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Contribution from the Department of Chemistry,
Case Western Reserve University, Cleveland, Ohio 44106

Copper(II) Chelation Kinetics. IV. N-Substituted Systems

STEPHEN M. FELTCH, JOHN E. STUEHR,* and GEORGE W. TIN

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Kinetic data, via stopped flow and temperature jump spectroscopy, are reported for the interaction of Cu^{2+} with *N*,*N*-dimethylglycine and L-proline at 25° and $I = 0.1\ M$ KNO_3. Two relaxation times, corresponding to the formation of mono and bis complexes, were characterized as a function of concentration and pH. Forward complexation rate constants were found to be 1.4×10^9 and $3.8 \times 10^8\ M^{-1}\ sec^{-1}$ for dimethylglycine, and 2.6×10^9 and $2.2 \times 10^8\ M^{-1}\ sec^{-1}$ for proline. Dissociation rate constants, for these and other α-amino acids, were shown to correlate with the pK of the amino group, the variation being greatest for nitrogen-substituted amino acids.

Since the development of rapid kinetic techniques, much effort has been directed toward the study of metal complex formation with labile metal ions.[1-3] For most metal ions with "simple" ligands, forward complexation rate constants have been consistent with a scheme whereby the formation of a solvent separated ion pair (outer sphere complex) was followed by the (rate determining) formation of an inner sphere complex via the loss of one or more intervening solvent molecules. Studies to date have shown[4-12] that, for Cu^{2+} complexation with α-amino acids, second-order rate constants for mono complex formation are on the order of $1-4 \times 10^9\ M^{-1}\ sec^{-1}$. These relatively large values have been attributed[13] to the fact that the axial $Cu^{2+}-H_2O$ bonds are elongated compared with the equatorial and that the axial and equatorial forms interconvert, rendering solvent molecules about Cu^{2+} kinetically equivalent. It was thought at first that there was very little dependence of the rate constants on the specific α-amino acid under study. Recently, however, it has been shown[12] that these rate constants decrease somewhat as the bulkiness of the substituent on the α carbon increases. This ligand dependence seemed to be even more pronounced when the substituents were placed on the amino group.

In this paper we further examine the dependence of Cu^{2+} rate constants upon the nature of the substituent on the amino group of α-amino acids. The ligands chosen for study were *N*,*N*-dimethylglycine (dMG) and L-proline. The latter, for which measurements have been reported in an earlier study,[11] is an especially interesting example in that the pyrrolidine ring system locks the $N-COO^-$ moiety into a rigid configuration compared with other amino acids.

Experimental Section

N,*N*-Dimethylglycine (dMG) obtained from Nutritional Biochemicals was recrystallized from 1-propanol prior to use. Sigma Chemicals L-proline was used without further purification. All other chemicals were standard analytical reagent grade. Kinetic runs were made at 25° employing a Gibson-Durrum Model D-110 stopped flow apparatus or a temperature jump spectrophotometer purchased from Messanlagen Studiengesellschaft, West Germany. The temperature jump spectrophotometer was thermostated at 20°, with a temperature jump of 5°. Stability constants and pK_a values for L-proline and dMG at 25° were determined by potentiometric titration using a Corning Model 101 digital electrometer. Details of this procedure have been described elsewhere.[14] The necessity of calibration of the instrument with accurate buffers (those used were prepared in our laboratory in accordance with NBS specifications) in the appropriate region for the pK_a determinations must be stressed. Otherwise substantial error may be introduced into the determinations, particularly in the lower pK region.

