_1 + (\mathrm{H}^+))}{(\mathrm{H}^+)} = \frac{(k_{12}/k_{21})k_{23} + k_{43}K_1(\mathrm{H}^+)^{-1}}{(k_{32}/k_{35}) + 1} \qquad (6)$$

The proton transfer steps k_{23} and k_{32} will have contributons from any base and acid, respectively, present in solution, and may be given by

$$k_{23} = k_1[\mathrm{H_2O}] + k_2[\mathrm{Bu}] + k_3[\mathrm{OH}^-] \qquad (7)$$

$$k_{32} = k_{-1}[\mathrm{H_3O}^+] + k_{-2}[\mathrm{BuH}^+] + k_{-3}[\mathrm{H_2O}] \qquad (8)$$

where [Bu] and [BuH$^+$] represent the basic and acidic forms of the buffer, respectively, which can be calculated readily from the total concentration and acid dissociation constant of the buffer (K_{Bu}) and the pH of the solution. Since $(k_{23}/k_{32}) = K_{23}/(\mathrm{H}^+)$, if eq 6 simplifies to a form containing k_{32} and k_{23} only as their ratio, then the acidic and basic components appearing in eq 8 will not appear in the final rate law.

In the case of copper(II) the reactions are generally studied at sufficiently low pH so that $k_3[\mathrm{OH}^-]$ does not contribute to k_{23}. In addition, previous work with copper(II) would lead one to expect that $k_{35} \approx 10^9$ s^{-1}, while proton transfer studies indicate $k_{-1} \approx 10^{10}$ s^{-1}, so that for pH 3-7 it will be true that $(k_{32}/k_{35}) \ll 1$ and eq 6 simplifies to

$$k_{\mathrm{obsd}} \frac{(K_1 + (\mathrm{H}^+))}{(\mathrm{H}^+)} = \frac{k_{12}}{k_{21}} k_{23} + k_{43}K_1(\mathrm{H}^+)^{-1} \qquad (9)$$

According to eq 9 the overall rate is dependent on two terms. The first represents a pathway where a fast preequilibrium is followed by rate controlling proton transfer and the second term is the contribution from the reaction between Cu(II) and the unprotonated ligand (N-N).

Choosing reasonable estimates for k_{12}/k_{21} and $k_{23} = k_1[\mathrm{H_2O}]$, Sharma and Leussing[11] calculated an overall rate constant ($= (k_{12}/k_{21})k_1[\mathrm{H_2O}]$) in good agreement with the experimental value, thus supporting their conclusion that the

Table I. Kinetic Data for the Reaction of Copper(II) with 2-Aminomethylpyridine[a]

pH	[TMHA],[b] M	[NaClO$_4$], M	[NaCl],[c] M	$10^{-4}\,k_{obsd}$, $M^{-1}\,s^{-1}$
3.75	0.20	0.30	0	3.78
3.64	0.20	0.30	0	3.44
3.63	0.20	0.30	0	3.48
3.61	0.20	0.30	0	3.05
3.50	0.20	0.30	0	2.76
3.81	0.10	0.40	0	3.43
3.67	0.10	0.40	0	2.72
3.64	0.10	0.40	0	2.64
3.55	0.10	0.40	0	2.42
3.74	0	0.30	0.20	2.62
3.64	0	0.30	0.20	2.17
3.50	0	0.30	0.20	1.97
3.30	0	0.30	0.20	1.60
3.75	0	0.40	0.10	2.52
3.61	0	0.40	0.10	2.11
3.51	0	0.40	0.10	1.93
3.29	0	0.40	0.10	1.49

[a] At 25 °C, $[Cu^{2+}] = 5.08 \times 10^{-4}$ M; [amp] = 5×10^{-5} M, ionic strength = 0.50 M. [b] Total concentration of trimethylhydroxylamine hydrochloride buffer. [c] Added to maintain the ionic strength at 0.50 M in the absence of buffer.

reaction of Cu(II) with $NH_2CH_2CH_2NH_3^+$ is proton transfer controlled. A comparable calculation led Roche and Wilkins[13] to the same conclusion for the reaction of Cu(II) with protonated 2-aminomethylpyridine ($ampH^+$).

Since the evidence for proton transfer controlled complexation is based on comparisons and expected rates, we were interested in providing more direct experimental evidence. If, in fact, rate determining proton loss from the intermediate, $MNNH^+$, is the cause of the anomalously slow rate of complex formation, then, according to eq 7, the proton transfer should be subject to general base catalysis. The basic component of a buffer of appropriate pK_a and at sufficiently high concentration should be able to assist the proton loss. The catalytic effect of the buffer could be manifested by an enhancement of the rate for complex formation. The complexing of Cu(II) by 2-aminomethylpyridine (amp) was examined in both the presence and absence of a bufer to test for general base catalysis.

From a preliminary study of the Ni(II)-amp system in the low pH region (pH <4), we observed a rate significantly less than that calculated on the basis of the earlier study of Cassatt and Wilkins[19] over a somewhat limited pH range (6-7). Consequently, the reaction of Ni(II) with amp was examined in more detail to try to account for this large discrepancy. The study included an examination of the effect of three different buffers on the complexation rate. Due to the much slower rate of substitution on Ni(II), at least compared to the very labile ions such as Cu(II), proton transfer controlled substitution on Ni(II) has generally been considered to be highly unlikely[13,18] (except possibly in the reaction Ni(II) with the enol form of β-diketones[20]). The results of the present study demonstrate that proton transfer can be more important with nickel(II) than previously thought.

