Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50010

Proton Nuclear Magnetic Resonance Studies of Some Paramagnetic Nickel(II)-Amino Acid Complexes

RICHARD V. SNYDER[1] and ROBERT J. ANGELICI*[2]

Received April 16, 1973

Proton nmr spectroscopy has been used to investigate the stereochemistry of paramagnetic Ni(II) complexes of α-amino acidates (A^-), *N*-carboxymethylamino acidates (*N*-Cm-AA^{2-}), and their mixed complexes. As has been observed previously in related systems, the α-proton contact shift of the $NH_2CH(R)CO_2^-$ ligand decreases as R becomes larger and noncoordinating; this presumably results from this proton becoming more axial as the bulky R becomes more equatorial. On adding an *N*-carboxymethyl group to the amino acidate to give the Ni(*N*-Cm-AA) complexes, the α proton is forced into a more equatorial position (larger contact shifts) as a consequence of facial coordination of the ligand to the Ni(II) and the resultant rigidity and puckering of the chelate rings. Puckering of the *N*-carboxymethyl chelate ring is reflected by the large differences observed for the contact shifts of the two methylene protons. Contact shifts for ligands in the mixed complexes Ni(*N*-Cm-AA)$(A)^-$ are very similar to those of the 1:1 compounds. Contact shifts of protons in the Ni(II) complexes of *N*-pyridylmethyl-L-aspartic acid and related ligands are also reported.

Introduction

In 1969 it was reported that copper(II) complexes of *N*-carboxymethyl-L-valine (*N*-Cm-L-Val) exhibit a stereochemical preference for L-amino acidates (L-A^-) over their D enantiomers.[3] That is, in general the equilibrium constant (K) is larger for reaction 1 than for reaction 2. Subsequent

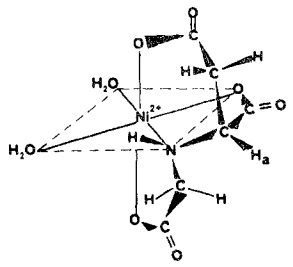
$$[Cu(N\text{-Cm-L-Val})] + \text{L-A}^- \overset{K}{\rightleftharpoons} [Cu(N\text{-Cm-L-Val})(\text{L-A})^-] \quad (1)$$

$$[Cu(N\text{-Cm-L-Val})] + \text{D-A}^- \overset{K}{\rightleftharpoons} [Cu(N\text{-Cm-L-Val})(\text{D-A})^-] \quad (2)$$

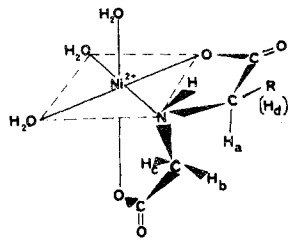
studies[4,5] have shown that the Cu(II) complexes of a variety of *N*-carboxymethylamino acids, $HO_2CCH_2NHCH(R)CO_2H$, exhibit a similar stereoselectivity.

In an effort to determine possible ligand conformations of metal ion complexes of these *N*-carboxymethylamino acid ligands, proton nuclear magnetic resonance spectra of a series of paramagnetic nickel(II) complexes were examined. The basic principles of the technique have been reviewed,[6-8] and the relationship between contact shift and chelate ring conformation has been well documented.[9-15] These latter studies have shown that the axial-equatorial nature of a ligand proton is reflected in its contact shift; *i.e.*, the more equatorial protons show a larger downfield contact shift than the axial ones (all other factors being constant). Thus it should be possible to determine relative conformations of the chelate rings in Ni(II) complexes for a series of *N*-carboxymethylamino acids by comparing contact shifts of similar protons.

The general structures of the (*N*-carboxymethylamino acidato)nickel(II) complexes, Ni(*N*-Cm-AA), to be considered here are shown in I and II.



I



II

Experimental Section

Materials. The amino acid derivatives were prepared as described previously.[4,5] The *N*-2-pyridylmethyl derivatives of aspartic acid were prepared by Dr. Pio Rechani.[16] The amino acids, $Ni(NO_3)_2 \cdot 6H_2O$, 2,2′-dipyridyl, and NaOH were analytical grade. The deuterium oxide contained 99.75% deuterium.