Triply distilled degassed water was used for the preparation of stock solutions of ligand and metal ion, from which the experimental solutions were prepared by volumetric dilution. The ionic strength of the solutions was maintained constant at 0.1 M using KNO_3. Typical concentrations were 0.01–0.05 M for copper and 0.003–0.50 M for the ligands. The pH range utilized extended from 2.8 to 4.5, with the majority of the measurements being taken below pH 3.8. Both temperature jump and stopped flow measurements were made on L-proline and dMG. The absorbance changes brought about by shifts in the metal complexation equilibria were monitored at 540–625 nm for dMG and 500–700 nm for L-proline, the best wavelengths being dependent upon metal and ligand concentrations. As with previous Cu^{2+} studies in this laboratory, no pH indicators were necessary since the absorbance changes were large enough to be monitored directly. In the stopped flow experiments, only the very last portions of the absorbance vs. time curves were utilized. As a consequence, the data obtained were able to be treated by close-to-equilibrium kinetics. Relaxation times were determined from two or more oscilloscope traces by first plotting on semilog paper to demonstrate linearity and then using a weighted least-squares technique on a Univac 1108 computer to determine the best straight line.

Table I. Equilibrium Constants[a] for Cu(II) Systems[b]

	L-Proline	dMG
pK_{a_1}	1.95 (1.80)[c]	1.90 (2.08)[d]
pK_{a_2}	10.63 (10.63)[c]	9.81 (9.80)[d]
log K_1	8.86 (8.92)[c]	7.21 (7.30)[d]
log K_2	7.59 (7.66)[c]	6.56 (6.35)[d]

[a] See reaction I for definitions of constants. [b] At 25° and $I = 0.1\ M$ KNO_3. [c] R. D. Gillard, H. M. Irving, R. M. Parkins, N. C. Payne, and L. D. Pettit, *J. Chem. Soc. A*, 1169 (1966). [d] 0.1 M $NaClO_4$: F. Basolo and T. T. Chen, *J. Am. Chem. Soc.*, 76, 953 (1954).

Results

Measured pK values and binding constants for Cu^{2+} are shown in Table I. For proline, the present thermodynamic results are in satisfactory agreement with previous measurements (in parentheses) under similar conditions. Our results for dMG differ somewhat from those of an earlier determination in a slightly different medium.

Table II summarizes initial concentrations and measured relaxation times for L-proline and dMG. Two relaxations times were found for both ligands which ranged as follows: dMG $\tau_1 = 0.47-6.7$ msec, $\tau_2 = 3.8-8.2$ msec; L-proline, $\tau_1 = 24-123$ msec, $\tau_2 = 6.5-278$ msec. Kustin and Liu[11] have previously reported kinetic results for the Cu^{2+}–proline system. Measurements, as reported in that study, were carried out at relatively high pH values under such conditions that only one relaxation time was observed for each system. In all instances, the observed time corresponded to the plus root in eq 1. They also reported, for the Ni^{2+}–proline system, that some of the relaxation times corresponding to the negative root in eq 1 were surprisingly long. Similar considerations should apply to the Cu^{2+} system. As Table II shows, we have been able to obtain τ_- values for almost all the solutions investigated. The longest τ_- value was found to be 0.28 sec, a time which overlaps considerably with the thermal disturbance present in T-jump measurements. These times were easily resolved by stopped flow spectroscopy.

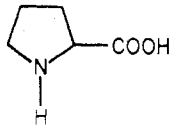
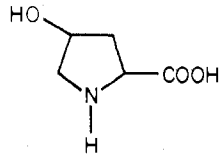
Analysis and interpretation of the data are consistent with the previously described two-step mechanism (reaction scheme I) for Cu^{2+}–amino acid complexation kinetics. This mechanism is based upon the assumption that the amino acid anion

Table II. Initial Concentrations and Measured Relaxation Times for Cu(II) Systems[a]