Experimental Section

Materials. 2-Aminomethylpyridine (amp) (99%, Aldrich) was used as supplied. Stock buffer solutions (0.125 M) of MES (2-(*N*-morpholino)ethanesulfonic acid) and PIPES (1,4-piperazinebis(ethanesulfonic acid)) were prepared from commercial products (Polysciences). The sparing solubility of pivalic acid (Eastman) in water necessitated the preparation of the sodium salt. This was accomplished by adding a stoichiometric amount of NaOH to a suspension of the acid in water and then by adding acetone to precipitate the salt. The product was oven-dried overnight at 80 °C. An integrated NMR spectrum of the sodium salt in anhydrous Me_2SO-d_8 indicated one water of hydration. Titration with standard base gave a neutralization equivalent 96% of the value expected for $NaO_2CC(CH_3)_3{\cdot}H_2O$. Using the method of Jones and Major,[21] trimethylhydroxylamine hydrochloride ($CH_3ON(CH_3)_2{\cdot}HCl$) was prepared by methylating the free base, CH_3ONHCH_3, obtained from *O,N*-dimethylhydroxylamine hydrochloride (Aldrich). The trimethylated hydroxylamine hydrochloride was recrystalized from a methanol-rich methanol/ether mixture and stored for several days in a vacuum desiccator over Drierite. An analysis of the product by titration with standard base gave a neutralization equivalent 99.4% of the theoretical value for $CH_3ON(CH_3)_2{\cdot}HCl$.

Aqueous nickel(II) perchlorate was prepared by mixing reagent grade nickel carbonate (Baker and Adamson) with perchloric acid. The Ni(II) and Cu(II) ($Cu(NO_3)_2{\cdot}3H_2O$, Fisher) solutions were standardized by titration with EDTA using murexide as indicator.

The ionic strength was maintained at 0.5 M by addition of $NaClO_4$ (Fisher, purified).

Kinetic Measurements. A tenfold (or greater) molar excess of metal ion over ligand was used to ensure pseudo-first-order kinetics. The pH conditions were such (pH 3.5-7.0) that the predominant form of the ligand amp (pK_a = 8.6) was the monoprotonated form, $ampH^+$. The net loss of H^+ ions which accompanied the formation of the Ni(II)-amp complex was used to follow the progress of the reaction by the indicator method. The transmittance change was monitored at 620, 405, 520, and 620 nm for the indicators bromothymol blue (p$K_a \sim$ 7.1), chlorophenol red (p$K_a \sim$ 6.0), methyl red (p$K_a \sim$ 5.0) and bromocresol green (p$K_a \sim$ 4.7), respectively. The formation of the copper(II)-amp complex was followed directly at 255 nm. The pseudo-first-order rate constant (k') determined for each run was used to evaluate the second-order rate constant, $k_{obsd} = k'[M(II)]^{-1}$. Each k_{obsd} value in Tables I and II is the average of at least six runs for each set of concentrations with a maximum deviation from the mean of 10%.

The recorded pH is the mean of the values at the beginning and end of each experiment.

The temperature of the reactants in the drive syringes of the stopped-flow system was controlled to 25 ± 0.2 °C.

Determination of Acid Dissociation Constants. The values of the pK_a for PIPES, MES, pivalic acid, and TMHA in 0.5 M $NaClO_4$ at 25 ± 0.2 °C were determined by pH titration using a Metrohm Herisau pH meter (E 300B)-titrator (Dosimat 373) assembly. From the half neutralization points the pK_a values (±0.04) were found to be 6.61, 6.06, 4.72, and 3.69 for PIPES, MES, pivalic acid, and TMHA, respectively.

Results and Discussion

If, as indicated by Roche and Wilkins,[13] the rate of reaction of Cu(II) with $ampH^+$ is controlled by proton transfer, then the rate should be subject to general base catalysis. To test this hypothesis it was necessary to find a buffer with a suitable pK_a, and that does not complex with Cu(II). For the Cu(II)-amp system a pH <4 was necessary to keep the pseudo-first-order rate constant, k', at a magnitude convenient for a stopped-flow study. Accordingly, the pK_a of the noncomplexing buffer should have a value between 3 and 4. Formic acid (p$K_a \approx 3.7$) was not considered suitable because of the probable formation of copper-formate complexes at higher formate ion concentrations (~0.1 M). Such complexing could lead to an ambiguity as to whether any observed rate enhancement is due to general base catalysis or increased reactivity of $ampH^+$ with the copper-formate species. However, trimethylhydroxylamine (TMHA) (pK_a = 3.69, 25 °C, 0.5 M $NaClO_4$) appeared to satisfy our requirements. Lack of significant complexing was demonstrated by the following experiments. The proton NMR spectrum of 0.2 M trimethylhydroxylamine hydrochloride (half-neutralized) in D_2O showed two sharp peaks, one (A) twice the intensity of the other (B), with line widths $\simeq$0.6 Hz. In the presence of Cu(II) (10^{-2} M) both peaks were slightly broadened, A (1.2 Hz) more than B (0.8 Hz). This slight broadening may be contrasted to the 30 Hz broadening of the *N*-methyl proton in a solution of Cu(II) (10^{-2} M) in 0.1 M

