of bicyclic tris(amino)boranes such as IV proceeds stepwise and involves a monocyclic intermediate.

The pmr spectrum of IV exhibits only three peaks. The overlapping multiplet centered at 3.4 ppm (8H) is due to the nitrogen-bonded methylene groups, a quintuplet (2.25 ppm, 2H) is observed for the CH_2–CH_2–CH_2 protons, and a broad singlet (1.34 ppm, 2H) can be assigned to the two NH protons.

In Table II the boron-11 nuclear magnetic resonance data for some boron-substituted 1,3-dimethyl-2-diazaboracycloalkanes are listed. It is noteworthy that the effect of the boron substituents on the deshielding of boron is analogous in order for the five-membered and the six-membered heterocycles independent of the ring size; however, the chemical shifts are slightly more negative for the smaller rings. On the other hand, the effect of nitrogen substituents on the boron-11 chemical shift appears to be much less pronounced. For example, in the series of 1,3,2-diazaboracyclohexanes, I, where $n = 3$, R′ = H, and R = H, CH_3, and C_2H_5, δ values of −25.1, −26.6, and −25.5 ppm, respectively, were observed with a coupling constant J_{BH} of 131, 132, and 128 Hz, respectively.

TABLE II
BORON-11 NMR DATA OF 1,3-DIMETHYL-2-DIAZABORACYCLOALKANES[a]

R′ of compd I	^{11}B nmr data, δ, ppm[b] $n = 2$	$n = 3$	R′ of compd I	^{11}B nmr data, δ, ppm[b] $n = 2$	$n = 3$
I	−21.3	−21.4	Cl	−27.0	−25.1
Br	−26.0	−24.8	H	−28.3	−26.0
$N(CH_3)_2$	−26.1	−25.2	CH_3	−31.6	−29.2

[a] Recorded at 19.3 MHz. [b] Neat liquids, external boron trifluoride etherate standard.

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Rates of Protonation of Some Amide and Peptide Nickel(II) Complexes

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A number of metal ions have the ability to promote proton ionization from a coordinated amide or peptide moiety. Nickel(II), for example, forms weak complexes with amino acid amides and glycine peptides in neutral solution but these lose protons from the ligand at about pH 9.[1] Judging from the structures of isolated solids,[2-4] as well as from indirect evidence, there is a Ni–O to Ni–N bond rearrangement at the amide or peptide site as a result of the proton ionization from the coordinated CONHR residue. This deprotonation is usually attended also by conformational change from an octahedral complex to a yellow or orange planar species.

The observation[1,5-9] of slow rates associated with either the deprotonation or the reverse protonation reaction supports the idea of such an attendant bond rearrangement, since this might conceivably limit the rate of an otherwise expected rapid proton–base reaction. Recently Billo and Margerum[9] have carried out an extensive investigation of the kinetics of reaction of a number of acids HX, including H_3O^+ and H_2O, with the deprotonated species derived from the nickel–triglycine complex $Ni(Gly_3\text{-}2H^+)^-$. The rate of reprotonation was given by rate = $\{k_{HX}[HX]\}[Ni(Gly_3\text{-}2H^+)^-]$. Distinct mechanisms were suggested for the reaction with HX and with H_2O. We have measured the acid-independent values (corresponding to k_{H_2O}) for the reprotonation of deprotonated nickel complexes of a number of amides and peptides and reached some conclusions as to their structures and the mechanism of the protonation.

Experimental Section

Materials.—These were commercially available and used as supplied. Triglycine and tetraglycine from different sources gave identical results. Nickel perchlorate (G. Frederick Smith) was the source of nickel ions.

Kinetic and Other Experiments.—The concentration of nickel ions was estimated by EDTA titration, and that of the ligands by direct weighing. Freshly prepared solutions were used in all cases. The metal ion inhibited hydrolysis of glycinamide and peptides is slow at 25°.[10] It was observed that on standing for some days solutions of nickel–tetraglycine underwent marked spectral changes, specifically, enhancement of absorption at 275 nm and the appearance of a new intense band at 325 nm. These changes were particularly noticeable in concentrated solution.[6] The causes for these changes are not understood, but the problem was avoided by using solutions prepared within 1 hr or so. Reproducible kinetic results were then obtained.