Dimethylglycine					L-Proline				
$[Cu]^0$,[b] M	$[L]^0$, M	pH[c]	τ_1^{-1},[d] sec^{-1}	τ_2^{-1}, sec^{-1}	$[Cu]^0$,[b] M	$[L]^0$, M	pH[c]	τ_1^{-1},[d] sec^{-1}	τ_2^{-1}, sec^{-1}
0.01	0.10	4.33	2152[e] (2036)	(382)	0.03	0.50	3.25	41 (45)	11 (11)
0.01	0.10	4.22	1431[e] (1508)	(318)	0.04	0.50	3.18	39 (39)	11 (11)
0.01	0.10	4.10	1118[e] (1082)	266 (264)	0.02	0.50	3.35	34 (56)	12 (12)
0.01	0.10	4.05	940[e] (943)	258 (246)	0.04	0.25	3.20	33 (28)	9.6 (9.5)
0.01	0.10	3.97	761[e] (756)	(221)	0.04	0.10	2.79	10[e] (12)	(6.0)
0.01	0.05	4.14	(1521)	171 (187)	0.05	0.0075	2.80	8.5 (8.6)	(5.6)
0.0125	0.025	4.10	(1695)	146 (140)	0.04	0.0075	2.82	8.1 (8.0)	(5.3)
0.01	0.025	4.00	(967)	135 (135)	0.04	0.40	4.31	(350)	154[e] (135)
0.01	0.0125	3.85	(477)	122 (116)	0.02	0.50	4.49	(712)	126[e] (127)
0.01	0.003	3.78	(206)	112 (109)	0.02	0.50	4.32	(484)	81[e] (87)
0.01	0.10	3.76	428[e] (429)	(174)	0.02	0.50	4.11	(301)	50[e] (54)
0.01	0.20	3.70	(360)	200 (213)	0.02	0.50	3.66	(110)	28[e] (21)
0.01	0.15	3.73	(382)	171 (198)	0.04	0.40	3.55	(71)	22[e] (21)
0.01	0.10	3.67	341[e] (341)	146 (159)	0.01	0.50	3.60	(98)	18 (16)
0.01	0.10	3.60	262[e] (289)	(150)	0.01	0.25	3.65	(58)	14 (14)
0.01	0.05	3.78	(480)	141 (130)	0.02	0.25	3.37	(34)	11 (11)
0.01	0.025	3.76	(426)	125 (123)	0.01	0.125	3.49	(27)	9.2 (9.4)
0.01	0.10	3.50	247[e] (231)	(138)	0.02	0.125	3.26	(22)	8.4 (7.8)
0.01	0.10	3.35	216[e] (176)	(124)	0.03	0.125	3.13	(20)	7.8 (7.2)
0.05	0.05	3.18	204 (263)	(114)	0.01	0.025	3.25	(13)	5.6 (6.0)
0.0125	0.05	3.18	151 (138)	(110)	0.04	0.0125	2.99	(14)	4.6 (5.7)
0.01	0.25	3.08	150 (160)	(108)	0.04	0.00625	3.08	(13)	4.3 (5.6)
0.01	0.15	3.00	150 (134)	(99)	0.04	0.003125	3.20	(13)	3.6 (5.6)

[a] At 25° and $I = 0.1$ M KNO_3. Data presented here represent only 80% of the total measurements made. The omitted data correspond to nearly overlapping measurements and agree well with those presented in the table. [b] Superscript refers to total stoichiometric concentration (M) after mixing. [c] $[H^+]$ was calculated by dividing measured a_H values by γ_H (≅0.83). [d] Values in parentheses are calculated as described in the text with best-fit rate constants. Other τ^{-1} values are experimental. [e] Refers to measurements made on the temperature jump apparatus apparatus. All others are stopped flow.

Table III. Chelate Formation Rate Constants of Cu(II) with α-Amino Acids ($I = 0.1$, $T = 25°$)