Sample Preparation. The nmr samples were prepared by weighing out enough of the desired amino acid and/or amino acid derivatives to make a 0.5 *M* solution when dissolved in 0.5 ml of D_2O and then adding an equivalent amount of $Ni(NO_3)_2$ as a 0.5 *M* solution. Sufficient 0.5 *M* NaOH to neutralize all of the replaceable protons was then added. The solution was reduced in volume at 50° as far as possible using a water aspirator vacuum, and then the residue was redissolved in 0.5 ml of D_2O. The evaporation was repeated, another 0.5 ml of D_2O was added, and then the solution was added to a standard nmr tube. A small amount of sodium 2,2-dimethyl-2-silapentane-5-sulfonate was added as an internal standard before recording each spectrum.

Operation of the Spectrometer. Two spectra were recorded for each complex on a Varian Associates HA-100 spectrometer at 31.6°. One spectrum was recorded on the instrument's bed recorder with the instrument in an unlocked mode using normal HR operating techniques and scanning from high to low field with the slow-sweep unit (V3507) and with the linear-sweep unit (V4352A) turned off. This type of scan was run to avoid the lower sensitivity of the external recorder for peaks occurring ~100 ppm downfield. The second spectrum was recorded on an external recorder with the ac sweep disconnected to avoid the side bands occurring every 2500 Hz; they appear in the spectra recorded by the other method. The spectra were calibrated by the side-band technique using an external oscillator.[11]

Results

The only serious problem encountered in preparing samples was solubility. Precipitates formed immediately upon

(1) National Science Foundation Trainee, 1968-1969.
(2) Fellow of the Alfred P. Sloan Foundation, 1970-1972.
(3) B. E. Leach and R. J. Angelici, *J. Amer. Chem. Soc.*, 91, 6296 (1969).
(4) R. V. Snyder, R. J. Angelici, and R. B. Meck, *J. Amer. Chem. Soc.*, 94, 2660 (1972).
(5) R. V. Snyder and R. J. Angelici, *J. Inorg. Nucl. Chem.*, 35, 523 (1973).
(6) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, 1, 103 (1965).
(7) D. R. Eaton and K. Zaw, *Coord. Chem. Rev.*, 7, 197 (1971).
(8) H. J. Keller and K. E. Schwarzhans, *Angew. Chem., Int. Ed. Engl.*, 9, 196 (1970).
(9) R. E. Richards, *Discuss. Faraday Soc.*, 34, 74 (1962).
(10) L. Pratt and B. B. Smith, *Trans. Faraday Soc.*, 65, 915 (1969).
(11) F. F. L. Ho and C. N. Reilley, *Anal. Chem.*, 41, 1835 (1969).
(12) F. F. L. Ho and C. N. Reilley, *Anal. Chem.*, 42, 600 (1970).
(13) F. F. L. Ho, L. E. Erickson, S. R. Watkins, and C. N. Reilley, *Inorg. Chem.*, 9, 1139 (1970).
(14) L. E. Erickson, F. F. L. Ho, and C. N. Reilley, *Inorg. Chem.*, 9, 1148 (1970).
(15) L. E. Erickson, D. C. Young, F. F. L. Ho, S. R. Watkins, J. B. Terrill, and C. N. Reilley, *Inorg. Chem.*, 10, 441 (1971).
(16) R. Nakon, P. R. Rechani, and R. J. Angelici, *Inorg. Chem.*, 12, 2431 (1973).