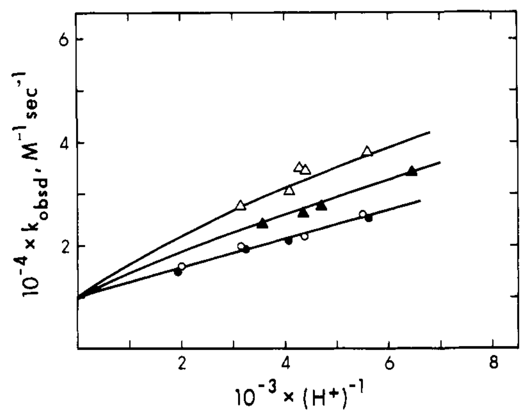
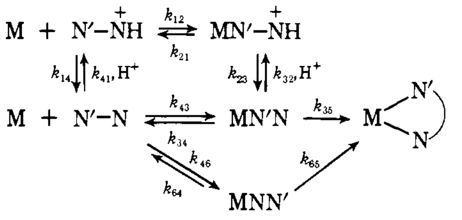


Figure 1. Plot of k_{obsd} vs. $(H^+)^{-1}$ for the reaction of aqueous copper(II) with 2-aminomethylpyridine (25 °C, $Cu^{2+} = 4.08 \times 10^{-4}$ M, amp = 5×10^{-5} M, $I = 0.5$ M): ●, 0.1 M NaCl, 0.4 M $NaClO_4$, no buffer; ○, 0.20 M NaCl, 0.30 M $NaClO_4$, no buffer; ▲, 0.40 M $NaClO_4$, 0.10 M trimethylhydroxylamine hydrochloride; △, 0.30 M $NaClO_4$, 0.20 M trimethylhydroxylamine hydrochloride.

(half-neutralized) *O,N*-dimethylhydroxylamine hydrochloride. These results show that there is little or no complexing of copper(II) by TMHA under our experimental conditions.

The reaction of copper(II) with amp has been studied both in the presence and absence of buffer. The latter studies were possible because of the relatively high (H^+) ($>10^{-4}$ M) and low amp concentration (5×10^{-5} M) so that very little pH change occurred during the reaction even without buffer present. The experimental results are given in Table I and plotted vs. $(H^+)^{-1}$ in Figure 1.

The results may be described in terms of a reaction scheme closely analogous to eq 3 except that the two nitrogen donor atoms in amp are chemically different so that the metal ion may complex at either the pyridine or amino nitrogen in the neutral ligand. If amp is represented by N′–N, where N′ is the pyridine nitrogen, then the reaction scheme is as shown in eq 10.



(10)

Kinetic analysis, with steady state assumptions for the nonchelated intermediates, yields two observed rate constants for this system. Substitution of estimated rate constants and normal metal ion concentrations and pH conditions shows that only the smaller of these two rate constants will be measurable. The complete expression, which is given in the Appendix, can be simplified with the reasonable approximation that $k_{65} \gg k_{64}$ and $k_{35} \gg k_{34}$. It is also true that $k_{41} > k_{12}[M]$, $k_{46}[M]$, $k_{43}[M]$, because of the low pH and low [M] in the case of copper(II), and because of the smaller expected values of k_{12}, k_{46}, and k_{43} for nickel(II). With these simplifications, and noting that $(k_{14}/k_{41}) = K_{14}/(H^+)$ and $k_{23}/k_{32} = K_{23}/(H^+)$ it is found that

$$k_{obsd}(K_{14} + (H^+))/(H^+) = \frac{\frac{k_{12}}{k_{21}}\left\{k_{23}\frac{K_{14}}{(H^+)}\left[\frac{(k_{21}+k_{23})}{k_{12}}(k_{43}+k_{46})\right]\right\}}{1 + \frac{k_{23}}{k_{21}} + \frac{k_{23}(H^+)}{k_{35}K_{23}}} \quad (11)$$

Table II. Kinetic Data for Reaction of Nickel(II) with 2-Aminomethylpyridine (25 °C, 0.5 M $NaClO_4$)[a]

pH	$10^{-1}k_{obsd}$, M^{-1} s^{-1}	pH	$10^{-1}k_{obsd}$, M^{-1} s^{-1}
(i) [PIPES] = 1.93×10^{-2} M[b]		[PIPES] = 9.63×10^{-3} M[b]	
6.90	28.3	6.89	23.0
6.86	27.2	6.86	21.1
6.84	28.0	6.78	20.9
6.76	23.9	6.68	19.3
6.74	25.0	6.73	18.5
6.70	22.5	6.60	15.9
6.66	21.7		
6.60	19.9		
6.60	19.8		
6.50	17.9		
6.40	16.2		
6.21	12.1		
(ii) [MES] = 1.81×10^{-2} M		[MES] = 9.06×10^{-3} M	
6.55	16.0[b]	6.46	10.9[b]
6.48	15.0[b]	6.43	9.99[b]
6.39	13.4[b]	6.34	9.12[b]
6.31	11.2[b]	6.28	8.91[b]
6.12	9.16[b]	6.20	7.92[b]
6.00	8.03[b]	6.13	7.50[b]
5.91	6.41[c]	5.96	5.45[c,d]
5.91	6.35[c,d]	5.82	4.33[c,d]
5.83	6.15[c,d]	5.72	3.73[c,d]
5.82	5.79[b]		
5.71	5.03[c]		
5.71	4.97[c,d]		
5.56	3.50[b]		
5.35	2.53[c]		
(iii) [PIV] = 1.91×10^{-2} M		[PIV] = 9.55×10^{-3} M	
5.47	3.90[c]	5.23	1.76[e,d]
5.25	2.90[c]	5.20	1.63[f,d]
5.20	2.49[e,d]	5.14	1.50[e,d]
5.11	2.08[e,d]	5.11	1.47[f,d]
5.01	1.76[e,d]	5.04	1.35[e,d]
4.91	1.45[f,d]	4.99	1.24[f,d]
4.81	1.20[f,d]	4.93	1.08[f,d]
4.72	0.905[f,d]	4.77	0.855[f,d]
		4.73	0.780[f,d]

[a] Ligand concentration 10^{-3} M in all cases and $[Ni^{2+}] = 10^{-2}$ M unless otherwise indicated. [b] Using 2.5×10^{-5} M bromothymol blue indicator. [c] 5×10^{-5} M chlorophenol red indicator. [d] $[Ni^{2+}] = 2 \times 10^{-2}$ M. [e] 2×10^{-5} M methyl red indicator. [f] 2×10^{-5} M bromocresol green indicator.