In the measurement of the protonation rates, the complex solution was adjusted to a pH (usually 11–11.5) at which >95% deprotonation had occurred. This solution was then plunged into a buffer (final complex concentration $\sim 10^{-3}$ M) at a pH at which >95% reprotonation of the amide or peptide took place. To effect this, a borate buffer at pH ~9 was used for amide and dipeptide complexes and a lutidine buffer at pH ~7 for the higher peptides. The reactions were followed directly at the yellow peak, around 430 nm, and/or indirectly by incorporating indicators (phenolphthalein or bromothymol blue) to monitor the small pH increase (controlled by the buffer concentration) as a result of the removal of protons from solution. Usually the conditions were such that only a small amount of dissociation of the complex occurred. Since this occurred rapidly, it did not interfere with the indicator experiments and was unimportant in following the loss of yellow peak. The reactions were carried out in a stopped-flow apparatus of the Gibson design[11] or a Cary

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14 spectrophotometer. For the mixed tripeptide and higher oligopeptide complexes the protonation reaction was sufficiently slow to allow its examination by the pH-Stat method using a Radiometer automatic titration assembly. The reactions were first-order for at least 3 half-lives. Unless otherwise specified all experiments were at 25° and an ionic strength 0.16 *M* with added KNO_3. The results are shown in Table I which also contains

TABLE I

SPECTRA AND PROTONATION RATE CONSTANTS FOR DEIONIZED Ni(II) COMPLEXES OF AMIDES AND PEPTIDES

Species	Absorption, nm	Absorption, ϵ	k_{obsd}, sec^{-1}
Ni(glycinamide-H^+)$_2$[a]	435[a]	61	1.7,[b] 1.5[c]
Ni(L-alaninamide-H^+)$_2$	430[a]	66	0.1[c]
Ni(glycylglycine-H^+)$_2$[a]			2.6[b]
Ni(glycyl-L-valine-H^+)$_2$			3.0[b]
Ni(L-alanyl-L-alanine-H^+)$_2$			1.5[b]
Ni(glycylproline-H^+)$_2$			>100[b]
Ni(glycylglycinamide-2H^+)	452	136	3.1[c]
Ni(triglycine-2H^+)[a]	430[a]	250	0.054,[b] 0.057[c]
Ni(glycylglycyl-L-alanine-2H^+)	430[a]	190	0.013,[b] 0.013,[c] 0.015,[d] 0.015[e]
Ni(triglycinamide-3H^+)	410	140	0.035[d,f]
Ni(tetraglycine-3H^+)[a]	412[a]	205	0.041[d,f] (0.003[d,f,g])
Ni(tetraglycinamide-3H^+)	410	170	0.016[d,f]
Ni(pentaglycine-3H^+)	410	170	0.016[d,f]

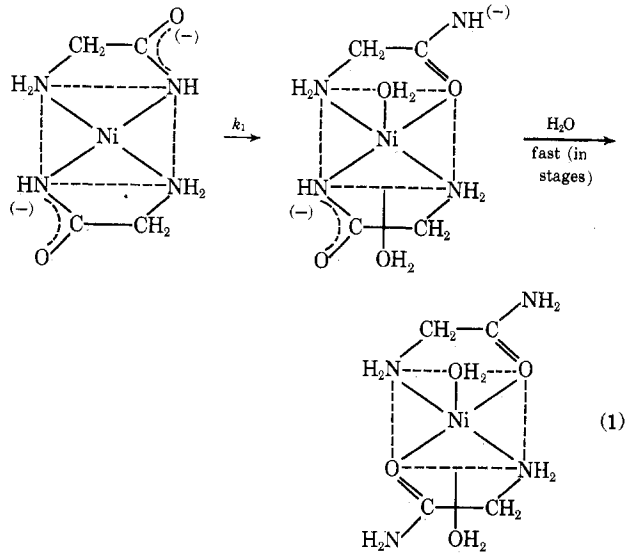
[a] Similar structures, absorption peaks, and intensities reported by R. B. Martin, M. Chamberlin, and J. T. Edsall, *J. Amer. Chem. Soc.*, **82**, 495 (1960), and J. W. Chang and R. B. Martin, *J. Phys. Chem.*, **73**, 4277 (1969). [b] H^+ change by indicator. [c] Spectrally at peak wavelength. [d] H^+ change by pH-Stat. [e] Optical rotation loss. [f] At 0°. [g] Second protonation stage (see text).

spectral data for the yellow deprotonated species (fuller details in ref 6). Because of extrapolation to low buffer and ligand concentrations, rate constants are only accurate to about ±15%. The spectra were used mainly to determine the beginning and final pH used in the kinetic experiments. Values for p*K* estimated from the spectral data[6] were in good agreement with those in the literature obtained potentiometrically. Solutions of a number of amide and peptide complexes were titrated with base. In these (and the other) experiments a ligand:metal ratio >3:1 was necessary with amides and dipeptides to prevent nickel hydroxide precipitation. For the others a ratio slightly more than 1 was sufficient. The additional equivalents of base per metal ion over that necessary to neutralize the free ligands were estimated, to determine the number of protons lost for the species shown in Table I. A Cary 60 recording spectropolarimeter was used to follow the ORD changes at 430 and 520 nm.