neutralization of 1:1 solutions of phenylalanine or leucine and $Ni(NO_3)_2$; precipitates formed within 4 hr with valine (Val), methionine, or isoleucine (Ileu). However, no precipitation occurred (within 3 days) for glycine (Gly), α-alanine (Ala), α-aminobutyric acid (Aba), serine (Ser), α-aminoisobutyric acid (Abu), or threonine (Thr). With the exception of iminodiacetic acid (IMDA), *N*-carboxymethyl-L-aspartic acid (*N*-Cm-L-Asp), and *N*-carboxymethyl-L-glutamic acid (*N*-Cm-L-Glu), all the *N*-carboxymethylamino acids reported here formed precipitates with $Ni(NO_3)_2$. Complete characterization of the precipitates was not undertaken, but Nujol and Fluorolube mull infrared spectra suggest that they are bis(amino acidato)nickel(II) or (*N*-carboxymethylamino acidato)nickel(II) complexes.[17]

Addition of a second ligand, such as glycine, prevented precipitation long enough to record the spectra. All evidence suggests that the complex present in these solutions is Ni(*N*-Cm-AA)(A)$^-$. This is supported by the nmr spectra which show large contact shifts for all ligands; all peaks can be assigned assuming only one complex is present. In addition, known stability constants for $Ni(IMDA)_2^{2-}$ ($\log \beta_2 = 14.61$),[18] $Ni(Gly)_2$ ($\log \beta_2 = 10.92$),[19] and Ni(IMDA)(Gly)$^-$ ($\log K_1K_2 = 13.28$)[20] allow the calculation of 1.1×10 for the equilibrium constant for the reaction $Ni(IMDA)_2^{2-} + Ni(Gly)_2 \rightleftharpoons 2Ni(IMDA)(Gly)^-$. This too indicates the preferred formation of Ni(*N*-Cm-AA)(Gly)$^-$ over the unmixed complexes.

Contact shifts for a series of (amino acidato)nickel(II) complexes (1:1) are listed in Table I along with some values from the literature. The assignments were made on the basis of relative peak areas and the distance of each proton from the delocalization center. The values reported here agree well with those reported by other authors. (In some cases, the results of other workers were not reported as contact shifts; in those cases, we estimated contact shifts from their reported spectra.) Uncertainties in peak positions vary. The extreme downfield peaks had widths of up to 20 ppm, while those near 0.0 ppm were much sharper (<1 ppm). It should be emphasized that these are contact shifts, not the observed chemical shifts of the protons. That is, they are the observed shifts minus the diamagnetic shifts (which were measured in basic solutions on the amino acidate anions with no metal ion present).

Contact shifts for a series of mixed nickel(II) complexes of glycine and some *N*-carboxymethylamino acids are listed in Table II. In general these assignments were made as before while also taking into account assignments made by Pratt and Smith[10] for the Ni(II) complex of *N*-carboxymethylalanine. In the case of *N*-benzyl-*N*-carboxymethyl-L-alanine (*N*-Bz-*N*-Cm-L-Ala), the assignments of Fitzgerald and Drago[21] for hexakis(benzylamine)nickel(II) tetrafluoroborate were used as guides for the benzyl proton assignments. They assigned resonances, with chemical shifts of −5.83, −8.71, and −5.75 ppm to the ortho, meta, and para protons, respectively. On this basis and considering relative intensities, the resonances of [Ni(*N*-Bz-*N*-Cm-L-Ala)(Gly)$^-$] appearing at −6.97, −9.00, and −7.57 ppm were assigned as the ortho, meta, and para protons.

Table I. Contact Shifts (in ppm) for the Protons of Some 1:1 Nickel(II)–Amino Acid Complexes

Amino acid	α H	β H
Gly[a]	−61	
Ala[b]	*c*	−18
Aba[d]	−30	−24, −14
Ser	−31	−16
Thr[e]	−32	−29
Abu		−16[f]
Asp[g]	−144	+8.1

[a] α H, −60.[13] [b] α H, −43; β H, −18.[13] [c] Not observed. [d] γ H, −1.0. [e] γ H, −1.5. [f] Reference 13. [g] α H, −140; β H, +8.2.[13]

Table II. Contact Shifts (in ppm) for the Protons of the *N*-Carboxymethylamino Acids in [Ni(*N*-Cm-AA)(Gly)$^{1,2-}$]