Classification	Ligand	Formula	pK_{a_2}	$k_{1f} \times 10^{-9}$, M^{-1} sec^{-1}	k_{1r}, sec^{-1}	$k_{2f} \times 10^{-9}$, M^{-1} sec^{-1}	k_{2r}, sec^{-1}	Ref
Nonhindered	Glycine	$HCHNH_2COOH$	9.6	4.3	23	1.0	120	12
	Alanine	CH_3CHNH_2COOH	9.7	1.7	14	0.42	93	12
	Serine	$HOCH_2CHNH_2COOH$	9.1	2.5	32	0.5	150	6
Hindered	Leucine	$(CH_3)_2CHCH_2CHNH_2COOH$	9.9	1.6	12	0.8	15	7
	Valine	$(CH_3)_2CHCHNH_2COOH$	9.7	1.1	8	0.23	23	12
	Phenylalanine	$PhCH_2CHNH_2COOH$	9.1	1.2	22	0.3	30	9
Nitrogen substituted	Sarcosine	$HCH(NHCH_3)COOH$	10.0	2.8	32	0.1	22	8
	N,N-Dimethylglycine	$HCHN(CH_3)_2COOH$	9.8	1.4	86	0.38	107	Present
	Proline		10.6	2.6 2.5	3.6 3.0	0.22 0.27	5.6 5.9	Present 11
	Hydroxyproline		9.5	0.74	3.1	0.28	2.8	11
	Bicine	$HCHN(C_2H_4OH)_2COOH$	8.1	0.95	5	0.032	145	12

(L^-) is the only species active in binding to the metal ion. There are two relaxation times corresponding to the formation of the mono and bis complexes

$$2L^- + Cu^{2+} \underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}} CuL^+ + L^- \underset{k_{2r}}{\overset{k_{2f}}{\rightleftharpoons}} CuL_2$$
$$H_2L^+ \overset{K_{a_1}}{\rightleftharpoons} H^+ + HL \overset{K_{a_2}}{\rightleftharpoons} H^+ + L^- \text{ (pre-equilibria)} \quad \text{(I)}$$

where the arrows indicate the slow steps. The two relaxation times for scheme I are given by

$$\frac{1}{\tau_\pm} = -\frac{1}{2}\left[a_{11} + a_{22} \pm \sqrt{(a_{11} + a_{22})^2 - 4(a_{11}a_{22} - a_{12}a_{21})}\right] \quad (1)$$

where τ_+ and τ_- correspond to the plus and minus signs respectively within the brackets and the a_{ij} coefficients are calculated from the mole balance and pre-equilibrium relationships[12] for this reaction scheme.

The forward rate constants were obtained by inserting trial values for these constants into a computer program which generated a set of theoretical τ^{-1} values. The best set of rate constants were taken as those which minimized the error function defined as follows:

$$\sigma = \Sigma\left(\frac{\tau_{calcd}^{-1} - \tau_{exptl}^{-1}}{\tau_{exptl}^{-1}}\right)^2 \quad (2)$$

For details of this procedure the reader is referred to ref 11 and 12.

The best computer fitted forward rate constants were found to be $k_{1f} = 1.4 \times 10^9$ M^{-1} sec^{-1}, $k_{2f} = 0.38 \times 10^9$ M^{-1} sec^{-1}

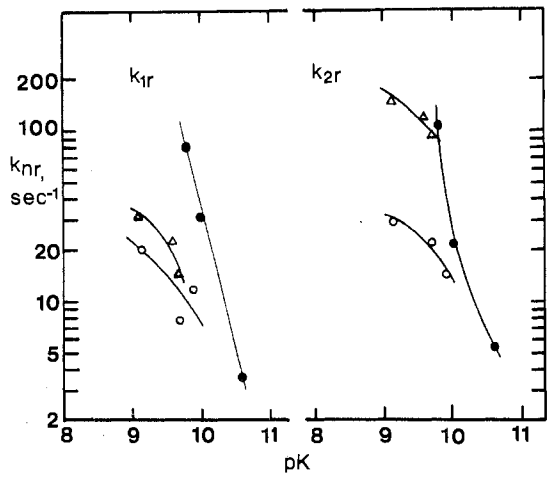


Figure 1. Variation of dissociation rate constants with the amino pK: ○, unhindered α substituted; △, hindered α substituted; ●, N-substituted systems.

for dMG and $k_{1f} = 2.6 \times 10^9\ M^{-1}$ sec^{-1}, $k_{2f} = 0.22 \times 10^9\ M^{-1}$ sec^{-1} for L-proline. The reverse rate constants as obtained from the forward rate constants and the corresponding equilibrium constants are $k_{1r} = 86$ sec^{-1}, $k_{2r} = 107$ sec^{-1} for dMG and $k_{1r} = 3.6$ sec^{-1}, $k_{2r} = 5.6$ sec^{-1} for L-proline. The best fit rate constants for proline are in excellent agreement with those reported in the earlier study[11] (Table III).