Results and Discussion

Amides.—We have confirmed that solutions containing nickel(II) and glycinamide release two protons (per Ni) on raising the pH, at the same time turning yellow.[1] Isosbestic points at 375 and 560 nm indicate that an intermediate monoprotonated species does not exist in appreciable amounts. Moreover, such ionization behavior is not confined to amides containing the glycyl residue since L-alaninamide, prolinamide, and even pyridine-2-carboxamide[10] complexes give up amide protons in basic solution and turn yellow or orange.

The value for the first-order rate constant for protonation of Ni(glycinamide-H^+)$_2$ was dependent on the concentration of buffer, excess ligand (added to prevent precipitation of nickel hydroxide), and hydrogen ion.[6] The value for k_{obsd} at pH ~9 is sensibly independent of a small change in pH. This value, extrapolated to small concentrations of excess ligand and buffer, is taken as the acid-independent protonation constant shown in Table I. It is believed to represent the rate constant k_1 for the Ni–N to Ni–O bond rearrangement shown in (1).[12] This rate-determining step leads to an octahedral complex which must then further protonate



(1)

and equilibrate rapidly to the composition (mono, bis, and tris) at pH ~9 demanded by the concentrations of metal ion and ligand.

We have determined that two protons are released from glycylglycinamide in the presence of nickel ion in basic solution with the production of a yellow species, unlike the behavior of glycylglycine (*vide infra*). It probably thus acts as a terdentate ligand with the amino, deprotonated peptide, and amide groups coordinated to the nickel, and a water molecule making up the planar arrangement. The value of k_{obsd} measured in the same way as with glycinamide would then represent the Ni–N to Ni–O bond rearrangement in the terminal (amide-H^+) linkage.

Dipeptides.—The nickel(II)-promoted ionization of protons from a number of dipeptides in basic solution has been reported,[1] although not observed in later work.[13] However, the structure of the solid complex Ni(Gly$_2$-H^+)$_2$ has been determined and this indicates an octahedral complex with proton loss from the peptide N and coordination of three groups from each ligand (I).[4] The ionization depicted in I in solution is supported by the slow rates of protonation for the dipeptide complexes in Table I. The values of k_{obsd} measured at pH ~9 will be related to the value of k_1 by a preequilibrium constant K_1 (eq 2). The similar values of k_{obsd} for glycinamide could be explained if the rearrangement and protonation occurred at the middle bond without the coordinated carboxylate having to be disturbed. This is unlikely. It is more probable that $K_1 \approx 1$ or that the carboxylate is not coordinated in solution, and we tend to favor the former likelihood. Glycylproline has no peptide hydrogen and the immeasurably rapid protonation for the deprotonated nickel complex must arise from the proton interaction with a hydroxy species formed at high pH.[1] The value for k_{obsd} for the glycyl-L-valine complex indicates that proton ionization has occurred from the peptide linkage also (rather

(12) We have no evidence as to the disposition of the glycinamide residues about the nickel. The amide groups are however trans in the blue octahedral $[Ni(piaH)_2(H_2O)_2]Cl_2$ and the derived orange-red planar $Ni(pia)_2 \cdot 2H_2O$, piaH = pyridine-2-carboxamide.[2,3]

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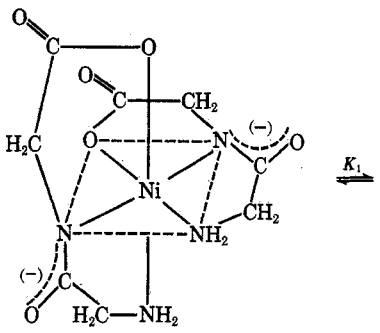