Ligand	α H	β H	γ,δ H	*N*-Cm
N-Cm-L-Asp	−115	+10.3, +7.2		−62
N-Cm-L-Glu	−90	−22	−6.6	−71, −45
N-Cm-L-Ser	−89	−7.3		−98, −16
N-Cm-L-Val	−60	−11.6	−0.6, −1.4	−97, −12.8
N-Cm-L-Ileu	−61	−10.3	−0.30	−98, −15.1
N-Cm-Gly (IMDA)	−93, −15			−23, −84
N-Bz-*N*-Cm-L-Ala[a]	−61	−6.1		−90, −11.9

[a] Benzyl contact shifts are as follows: CH_2, −5.3; ortho H, +0.26; meta H, −1.67; para H, −0.24.

Table III. Ligand Combinations Studied as Mixed-Ligand-Nickel(II) Complexes [Ni(*N*-Cm-AA)(A)$^{1,2-}$]

	A$^-$			
N-Cm-AA	Thr	Ser	Ala	Aba
N-Cm-L-Asp	×	×	×	×
N-Cm-L-Glu	×	×	×	×
N-Cm-L-Ser	×	×	×	×
N-Cm-L-Val	×	×	×	
N-Cm-L-Ileu	×	×	×	×
N-Bz-*N*-Cm-L-Ala		×	×	

In addition to the mixed complexes of Gly given in Table II, mixed complexes of the general formula Ni(*N*-Cm-AA)(A)$^{1,2-}$ indicated in Table III were also investigated. Contact shifts of the *N*-Cm-AA ligands in these complexes are not tabulated since for a given ligand they are within experimental error, the same (as in Table II) in all of the mixed-ligand complexes.

It has been shown by others[10,14] that in Ni(IMDA), structure II, H_a and H_b are different than H_c and H_d. In Ni(IMDA)(Gly)$^-$ (Table II), all four protons are different presumably because both carboxymethyl groups of the IMDA are no longer equivalent relative to the added Gly$^-$ ligand. Although exact assignments are not possible, the two equatorial protons (H_a and H_b) are associated with the large contact shifts (−93 and −84 ppm), while H_c and H_d are associated with those at −15 and −23 ppm.

As compared to the contact shifts in the 1:1 nickel(II)–amino acid (NiA) complexes, contact shifts of the amino acids in the Ni(*N*-Cm-AA)(A) complexes were 2–5 ppm smaller. A similar trend was noted for the *N*-Cm-AA ligand when comparing Ni(*N*-Cm-AA) and Ni(*N*-Cm-AA)(A). The solubilities of the complexes permitted comparisons in only a few cases; thus the contact shifts of the protons in Ni(*N*-Cm-L-Asp) (contact shifts: α H, −144; β H, +9.6, +5.3; *N*-Cm, −65 ppm) are larger than in Ni(*N*-Cm-L-Asp)(Gly)$^{2-}$ (see Table II). Likewise, contact shifts for $IMDA^{2-}$ are on the

(17) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Interscience, New York, N. Y., 1970, p 232.

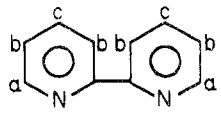
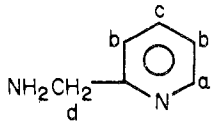
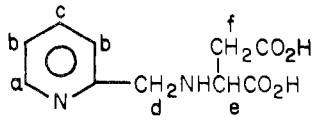
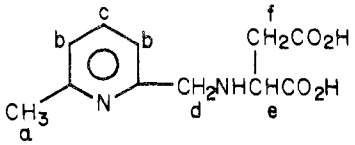
(18) S. Chaberek and A. E. Martell, *J. Amer. Chem. Soc.*, 74, 5052 (1952).

(19) J. M. White, R. A. Manning, and N. C. Li, *J. Amer. Chem. Soc.*, 78, 2367 (1956).

(20) G. Sharma and J. P. Tandon, *Talanta*, 18, 1163 (1971).

(21) R. J. Fitzgerald and R. S. Drago, *J. Amer. Chem. Soc.*, 89, 2879 (1967).

