Proton Resonance Spectra of some Nickel Complexes in Aqueous Solution

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The proton resonance spectra of some aminopolycarboxylate complexes of nickel have been measured. The assignments of the large contact shifts of the CH protons are discussed, and it is suggested that the two protons of the N—CH_2 group in a chelate ring are often non-equivalent. This is ascribed to the puckering of the rings, and a consideration of the structures of the complexes indicates that the magnitude of the shift for an N—CH proton depends on the dihedral angle across the group Ni—N—C—H in a manner similar to that found for the vicinal proton-proton coupling in aliphatic groups in diamagnetic compounds. The ligands N-2-hydroxyethyl iminodiacetate and nitrilo β-propionate diacetate, which are tetradentate in the 1 : 1 complexes, are shown to be tridentate in the 2 : 1 complexes. With the 2 : 1 complexes of iminodiacetate and N-methyl iminodiacetate, spatial isomers appear to be present.

The proton resonance spectra of many paramagnetic complexes of nickel(II) show large contact shifts [1, 2] resulting from the presence on the ligand hydrogen atoms of small fractional unpaired electron densities, which are transmitted from the nickel atom. Previous measurements [3] on nickel complexes of aminoacids had suggested that the magnitude of the shifts for N—CH protons in chelate rings depends on the conformations of the rings. This suggestion has been studied further by measuring the spectra of complexes in which the ligands are the tri- and tetra-dentate anions of aminopolycarboxylic acids.

EXPERIMENTAL

MATERIALS

The structural formulae of the anions of the following acids are shown in the legends to fig. 1, 2 and 3.

IMINODIACETIC ACID, N-METHYL IMINODIACETIC ACID AND NITRILOTRIACETIC ACID were obtained from Hopkin and Williams Ltd. and from Koch-Light Laboratories Ltd. L-histidine hydrochloride and L-proline were obtained from B.D.H. Ltd.

C-METHYL IMINODIACETIC ACID (imino α-propionic acetic acid) was prepared by the reaction of α-alanine with monochloroacetic acid.[4] The initial product (the hydrochloride) was dissolved in ethanol, ether was added and the solution cooled in ice. The iminoacid crystallized out, and was filtered off and dried in vacuum.

N-ETHYL IMINODIACETIC ACID was prepared by a method analogous to that given [5] for the N-methyl derivative, i.e., the reaction in aqueous solution of ethylamine (1 mole) with monochloroacetic acid (2 moles). Yield 55 %. Analysis, found C 44·98, H 7·00, N 8·57; $C_6H_{11}NO_4$ requires C 44·70, H 6·88, N 8·69 %.

N-2-HYDROXYETHYL IMINODIACETIC ACID was prepared from ethanolamine (1 mole) and monochloroacetic acid (2 moles), again using conditions similar to those given [5] for the N-methyl derivative. Yield 44 %. Analysis, found C 40·49, H 6·21, N 7·68; $C_6H_{11}NO_5$ requires C 40·47, H 6·26, N 7·91 %.

IMINO DI-β-PROPIONIC ACID was prepared by the hydrolysis of imino di-β-propionitrile (obtained from Eastman Kodak Co.) by $Ba(OH)_2$ in aqueous solution,[6] and recrystallized from methanol.

IMINO β-PROPIONIC ACETIC ACID was obtained by hydrolyzing the mono N-2-cyanoethyl derivative of glycine which was prepared from glycine and acrylonitrile[7]; the product crystallized as the dihydrate. Yield 74 %. Analysis, found C 33·15, H 7·23, N 7·56; $C_5H_{13}NO_6$ requires C 32·78, H 7·15, N 7·64.

IMINO α-PROPIONIC β-PROPIONIC ACID was prepared by the same method, using α-alanine. Yield 78 %. Analysis, found C 44·60, H 6·89, N 8·59; $C_6H_{11}NO_4$ requires C 44·70. H 6·88, N 8·69 %.