As noted in the introduction, for the very labile copper(II) ion $k_{23}/k_{21} \ll 1$ and $k_{23}(H^+)/K_{23}k_{35} = k_{32}/k_{35} \ll 1$, so that

$$k_{obsd}\frac{(K_{14} + H^+)}{(H^+)} = \frac{k_{12}}{k_{21}}k_{23} + K_{14}\left(\frac{(k_{43}+k_{46})}{(H^+)}\right) \quad (12)$$

If k_{23} is expanded as given by eq 7, with $k_3[OH^-]$ dropped because pH <4 in the study with copper(II), and substituting for [Bu] in terms of the total buffer concentration $[Bu]_T$ and the acid dissociation constant of the buffer K_{Bu}, then

$$k_{obsd}\frac{(K_{14} + (H^+))}{(H^+)} = \frac{k_{12}}{k_{21}}\left\{(k_1[H_2O]) + \frac{k_2K_{Bu}}{(K_{Bu} + (H^+))}[Bu]_T\right\} + K_{14}\frac{(k_{43}+k_{46})}{(H^+)} \quad (13)$$

The results in Figure 1 are consistent with this equation in that k_{obsd} increases with $[Bu]_T$, and is not an exactly linear function of $(H^+)^{-1}$ in the presence of buffer because K_{Bu} is of the order of magnitude of (H^+). A least-squares analysis of the results yields the kinetic parameters summarized in Table III. The magnitudes of these parameters will be discussed in connection with values from the nickel(II) study.

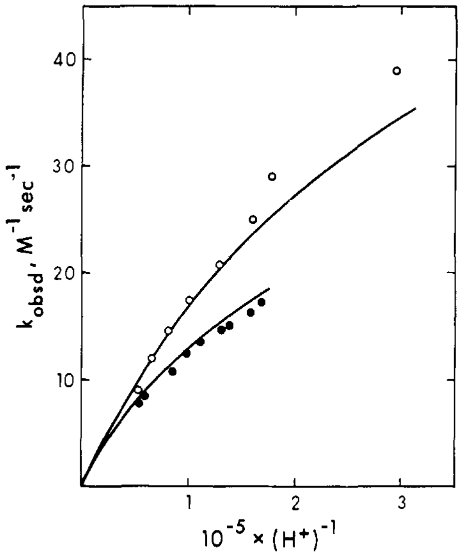


Figure 2. Plot of k_{obsd} vs. $(H^+)^{-1}$ for the reaction of aqueous nickel(II) with 2-aminomethylpyridine (25 °C, $I = 0.5$ M), in the presence of pivalic acid buffer at 9.55×10^{-3} M (●), and 1.9×10^{-2} M (○).

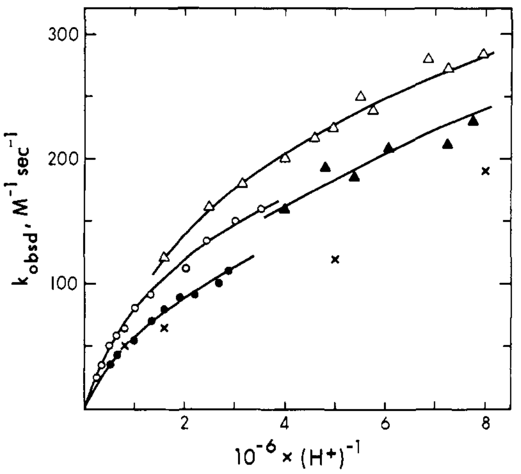
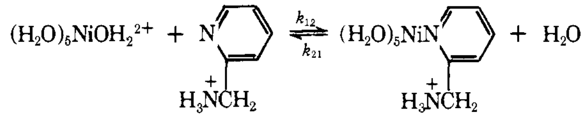


Figure 3. Plot of k_{obsd} vs. $(H^+)^{-1}$ for the reaction of aqueous nickel(II) with 2-aminomethylpyridine (25 °C, $I = 0.5$ M), in the presence of MES buffer at 9.06×10^{-3} M (●), and 1.81×10^{-2} M (○); and in the presence of PIPES buffer at 9.63×10^{-3} M (▲), and 1.93×10^{-2} M (△); data of Cassatt and Wilkins, ref 19 (×), lutidine buffer at ~10^{-2} M.

The reaction of nickel(II) with amp was studied as a function of pH and buffer concentration for several buffers. The results are given in Table II and plotted in Figures 2 and 3. It was somewhat surprising to find that the reaction with nickel(II) was also catalyzed by buffer. Generally it has been assumed that substitution on nickel(II) is sufficiently slow that proton transfer effects should not interfere. However, further analysis of eq 11 reveals the source of the buffer catalysis.