Table IV. Chemical Shifts[a,b] of 1:1 Nickel(II) Complexes

Ligand	a	b	c	d	e	f
	−159	−44.3 −57.0	−15.0			
	−157	−44.2 −46.5	−14.7	−76.8		
	−152	−44.7 −46.5	−14.2	−91.7 −84.6	−160	+2.1 +7.3
	−2.85	−24.6 −46.6	−11.5	−102	−163	+2.1 +7.3

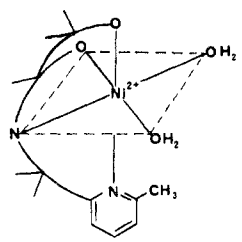
[a] In ppm relative to the internal standard, sodium 2,2-dimethyl-2-silapentane-5-sulfonate. [b] Nmr (ppm) of free ligand in D_2O with multiplicities and relative intensities given in parentheses: *N*-pyr-L-Asp, −3.00 (d, 2), −3.95 (t, 1), −4.55 (s, 2), −7.5 to −8.9 (m, 4); *N*-mepyr-L-Asp, −2.70 (s, 3), −2.90 (d, 2), −3.90 (t, 1), −4.55 (s, 2), −7.5 to −8.25 (m, 3).

average smaller in Ni(IMDA)(Gly)$^-$ (Table II) than in Ni(IMDA) (contact shifts are −95 and −26 ppm[14]). The observed reduction in contact shifts on adding a second ligand may reflect a weakening of Ni(II)–ligand bonds as more electron density is placed on the metal ion by the second ligand. One minor exception to this trend is the *N*-Cm-L-Glu ligand in Ni(*N*-Cm-L-Glu)$^-$ and Ni(*N*-Cm-L-Glu)(Gly)$^{2-}$; in this case the contact shift of the ligand is essentially the same in both complexes.

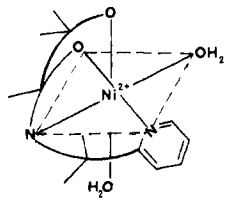
With one exception, contact shifts of ligands in complexes containing different enantiomers of the amino acid, as in Ni(*N*-Cm-L-AA)(L-A)$^-$ and Ni(*N*-Cm-L-AA)(D-A)$^-$, are the same within experimental error. The spectrum of the exception Ni(*N*-Cm-L-Asp)(L-Ala)$^{2-}$ exhibited a shoulder on the downfield side of the methyl resonance of the alanine. The complex with D-Ala showed a single resonance. The split resonance in the L-Ala complex is possibly due to the presence of isomers in which the nitrogen of the alanine is either cis or trans to the nitrogen of the *N*-Cm-L-Asp in the complex (structure I).

Chemical shifts and assignments for the 1:1 Ni(II) complexes of 2,2′-dipyridyl, α-picolylamine, *N*-(2-pyridylmethyl)-L-aspartic acid (*N*-pyr-L-Asp), and *N*-(6-methyl-2-pyridylmethyl)-L-aspartic acid (*N*-mepyr-L-Asp) are listed in Table IV. Assignments for the latter two ligands were made by comparison of their shifts to those of 2,2′-dipyridyl, α-picolylamine, and aspartic acid. These latter assignments were in turn made from comparisons to previously reported data.[22] Unequivocal assignment of the two pyridine meta protons (labeled b) to the two observed resonances could not be made. These assignments, however, are not central to the problem of ligand conformations. The para- and meta-proton resonances were relatively sharp whereas those of the ortho protons were very broad.

Spectra of the 1:1 Ni(II) complexes of *N*-pyr-L-Asp and *N*-mepyr-L-Asp are similar with the exception that the benzyl CH_2 group is a singlet in the *N*-mepyr-L-Asp complex and a doublet in the other. Models indicate that the two CH_2 protons have the same axial-equatorial character when the ligand has structure III; *i.e.*, in this isomer the chelate ring is puckered in structure IV giving rise to nonequivalence of the



III



IV

two CH_2 protons. The CH_2 doublet observed for Ni(*N*-pyr-L-Asp) therefore supports the more strained structure IV for this complex. It should be emphasized, however, that too little is currently known about the origins of such splitting to make unequivocal structural assignments.