Discussion

Kinetic results are now available for the interactions of Cu^{2+} with 11 α-amino acids. Table III compares the forward and reverse rate constants of dMG and proline with those of the other α-amino acids. The forward rate constants for dMG and proline are seen to be comparable with those of the systems studied earlier. That is, substitution on the α carbon or the nitrogen produces small but significant changes in the rates of metal complexation. In this respect the rates of formation of the mono and bis complexes of proline and dMG are "normal", and the rigid configuration imposed by the five-membered ring in proline is seen not to additionally influence these rates. This was initially pointed out in the earlier study[11] on proline. The additional *N*-methyl group on dMG slows the rate of formation of the mono complex by a factor of 2 as compared with sarcosine; there is, however, no additional slowing of the rate of formation of the bis complex.

Forward Rate Constants. Examination of the forward rate constants in Table III indicates that there are two sets of values, those which correspond to (essentially) *nonhindered* complexation and those which correspond to *hindered* complexation, on the basis of the bulkiness of the substituent groups (relative to glycine). The amino acids which permit unhindered or virtually unhindered reaction have k_{1f} values of 2–4 × 10^9 M^{-1} sec^{-1} for k_{2f} values of 0.4–1 × 10^9 M^{-1} sec^{-1}. The corresponding rate constants for the hindered groups are 1–1.6 × 10^9 and 0.2–0.8 × 10^9 M^{-1} sec^{-1}, respectively. Although values for the two groups overlap somewhat, there is clearly a decrease from glycine through phenylalanine. We had called attention to this trend in an earlier paper.[12] Rate constants for the N-substituted systems fall into both the above categories; sarcosine and proline appear to be unhindered, and dMG hindered. (The value of k_{2f} for sarcosine seems to be somewhat small.) As pointed out previously[12] bicine is an unusual system in that it appears to be behaving as a tridentate ligand.

Reverse Rate Constants. Differences among the three groups, which manifest themselves only slightly in terms of the forward rate constants, are much more pronounced when one examines the reverse rate constants. The values of k_{1r} for the unhindered group are 15–30 sec^{-1}; for the hindered, 10–20 sec^{-1}; and for the N-substituted, 3–100 sec^{-1}. The considerable overlap results from the fact that we are comparing ligands of different pK_{a2} values. Figure 1 shows how k_{1r} and k_{2r} depend, for a given class, upon the amino pK. In all instances, there is a decrease in k_{nr} values as the basicity of the amino nitrogen increases. At a given pK, k_{1r} and k_{2r} increase in the order hindered < nonhindered < N substituted. The ratio of nonhindered/hindered values is only about 1.5 for k_{1r}, but is about 5 for k_{2r}. The values for k_{nr} for the N-substituted systems are consistently higher than those for the α-carbon-substituted amino acids, with a much larger variation over the pK range involved.

N-Substituted Systems. There are several features of the rate constants for N-substituted α-amino acids that merit special comment. First, the numerical spread of the rate constants is quite large. Values of k_{1f} vary by a factor of 4: 0.74–2.8 × 10^9 M^{-1} sec^{-1}. The variation among values of k_{2f} is even larger: 3.2 × 10^7 to 3.9 × 10^8 M^{-1} sec^{-1}. The former is the smallest rate constant yet observed for the reaction of Cu(II) with an α-amino acid. Second, values of k_{nr} not only vary quite widely, compared with the other classes of amino acids shown in Table III, but also are the most dependent upon the amino acid pK (Figure 1). Dissociation rate constants for dimethylglycine are substantially larger than those reported for sarcosine, while the rate constants for proline are approximately an order or magnitude smaller as compared with sarcosine. The great dissociation stability of proline is presumably not due to any additional stability conferred by the pyrrolidine ring system, but rather to the fact that the amino pK is the highest for this system.