An important feature of the reduction of eq 11 to various limiting forms is the relative magnitudes of k_{21} and k_{23}. If $k_{23} > k_{21}$ then no proton transfer effects should be noted. In previous work on nickel(II) it has been assumed, albeit implicitly, that (k_{12}/k_{21}) was large and $k_{12} \approx 10^3$ M^{-1} s^{-1}, so that k_{21} would be small enough to satisfy the condition $k_{23} > k_{21}$. However, a more detailed consideration shows that it is quite possible for some common systems that $(k_{12}/k_{21}) \approx 1$, in which case k_{21} and k_{23} may be of similar magnitude.

In the specific case of amp the equilibrium in question is



(14)

The equilibrium constant for this reaction can be roughly estimated by assuming that the ratio of complex formation constants with nickel(II) of 2,4-dimethylpyridine (3.6 M^{-1})[22] to ethylamine (66 M^{-1})[23] is the same as the ratio for ampH^+ to *N,N,N*-trimethylethylenediamine (10 M^{-1})[24] from which one obtains $(k_{12}/k_{21}) \approx 0.5$ for eq 14. If $k_{12} \approx 500$ M^{-1} s^{-1}, as found for *N,N,N*-trimethylethylenediamine, then $k_{21} \approx 1 \times 10^3$ s^{-1}. From eq 7 at pH 7 in the absence of buffer the $k_3[OH^-]$ term dominates and $k_{23} \approx 10^{10} \times 10^{-7}$ s^{-1}, close to an upper limit for the present work because the pH was always <7. These estimates show that it may not be generally true that $k_{23} > k_{21}$, and that buffer catalysis may be necessary to give this inequality.

Substitution for k_{23} from eq 7 into eq 11 yields a function with the experimental dependence of k_{obsd} on (H^+) and [Bu]. In preliminary least-squares fits of the data to eq 11 it became apparent that the second term in the numerator of eq 11 was not significant relative to the first term. This is reasonable in retrospect because $K_{14} = 2 \times 10^{-9}$ M^{-1} and $(k_{43} + k_{46}) \approx 4 \times 10^3$ M^{-1} s^{-1}, and $k_{12} \approx 5 \times 10^2$ M^{-1} s^{-1}, and $k_{21} \lesssim k_{23}$. With these values the second term is 12% of the first at pH 6.9, and the contribution decreases as the pH decreases. Similarly, it was found that the $k_1[H_2O]$ contribution to k_{23} (eq 7) was negligible compared to the other terms for the pH and buffer concentrations used in the nickel(II) system. With these simplifications, combination of eq 7 and eq 11 gives

$$k_{obsd}\ \frac{K_{14} + (H^+)}{(H^+)} = \frac{\dfrac{k_{12}}{k_{21}}\left\{\dfrac{k_2K_{Bu}[Bu]_T}{K_{Bu} + (H^+)} + \dfrac{k_3K_w}{(H^+)}\right\}}{1 + \left\{\dfrac{1}{k_{12}} + \dfrac{k_{21}(H^+)}{k_{12}k_{35}K_{23}}\right\}\left(\dfrac{k_{12}}{k_{21}}\right)\left\{\dfrac{k_2K_{Bu}[Bu]_T}{K_{Bu} + (H^+)} + \dfrac{k_3K_w}{(H^+)}\right\}} \tag{15}$$

The k_{obsd} values from all three buffers were analyzed simultaneously in a least-squares program which made values of k_{12}, $(k_{12}/k_{21})k_3K_w$, and $(k_{12}/k_{21})k_{35}K_{23}$ independent of the buffer and varied $(k_{12}/k_{21})k_2$ for each buffer. The results of this analysis are summarized in Table III and are used to draw the solid lines in Figures 2 and 3. Because of the complexity of eq 15 and the fact that four independent variables (three buffer concentrations and (H^+)) were used in the fit, and to justify the simplifications used to obtain eq 15, several different sets of least-squares fitting parameters are given in Table III. In fit A all seven parameters were included, and the $(k_{12}/k_{21})k_1(H_2O)$ value is unreasonably small. In fit B this term was omitted and essentially the same fit was obtained as judged by the standard error of the fit. Finally, in fit C, a reasonable value of $(k_{12}/k_{21})k_1[H_2O]$ was estimated and held fixed and the fit was not significantly different from fit A. This simply shows that inclusion of $k_1[H_2O]$ does not greatly affect the analysis. A comparison of the parameters from fits A, B, and C also shows that they are reasonably insensitive to assumptions made in the fitting. As expected $(k_{12}/k_{21})k_2$ for pivalate is most affected by inclusion of $k_1(H_2O)$ (fit C) because the latter term will be most significant at low pH and for a less basic buffer wit a smaller k_2 value.

The model proposed does account quantitatively for the observed buffer catalysis. However, the kinetic parameters obtained should be consistent with previous work on metal ion substitution and proton transfer reactions. The major difficulty in making comparisons to previous work is that (k_{12}/k_{21}) and K_{23} are unknown. One estimate of (k_{12}/k_{21}) has been made on the basis of formation constants. It is also possible to use the experimental value of $(k_{12}/k_{21})k_3K_w$ and the fact that k_3

Table III. Summary of Kinetic Results for the Reaction of Copper(II) and Nickel(II) with 2-Aminomethylpyridine

		Ni^{2+}		
	Cu^{2+}	A	B	C
$(k_{12}/k_{21})k_1[H_2O]$	1.01×10^4	4.80×10^{-9}		4.0
$(k_{12}/k_{21})k_2$ TMHA	1.12×10^5			
$(k_{12}/k_{21})k_2$ PIPES		3.40×10^4	3.33×10^4	3.20×10^4
$(k_{12}/k_{21})k_2$ MES		1.30×10^4	1.26×10^4	1.22×10^4
$(k_{12}/k_{21})k_2$ PIV		3.80×10^3	3.59×10^3	3.28×10^3
$(k_{12}/k_{21})k_3K_w$		2.80×10^{-5}	2.85×10^{-5}	2.69×10^{-5}
$(k_{43} + k_{46})K_{14}$	2.78			
k_{12}		635	630	680
$(k_{12}/k_{21})K_{23}k_{35}$		2.55×10^{-4}	2.67×10^{-4}	2.57×10^{-4}

should have a diffusion controlled value of $\sim 2 \times 10^{10}$ M^{-1} s^{-1},[25] to obtain $(k_{12}/k_{21}) \approx 0.14$ M^{-1}.