Discussion

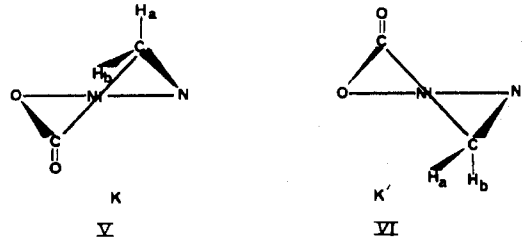
As pointed out by others,[9-15] contact shifts of α protons of α-amino acid complexes of Ni(II) are influenced by the relative axial-equatorial nature of those protons. Equatorial protons show much larger contact shifts than axial protons. In amino acids with bulky side chains, the side chain prefers a more equatorial position which forces the α proton into a more axial site. Thus for the 1:1 nickel-amino acid complexes the α-H contact shifts (Table I) decrease with increasing bulkiness of the side chain as expected: $H > CH_3 > CH_2CH_3 \sim CH_2OH$.

Because of the bulkiness of the $-CH(OH)CH_3$ side chain of threonine, it would be anticipated that α H would have a smaller contact shift than is observed. The β H in threonine also has an unusually large contact shift as compared to those for Ala, Aba, and Ser. These results could be rationalized by assuming that the OH group of threonine either coordinates directly to the Ni(II) or hydrogen bonds to an H_2O ligand coordinated to the metal ion. This would have the effect of increasing the contact shift of the β H. It should be noted that there is no similar evidence for -OH binding

(22) R. E. Cramer and R. S. Drago, *J. Amer. Chem. Soc.*, 92, 66 (1970).

in the serine complex. While such -OH coordination accounts for the large β-H contact shift of Thr, its α H should also have a larger contact shift than Ser as a result of being forced into a more equatorial position; this is not observed. Thus these results leave the question of OH coordination unsettled. Some support for -OH coordination with Thr but not with Ser comes from circular dichroism studies[23] of Cu(Thr)$^+$ and Cu(Ser)$^+$. On the other hand, stability constants[24,25] for the formation of Ni(Thr)$^+$ and Ni(Ser)$^+$ are essentially the same. An X-ray crystal structure[26] of Ni(Ser)$_2$(H$_2$O)$_2$ shows no -OH coordination.

A comparison of some of the shifts in Tables I and II gives an indication of the stereochemical changes that take place when an *N*-carboxymethyl group is added to an amino acid to form a tridentate ligand. In general, when the two chelate rings are linked together, they are forced to adopt conformations different from those of the separate rings. That is, the R groups of the amino acids which would be relatively equatorial in the free amino acid are forced into a more axial position in the *N*-carboxymethyl derivatives (structure II). Also the two protons of the *N*-carboxylmethyl group would no longer be equivalent (as they are in glycine) because one would become more equatorial while the other would become more axial. In terms of structures V and VI, either k or k′



V VI

would be favored causing H_a and H_b to become inequivalent. The two forms (k and k′) are continually interconverting but one predominates. These changes are reflected in the changing contact shifts. Adding a carboxymethyl group to glycine results in H_d and H_c becoming more axial on the average than before so that their contact shifts become less negative (*i.e.*, move from −61 to −23 and −15 ppm). An opposite effect is seen for H_a and H_b. They become more equatorial and their contact shifts become more negative (*i.e.*, move from −61 to −93 and −84 ppm). Similar changes occur for the other *N*-carboxymethylamino acid derivatives. For example, in *N*-Cm-L-Ser(R=CH_2OH), the R group will be more axial on the average than for L-Ser (due to crowding it cannot be equatorial),[10] and H_a will thus be more equatorial on the average. The expected changes in the contact shifts are observed (the β H moves up from −16 to −7.3 ppm and the α H moves down from −31 to −89 ppm). The *N*-carboxymethyl group parallels these changes as its protons exhibit contact shifts of −98 and −16 ppm.