Both bicine and hydroxyproline are exceptions to these generalizations and to the trends displayed in Figure 1. The former is almost certainly acting as a *tridendate* ligand. Evidence[12] for this is the anomalously low k_{1r} value, accompanied by a larger k_{2r} value. Dissociation rate constants for hydroxyproline are also different (smaller) than would be expected on the basis of its pK. Kustin and Liu[11] explained the low dissociation rate constants for this compound on the basis of hydrogen bonding effects between the hydroxy group and solvent molecules. This hydrogen bonding could result in a greater difficulty in breaking up the complex.

In conclusion, we have demonstrated that substitution upon the nitrogen is more effective in bringing about changes in kinetic behavior than is substitution of the α carbon for these amino acid systems. We have further shown that there are three groups of complexes formed, and that within each group the dissociation rate constants vary in a predictable manner with the amino pK.

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Registry No. Cu^{2+}, 15158-11-9; *N,N*-dimethylglycine, 1118-68-9; L-proline, 147-85-3.

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Contribution from the Department of Chemistry, Indian Institute of Technology, Kanpur 208016, U.P., India

Chemistry of Tetravalent Nickel and Related Species. I. MN_6 Coordination Octahedra Generated from Hexadentate Oxime Ligands

J. G. MOHANTY, RAJENDRA P. SINGH, and A. CHAKRAVORTY*

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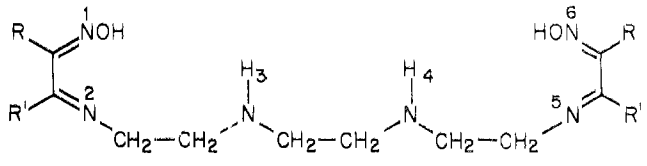
Hexadentate ligands ($H_2RR'L$) of type **1** readily yield high-spin nickel(II) complexes, $Ni(H_2RR'L)X_2$ (X = ClO_4, NO_3), in which the coordination polyhedron is octahedral NiN_6 and Dq is ~1300 cm^{-1}. These are readily oxidized to red diamagnetic $Ni(RR'L)X_2$ by chemical and electrochemical means. The oxidized complexes contain tetravalent nickel held in an octahedral NiN_6 core. They show two intense ligand → metal charge transfer transitions in the visible region. The charge transfer state also makes some contribution to the ground state (ir data). $Ni(RR'L)^{2+}$ oxidizes quantitatively 2 mol of Fe^{2+} to Fe^{3+}. The potential of the half-cell reaction $Ni(RR'L)^{2+} + 2H^+ + 2e^- \rightleftharpoons Ni(H_2RR'L)^{2+}$ is determined using a direct potentiometric method. $E°_{298}$ (vs. normal hydrogen electrode) is found to lie in the range 0.90–0.94 V for the systems studied. The possible role of the negative charge on the =N—O⁻ moiety in minimizing the effective positive charge on the metal in $Ni(RR'L)^{2+}$ is discussed. The spectroscopic properties of the low-spin complexes of H_2Me_2L with two other d^6 ions, viz., iron(II) and cobalt(III) are compared with those of the nickel(IV) species.