Unfortunately, it is not possible to make a similar estimate of (k_{12}/k_{21}) for the copper(II) system. It may be noted that $(k_{12}/k_{21})k_2$ for copper(II)-TMHA is larger than for nickel(II)-pivalate. Since pivalate ion is a stronger base than TMHA the k_2 value would be expected to be larger for pivalate, therefore (k_{12}/k_{21}) must be larger for copper(II) than for nickel(II). The latter is not unexpected because formation constants with nitrogen donor ligands are generally larger with copper(II) than with nickel(II).[26] There is an added factor in that copper(II) may produce a larger increase in acidity of coordinated ligands than nickel(II). This would have the effect of making k_2 larger for copper(II) than for nickel(II) systems.

The values of $(k_{12}/k_{21})k_2$ with PIPES, MES, and pivalate show the expected decrease with decreasing pK_{Bu} (decreasing basicity) of the buffer. It is interesting to estimate values of k_{-2} because they might be close to, but should not exceed, the diffusion controlled limit. It is readily shown that $k_{-2} = k_2K_{Bu}/K_{23}$. If k_2 is estimated with $(k_{12}/k_{21}) \approx 0.1$ M^{-1}, and noting that $K_{23} \geq K_{14}$, then it is possible to estimate upper limits on k_{-2} by using $K_{23} = K_{14}$, to obtain $k_{-2} \leq 3.2 \times 10^7$, 4.4×10^7, 2.5×10^8 M^{-1} s^{-1} for PIPES, MES, and pivalate, respectively. All of these upper limits are below the diffusion controlled limit, although, at least for pivalate, for which most certainly $pK_{23} - pK_{Bu} > 2$, k_{-2} normally would be expected to be diffusion controlled.[27] It is possible that charge, steric effects, and hydrogen bonding between the uncoordinated amino group and coordinated water molecules may all conspire to make k_{-2} smaller than anticipated from simpler systems.

The rate constants for metal ion substitution can be discussed with a great deal more confidence. The value of k_{12} obtained for amH^+ is in agreement with he value of 500 M^{-1} s^{-1} obtained for the *N,N,N*-trimethylethylenediamine cation reacting with nickel(II).[24] It is possible to estimate k_{35} from $(k_{12}/k_{21})K_{23}k_{35} = (k_{43}/k_{34})K_{14}k_{35}$ if the formation constant of the nickel(II)-2-methylpyridine complex[22] is used to estimate $(k_{43}/k_{34}) \approx 10$, then $k_{35} \approx 1 \times 10^4$ s^{-1}. Since coordinated pyridine ligands do not appear to labilize coordinated water molecules significantly,[28] the value of k_{35} would be expected to be similar to the water exchange rate constant of 3×10^4 s^{-1}, for $Ni(OH_2)_6^{2+}$.[28]

In the case of copper(II) the value of $(k_{43} + k_{46})$ can be calculated directly and is found to be 1.1×10^9 M^{-1} s^{-1}. This value seems normal for a neutral ligand reacting with copper(II).[29,30]

In summary, the general base catalysis of the complexing of copper(II) and nickel(II) by 2-aminomethylpyridine can be accounted for on the basis of reasonable proton transfer rates and by extrapolation of rates of substitution on these metal ions by simpler ligands. The results also indicate that general base catalysis may be observed in other previously studied systems, and these possibilities are being explored. It might be asked why buffer catalysis was not observed in our previous study of picolinic acid reacting with nickel(II).[8] A detailed analysis is not warranted here, but the main difference is the greater acidity of the pyridine nitrogen in picolinic acid ($pK_a \approx 5.0$), compared to the amino nitrogen in amp ($pK_a = 8.6$). This difference makes proton transfer sufficiently fast that it does not influence the kinetics in the picolinic acid-nickel(II) system.

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Appendix

If the reaction scheme in eq 10 is treated assuming steady state conditions for the three nonchelated intermediates, then the time dependence of the concentration of the ith species is given by

$$[\text{concn}]_i = A_i e^{\gamma_+ t} + B_i e^{\gamma_- t} \tag{A1}$$

where A_i and B_i are time independent constants, and γ_+ and γ_- are the roots of the quadratic equation

$$a\gamma^2 + b\gamma + c = 0 \tag{A2}$$

where

$$a = (k_{65} + k_{64})\{(k_{23} + k_{21})(k_{35} + k_{34}) + k_{32}k_{21}\}$$

$$\begin{aligned} b = {} & k_{65}k_{46}[M]\{(k_{23} + k_{21})(k_{35} + k_{34}) + k_{32}k_{21}\} \\ & + k_{35}(k_{65} + k_{64})\{(k_{23} + k_{21})(k_{14} + k_{41} + k_{43}[M]) \\ & + k_{23}k_{12}[M]\} + (k_{65} + k_{64})\{k_{34}(k_{23} + k_{21})(k_{14} + k_{41}) \\ & + k_{21}[k_{34}k_{23} + k_{32}(k_{14} + k_{41})[M]]\} \end{aligned}$$

$$\begin{aligned} c = {} & \{k_{14}(k_{23} + k_{21}) + k_{23}k_{12}[M]\}\{k_{65}k_{46}[M](k_{35} + k_{34}) \\ & + k_{35}k_{43}[M](k_{65} + k_{46}[M]) + k_{21}k_{14}k_{32}k_{65}[M]\} \\ & + k_{12}[M]k_{23}k_{41}k_{35}(k_{65} + k_{64}) \end{aligned}$$