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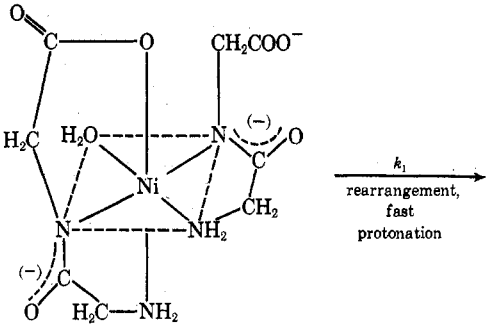
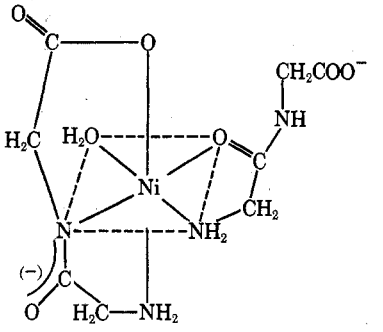
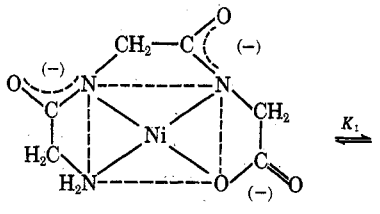




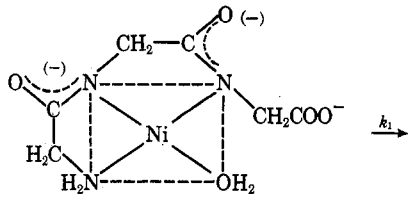
(2)

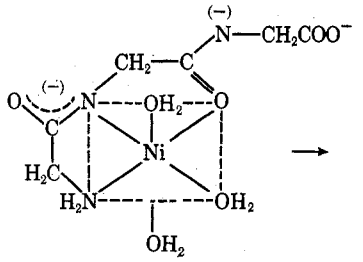
than a coordinated aquo ligand), a point which was not fully resolved in the original potentiometric study.[1] The observation of slow protonation rates with the octahedral dipeptide complexes indicates that the planar–octahedral interconversion is not directly implicated. This is not unexpected in view of the known lability of this conformational change.[14]

Tripeptides.—Both triglycine[1,13] and glycylglycyl-L-alanine lose two protons on complexing with Ni^{2+} in basic solution. As well as showing similar absorption maxima at 430 nm, the glycylglycyl-L-alanine complex in the deprotonated form shows strong ORD curves in the visible spectrum which disappear on protonation. This has been observed also by Chang and Martin,[15] who measured the circular dichroism of a number of planar nickel complexes of peptides. Because the reprotonation rate for the glycylglycyl-L-alanine complex was relatively slow, it was possible to measure this by a number of methods, including the pH-Stat and optical rotation loss. The results were in excellent agreement with one another (Table I). In the case of the triglycine complex the value agreed with that estimated by Billo and Margerum (~0.05 sec^{-1} at 25°).[9] At pH 7.3 contribution from $k_{H_3O^+}$ would be less than 10%.[9] The mechanism shown in (3) was suggested. A value



II

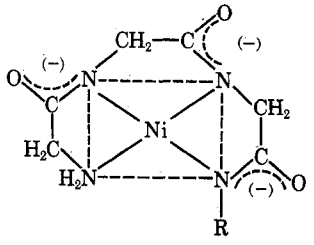




(3)

for $k_1 \approx 3$ sec^{-1} (from the results with glycylglycinamide) would lead to $K_1 = 0.05/3 \approx 0.02$ which does not seem an unreasonable value for the dissociation constant of such a nickel–carboxylate moiety. The reduced value for k_{obsd} for the glycylglycyl-L-alanine complex could then result from lowered K_1 and/or k_1 values. The identical first-order loss of optical absorption, optical rotation, and H^+ uptake for the alanine tripeptide shows that it is the *terminal* peptide group associated with the L-alanyl chromophore which is implicated and that protonation of this destroys the planar character and leads to rapid further protonation and dissociation. From (rather difficult) indicator experiments it appeared that there was a rapid consumption of *one* proton, prior to the measurable *two*-proton uptake, which was too fast to be measured by stopped flow. This could be due to the protonation of a coordinated hydroxy form ($pK = 10.5$) reported by Kim and Martell[13] although the occurrence of this ionization, as well as our rapid protonation, has been disputed.[9] In any event it appears that the yellow species examined kinetically by us is II.

Higher Peptides.—The triglycinamide–, tetraglycinamide–, and pentaglycine–nickel complexes give very similar potentiometric titration curves to that of tetraglycine,[1,13] losing three protons per Ni and giving yellow species completely formed at pH ~11 with absorption peaks at 410 nm. These species are believed to have similar structures (IV), with R = H, CH_2CONH_2,



IV

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$CH_2CONHCH_2COO^-$, and CH_2COO^- (for this structure in the solid state see ref 4), respectively. It is not possible for the CH_2CONH_2 and CH_2COO^- arms to coordinate to a fifth (apical) position.[4] The tetraglycinamide and pentaglycine complexes are remarkably stable and do not decompose completely at pH >5.