The same conclusions do not hold for aspartic acid and *N*-carboxymethyl-L-aspartic acid. In this case, H_a in structure I may not be expected to change its axial-equatorial nature much because the tridentate aspartic acid ligand is fixed in one conformation. Thus, it is observed that there is no change in the contact shift of the α proton from [Ni(L-Asp)] to [Ni(*N*-Cm-L-Asp)$^-$] (−144 ppm).

Relative conformations of the chelate rings in different *N*-carboxymethylamino acid complexes can be estimated by comparing contact shifts of the α protons of the ligands. The H_a and H_b protons of IMDA in Ni(IMDA)(Gly)$^-$ have contact shifts of −93 and −84 ppm. Compared to these values, the methine α H (H_a of structure I) of *N*-Cm-L-Asp in Ni(*N*-Cm-L-Asp)(Gly)$^{2-}$ has a larger contact shift (−115 ppm). This indicates that the α H is more equatorial as a result of -$CH_2CO_2^-$ side-chain coordination to the metal ion. For *N*-Cm-L-AA ligands with noncoordinating side chains, the bulky α substituents force H_a (structure II) into a more axial position; thus the contact shifts for the α H of the complexes of *N*-Cm-L-Val and *N*-Cm-L-Ileu are smaller than those of IMDA. Thus, as the α substituent on the *N*-carboxymethylamino acid changes from coordinating to noncoordinating, the ring inverts from one enantiomeric conformation (k) to the other (k′) (see V and VI).

A comparison of the contact shifts for the *N*-carboxymethyl group in Table II indicates that there is a change from an essentially planar ring to a puckered one. There is but a single resonance for the two *N*-carboxymethyl protons in [Ni(*N*-Cm-L-Asp)(Gly)$^{2-}$], indicating that they are equivalent. Models show that this can only happen when the *N*-carboxymethyl chelate ring is planar. As the α substitutent becomes less coordinating (*N*-Cm-L-Asp > *N*-Cm-L-Glu > *N*-Cm-L-Ser > *N*-Cm-L-Val ≃ *N*-Cm-L-Ileu ≃ *N*-Cm-L-Ala), the two *N*-carboxymethyl protons become less equivalent, which is reflected by an increasing difference in their contact shifts (Table II). This is caused by increased puckering of the ring which forces one of the two protons into a more equatorial position while the other moves to a more axial position.

Acknowledgment. We are grateful to the National Institute of General Medical Sciences (Grant GM12626) of the U. S. Public Health Service for support of this research. The nuclear magnetic resonance spectrometer used in this research was purchased with grant funds provided by the National Science Foundation.

Registry No. Ni(*N*-Cm-L-Asp)(Gly)$^{2-}$, 42578-25-6; Ni(*N*-Cm-L-Glu)(Gly)$^{2-}$, 42578-26-7; Ni(*N*-Cm-L-Ser)(Gly)$^-$, 42578-27-8; Ni(*N*-Cm-L-Val)(Gly)$^-$, 42578-28-9; Ni(*N*-Cm-L-Ileu)(Gly)$^-$, 42578-29-0; Ni(*N*-Cm-Gly)(Gly)$^-$, 35090-13-2; Ni(*N*-Bz-*N*-Cm-L-Ala)(Gly)$^-$, 42578-31-4; Ni(*N*-Pyr-L-Asp), 41203-04-7; Ni(*N*-MePyr-L-Asp), 42578-33-6.

(23) J. M. Tsangaris and R. B. Martin, *J. Amer. Chem. Soc.*, **92**, 4255 (1970).
(24) V. S. Sharma, *Biochim. Biophys. Acta*, **148**, 37 (1967).
(25) A. Gergely, J. Mojzes, and Zs. Kassai-Bazsa, *J. Inorg. Nucl. Chem.*, **34**, 1277 (1972).
(26) D. van der Helm and W. A. Franks, *Acta Crystallogr., Sect. B*, **25**, 457 (1969).