If reasonable estimates of the rate constants are substituted into these expressions it is found that $4ac/b^2 \ll 1$. Therefore, the binomial expansion can be applied to obtain the roots as

$$\gamma_- = -\frac{b}{a} \text{ and } \gamma_+ = -\frac{c}{b} \tag{A3}$$

where only the latter and smaller root is of a magnitude to be measured by stopped-flow methods. If it is noted that generally proton transfer to the basic forms of the ligand will be faster than substitution on the metal ion i.e., $k_{41} \gg k_{43}[M]$, $k_{46}[M]$, $k_{12}[M]$, and that chelate ring, closure will be faster than dissociation of the most basic ligand atom from the metal ($k_{65} \gg k_{64}$), then

$$\frac{-\gamma_+}{[M]} = k_{obsd}$$

$$= \frac{k_{41}k_{12}k_{23}k_{35} + k_{14}[(k_{23} + k_{21}) \times \{k_{46}(k_{35} + k_{34}) + k_{35}k_{43}\} + k_{21}k_{32}k_{46}]}{(k_{14} + k_{41})\{(k_{21} + k_{21})(k_{35} + k_{34}) + k_{21}k_{32}\}} \tag{A4}$$

This equation may be rearranged by dividing numerator and denominator by k_{41} and noting that $k_{14}/k_{41} = K_{14}/(\mathrm{H}^+)$, and $(k_{14} + k_{41})/k_{41} = (K_{14} + (\mathrm{H}^+)/(\mathrm{H}^+)$ and that $k_{32} = k_{23}(\mathrm{H}^+)/K_{23}$. In addition from the point of view of the present work it is useful to divide numerator and denominator by $k_{21}(k_{34} + k_{35})$ to obtain eq A5.

$$k_{\mathrm{obsd}}\ \frac{K_{14} + (\mathrm{H}^+)}{(\mathrm{H}^+)} = \frac{\dfrac{k_{23}}{(k_{35} + k_{34})}\left\{\dfrac{k_{12}}{k_{21}}k_{35} + \dfrac{K_{14}}{K_{23}}\right\} + k_{46}\dfrac{K_{14}}{(\mathrm{H}^+)}\left\{\dfrac{(k_{23} + k_{21})}{k_{21}}\left[k_{46} + \dfrac{k_{35}k_{43}}{(k_{35} + k_{34})}\right]\right\}}{1 + k_{23}\ \ k_{21} + k_{23}(\mathrm{H}^+)/K_{23}(k_{35} + k_{34})} \tag{A5}$$

The first term in brackets in the numerator can be written as $(K_{14}/K_{23})\{(k_{43}k_{35}/k_{43} + k_{46}\}$. It seems reasonable that $k_{43} \approx k_{46}$, and $k_{35} \gg k_{34}$, in which case eq A5 reduces to eq 11. It should be noted that the last two assumptions do not affect the (H^+) dependence predicted by eq A5, but simply produce a more tractable equation.