The kinetics of protonation of the tetraglycine complex was most extensively studied. A biphasic protonation was observed at 25° in which there was (a) the uptake of one proton (k = 0.22 sec^{-1}) with an attendent small optical density change at 410 nm (~10%) and (b) the consumption of remaining protons, k = 0.023 sec^{-1} (indicator), 0.020 sec^{-1} (pH-Stat), accompanied by the complete loss of absorption (k = 0.028 sec^{-1}) at the 410-nm peak. Both protonations could be easily measured by the pH-Stat method at 0° with rate constants of 0.041 and 0.003 sec^{-1} both at pH 6.7 and 7.3. A final very slow proton change recorded by an indicator in lutidine buffer[6] disappeared in their absence when examined by pH-Stat. Only the first stage was measured by pH-Stat for the other peptides listed, and the rate constant was shown to be pH independent over some 0.5-unit range of pH. The similar rate constants for the first stage at 0° suggest that we are measuring a Ni–N, Ni–O bond rearrangement in the terminal residue in all cases and that, from tetraglycine work, the product is still planar and then undergoes a second discernible protonation at the next peptide residue. The reason for this being so much slower than with triglycine may reside in the long attached grouping hindering inversion.

Conclusion

The acid-independent protonation rate constant for deionized amide and peptide complexes can be rationalized in terms of a mechanism in which an Ni–N bond switch to Ni–O is rate determining. The rate constant for the rearrangement is usually measured directly by k_{H_2O} (k_{obsd}), but when a carboxylate group has to be broken prior to protonation (as with triglycine), a preequilibrium constant is incorporated in k_{H_2O}. The values for k_{H_2O} are not strongly dependent on the structure of the amide or peptide and resemble more closely those for dissociation of nickel(II) complexes with unidentate than bidentate nitrogen ligands.[16]

Acknowledgment.—We are grateful to the National Science Foundation, which supported this work (Grants GP 1963 and GP 8099). We thank the late Mr. Arthur Baase for constructing the stopped-flow apparatus.

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The Reaction of Some Molybdenum and Tungsten Halides with β-Diketones

BY GERALD DOYLE

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Dihalobis(β-diketonate) complexes of the group IV metals, in particular $Ti(acac)_2Cl_2$, have been reported in the literature since just after the turn of the century.[1] Although some of the conclusions in the earlier work regarding the geometry[2] and even the polymeric nature[1] of complexes of this type were apparently in error, a number of more recent investigations[3-12] have determined the geometry of a variety of these complexes with some certainty. In all cases studied, including a number of germanium,[4] tin,[3-8] titanium,[9,12] zirconium,[10,12] and hafnium[10-12] compounds, there is overwhelming support for a monomeric cis octahedral structure, based on dipole moment and various spectroscopic results.

Besides the group IV metals, it appears that the only other documented preparation of complexes of the general type $M(diket)_2X_2$ is the preparation of $VCl_2(C_5H_7O_2)_2$ and $VCl_2(C_{10}H_9O_2)_2$ by the reaction of VCl_4 with acetylacetone and benzoylacetone, respectively.[13] In a short paper Larson and Moore reported[14] that $MoCl_4$ reacted with acetylacetone to give a red-purple solid whose elemental analysis approached that of $MoCl_2(acac)_2$. It was postulated that this product was polymeric with a coordination number greater than 6 although no data were given to support this or the proposed formula. This is apparently the only reference to a diketonate complex of either Mo or W in the 4+ oxidation state, although well established complexes in both higher and lower oxidation states are known. The best known of these include $Mo(acac)_3$,[15] $MoO_2(acac)_2$,[16] and $WO_2(acac)$.[17] A number of acetylacetonate complexes of oxymolybdenum species in the 5+ oxidation state have been reported,[18-20] but the existence of some of them has been questioned.[21] This present paper describes a convenient method of preparation of a variety of dihalobis(β-diketonate) complexes of Mo(IV) and W(IV) and discusses the probable structure of these compounds deduced mainly from infrared spectroscopic measurements.

Experimental Section

Preparation of Complexes.—Most of the compounds were synthesized several times. Microanalyses were carried out by Clark Microanalytical Laboratory, Urbana, Ill., and by the Analytical and Information Division, Esso Research and Engineering Co., Linden, N. J. Elemental analyses for all compounds reported in this paper are given in Table I.

Preparation of the Dichlorobis(diketonato)molybdenum(IV) Complexes. Method A. From Molybdenum(V) Chloride.—To a flask containing 5.4 g of $MoCl_5$ (0.02 mol) was slowly added a sufficient quantity of an appropriate solid or liquid β-diketone

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