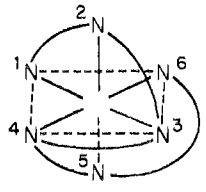
Introduction

Uncommon oxidation states of elements, transition elements in particular, have always fascinated inorganic chemists.[1] Such oxidation states are often implicated as transient intermediates in chemical and biochemical redox reactions. To obtain "stable" compounds containing such oxidation states is then of obvious interest. In the particular case of nickel the most common oxidation state is nickel(II). The higher oxidation states, nickel(III) and nickel(IV), are scarce and have aroused considerable interest. The existing literature was recently summarized elsewhere.[2,3] It has been postulated[4,5] that higher oxidation states of nickel are favored by localized accumulation of negative charge on donor atoms and by formation of strong metal–ligand σ bonds. The roles of these factors were illustrated using pyridine–oxime type ligands.[4,5] In general, oxime ligands appear to be particularly suitable for stabilization of higher oxidation states of nickel.[3]

In the present work, hexadentate ligands of type **1** simultaneously containing oxime, azomethine, and amine functions are shown to yield cationic nickel(II) and nickel(IV) species, both of which are quite stable. Selected properties of iron(II) and cobalt(III) complexes are also reported for the purpose of comparison. Directly determined thermodynamic redox potential data for nickel(IV)–nickel(II) couples are virtually unobtainable in literature. For the systems described in this paper, it has been possible to obtain such data. In what follows the ligand system **1** will be abbreviated as $H_2RR'L$; when R = R', the abbreviation will be H_2R_2L.



1



2

Results and Discussion

A. Nickel(II) Species. The ligand H_2Me_2L and its cobalt(III) complexes were reported recently.[6,7] The nickel(II) complexes of this and other ligands of type **1** are brown crystalline solids of composition $Ni(H_2RR'L)X_2$ (X = ClO_4, NO_3) (Table I). These are obtained by reacting **1** with NiX_2 or by the in situ reaction of NiX_2 with the appropriate isonitroso ketone and triethylenetetramine.

Electrical conductivity data (Table II) require[8] that the chelates are 1:2 electrolytes. The complexes are all high spin with magnetic moments lying close to 3.1 BM (Table II). In aqueous solution an electronic band is seen at ~12,800 cm^{-1} and a shoulder appears at ~20,000 cm^{-1} superimposed on a rising ultraviolet tail (Table III). These are assigned to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (ν_1) and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) respectively in idealized O_h symmetry. We therefore have $Dq \sim 1280$ cm^{-1} and $B(\text{found})/B(\text{free ion}) \sim 0.85$ where B is the Racah parameter. The above physical data show that $Ni(H_2RR'L)^{2+}$ contains pseudooctahedral nickel(II) most probably of the structural type **2**, which has been shown to be present in $Co(HMe_2L)Br_2 \cdot 4H_2O$ and $Co(H_2Me_2L)Br_3 \cdot 3H_2O$ from X-ray work.[7] $H_2RR'L$ produces a Dq which is larger than those of many other NiN_6 species.[5,9,10]

B. An Iron(II) Complex. For comparison with nickel(II), nickel(IV), and cobalt(III) species, we synthesized the iron(II) complex $Fe(H_2Me_2L)(ClO_4)_2$ which is red and diamagnetic both in the crystalline state and in aqueous solution. It is a 1:2 electrolyte[8] in acetonitrile (molar conductivity at 305°K = 285 ohm^{-1} cm^2 mol^{-1}). It gives rise to two intense electronic bands (Figure 1) in aqueous solution (19,400 cm^{-1}, ϵ 6300; ~23,000 cm^{-1} (shoulder), ϵ 2000). The same bands also appear in the crystalline state. The band at 19,400 cm^{-1} can be safely assigned to a charge transfer transition from the metal t_{2g} orbital (idealized O_h) to the lowest empty diimine π^* orbital.[10-13] The origin of the shoulder at 23,000 cm^{-1} is less certain.[14]

C. Nickel(IV) Species.[15] **(a) Synthesis and Characterization.** When H_2Me_2L is treated with concentrated HNO_3 a violent reaction occurs with the evolution of nitrous fumes. The solution thus obtained has no chelating properties toward metal ions. It has not been possible to isolate any definite compound from the oxidized solution. Evidently the free ligand is destroyed by concentrated HNO_3. On the other hand, on