References and Notes

(1) (a) R. G. Wilkins, *Acc. Chem. Res.*, **3**, 408 (1970); (b) *Pure Appl. Chem.*, **33**, 583 (1973).
(2) (a) M. Eigen and K. Tamm, *Z. Electrochem.*, **66**, 107 (1962); (b) M. Eigen and R. G. Wilkins, *Adv. Chem. Ser.*, **No. 49**, 55 (1965).
(3) K. Kustin, R. F. Pasternack, and E. M. Weinstock, *J. Am. Chem. Soc.* **88**, 4610 (1966).
(4) H. Hoffmann, *Ber. Bunsenges. Phys. Chem.*, **73**, 432 (1969).
(5) D. B. Rorabacher and D. B. Moss, *Inorg. Chem.*, **9**, 1314 (1970).
(6) D. B. Rorabacher, T. S. Turan, J. A. Defever, and W. G. Nickels, *Inorg. Chem.*, **8**, 1498 (1969).
(7) R. G. Pearson and O. P. Anderson, *Inorg. Chem.*, **9**, 39 (1970).
(8) R. H. Voss and R. B. Jordan, *J. Am. Chem. Soc.*, **98**, 2173 (1976).
(9) D. L. Rabenstein and R. J. Kula, *J. Am. Chem. Soc.*, **91**, 2492 (1969).
(10) L. J. Kirschenbaum and K. Kustin, *J. Chem. Soc. A*, 684 (1970).
(11) V. S. Sharma and D. L. Leussing, *Inorg. Chem.*, **11**, 138 (1972).
(12) D. B. Moss, C. T. Lin, and D. B. Rorabacher, *J. Am. Chem. Soc.*, **95**, 5179 (1973).
(13) T. S. Roche and R. G. Wilkins, *J. Am. Chem. Soc.*, **96**, 5082 (1974).
(14) J. Maguire, *Can. J. Chem.*, **52**, 4106 (1974).
(15) W. K. Ong and R. H. Prince, *J. Chem. Soc. A*, 458 (1966).
(16) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).
(17) J. E. Letter, Jr., and R. B. Jordan, *J. Am. Chem. Soc.*, **97**, 2381 (1975).
(18) J. C. Cassatt, W. A. Johnson, L. M. Smith, and R. G. Wilkins, *J. Am. Chem. Soc.*, **94**, 8399 (1972).
(19) J. C. Cassatt and R. G. Wilkins, *J. Am. Chem. Soc.*, **90**, 6045 (1968).
(20) M. R. Jaffe, D. P. Fay, M. Cefola, and N. Sutin, *J. Am. Chem. Soc.*, **93**, 2878 (1971); D. P. Fay, A. R. Nickels, Jr., and N. Sutin, *Inorg. Chem.*, **10**, 2046 (1971).
(21) L. W. Jones and R. T. Major, *J. Am. Chem. Soc.*, **50**, 2762 (1928).
(22) Z. Warnke and B. Lenarcik, *Rocz. Chem.*, **45**, 1385 (1971).
(23) D. B. Rorabacher and C. A. Melendez-Cepeda, *J. Am. Chem. Soc.*, **93**, 6071 (1971).
(24) C. T. Lin and D. B. Rorabacher, *Inorg. Chem.*, **12**, 2402 (1973).
(25) M. Eigen, G. Maass, and G. Schwarz, *Z. Phys. Chem.* (*Frankfurt am Main*), **74**, 319 (1971).
(26) L. G. Sillen and A. E. Martell, Ed., *Chem. Soc., Spec. Publ.*, **No. 17** (1963).
(27) R. P. Bell, "The Proton in Chemistry", 2d ed, Cornell University Press, Ithaca, N.Y., 1973, pp 126–131.
(28) M. Grant, H. W. Dodgen, and J. P. Hunt, *J. Am. Chem. Soc.*, **92**, 2321 (1970).
(29) H. Diebler and P. H. Rosen, *Ber. Bunsenges. Phys. Chem.*, **76**, 1031 (1972).
(30) S. M. Feltch, J. E. Stuehr, and G. W. Tin, *Inorg. Chem.*, **14**, 2175 (1975).

Synthesis, Characterization, and X-Ray Structure of η^5-Cyclopentadienyltris(*N*,*N*-dimethyldithiocarbamato)-zirconium(IV)

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Abstract: η^5-Cyclopentadienyltris(*N*,*N*-dimethyldithiocarbamato)zirconium(IV), $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$, has been prepared by reaction of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ with anhydrous $NaS_2CN(CH_3)_2$ in refluxing dichloromethane and has been characterized by analysis, ^{1}H NMR, and infrared spectroscopy. The structure of this molecule has been determined by a single-crystal x-ray diffraction study of the chlorobenzene solvate, $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3\cdot C_6H_5Cl$. The solvate crystallizes in the monoclinic space group $P2_1/c$ with four formula units in a unit cell of dimensions: a = 11.582 (2), b = 16.756 (3), c = 14.016 (2) Å; β = 90.58 (1)° (ρ_{obsd} = 1.545, ρ_{calcd} = 1.537 g cm^{-3}). The final anisotropic least-squares refinement, which employed 7384 independent diffractometer-recorded reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} \leq 62.07°$ and $I \geq 2.0\sigma(I)$, afforded residuals R_1 = 0.079 and R_2 = 0.090. The crystal contains discrete seven-coordinate molecules of the zirconium complex which have a pentagonal bipyramidal structure of approximate symmetry C_s-m. The η^5-cyclopentadienyl ligand occupies one axial position (Zr–C = 2.511–2.519 Å), dithiocarbamate ligand a spans the other axial position and one equatorial position, while dithiocarbamate ligands b and c take the remaining equatorial positions. Zr–S bond lengths vary from 2.655 (1) to 2.717 (2) Å (av value, 2.690 Å). The chief distortions from ideal pentagonal bipyramidal geometry are rotation of the axial Zr–S bond off the quasi-fivefold axis (by 8.9°) and displacement of the Zr atom from the plane of the equatorial sulfur atoms (by 0.60 Å) in the direction of the C_5H_5 group. As expected, there is considerable crowding in the ZrS_6C_5 coordination group, most of the S···S and C···S nonbonded contacts being less than the sum of the van der Waals radii.

In the course of our investigations of *N*,*N*-dialkyldithiocarbamate complexes of early transition metals[1-3] we have prepared the potentially seven-coordinate cyclopentadienylzirconium(IV) complex $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$. This compound is closely related to the dithiocarbamate complexes $Ti[S_2CN(CH_3)_2]_3Cl$,[1,2] $VO[S_2CN(C_2H_5)_2]_3$,[4] $NbO[S_2CN(C_2H_5)_2]_3$,[4] and $Mo(NO)[S_2CN(n\text{-}C_4H_9)_2]_3$[5] and to the cyclopentadienyltris(hexafluoroacetylacetonate) $(\eta^5\text{-}C_5H_5)Zr(hfac)_3$,[6] all of which have been shown by x-ray diffraction to possess pentagonal bipyramidal structures in which the monodentate ligand occupies an axial position. A similar structure for $(\eta^5\text{-}C_5H_5)Zr[S_2CN(CH_3)_2]_3$ is suggested by the proton NMR spectrum which exhibits four methyl resonances of relative intensity 2:1:2:1 at ambient probe temperature (37 °C). Thus, this compound is of special interest since it is one of only a few seven-coordinate complexes which