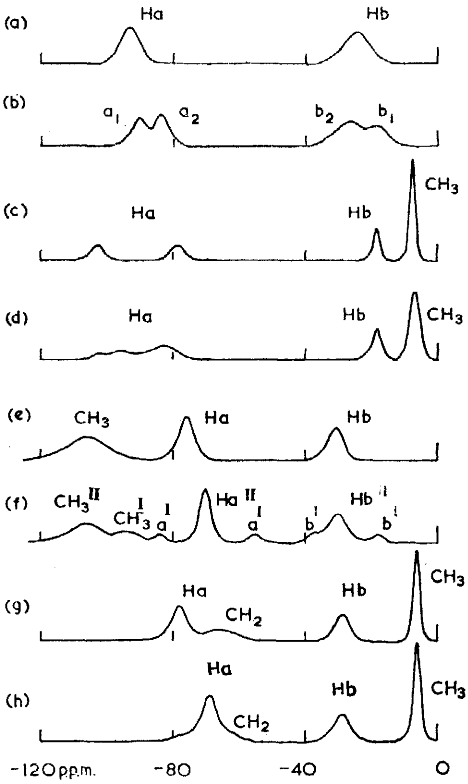

FIG. 1.—Spectra of nickel complexes with tridentate ligands forming 5-membered chelate rings only. Magnetic field increases from left to right; the scale zero is defined by the methyl line of t-butanol. (*a*) 1 : 1 and (*b*) 2 : 1 complexes with iminodiacetate, $HN(CH_aH_b{-}COO^-)_2$; (*c*) 1 : 1 and (*d*) 2 : 1 complexes with imino α-propionate acetate, $^-OOC{-}CH_a(CH_3){-}NH{-}CH_aH_b{-}COO^-$; (*e*) 1 : 1 and (*f*) 2 : 1 complexes with N-methyl iminodiacetate, $CH_3{-}N(CH_aH_b{-}COO^-)_2$; (*g*) 1 : 1 and (*h*) 2 : 1 complexes with N-ethyl iminodiacetate, $CH_3CH_2{-}N(CH_aH_b{-}COO^-)_2$.

IMINO β-BUTYRIC ACETIC ACID.[8] Glycine, crotonic acid (in slight excess) and barium hydroxide, in aqueous solution of pH about 9, were heated at 100°C for 24 h. Dilute sulphuric acid was added to precipitate the barium as $BaSO_4$, which was separated, the remaining solution then being evaporated to dryness in vacuum. The product was washed with ethanol and recrystallized from hot water. Yield 70 %. Analysis, found C 45·15, H 6·71, N 8·56; $C_6H_{11}NO_4$ requires C 44·70, H 6·88, N 8·69 %.

NITRILO TRI-β PROPIONIC ACID. Solutions of β-alanine (1 g in 3 ml water) and β-bromopropionic acid (3·5 g in 7 ml water) were separately treated with sodium hydroxide until each reached a pH of 8-9. The solutions were then mixed and heated at 100°C for 4 h, more sodium hydroxide being added from time to time to keep the pH in this range.

The solution was cooled, and concentrated hydrochloric acid was added until the pH was about 2; after further cooling, the solid (containing sodium chloride) was filtered off and the filtrate evaporated to smaller bulk. The crystals which formed on cooling were filtered off and dried in vacuum.

NITRILO β-PROPIONIC DIACETIC ACID. β-alanine (5 g in 10 ml water) and monochloroacetic acid (9 g in 17·5 ml water) were separately neutralized with sodium hydroxide until each solution reached a pH of about 8. The solutions were mixed and the mixture heated at 100°C for 5 h, more sodium hydroxide being added to keep the pH in the range 8-9. The solution was cooled, concentrated hydrochloric acid added until the pH was about 2, sodium chloride was filtered off and the filtrate kept at ice temperature. After several hours, crystals separated; they were filtered off and dried under vacuum. Yield 82 %. Analysis, found C 40·61, H 5·40, N 6·80; $C_7H_{11}NO_6$ requires C 40·97, H 5·40, N 6·83 %.

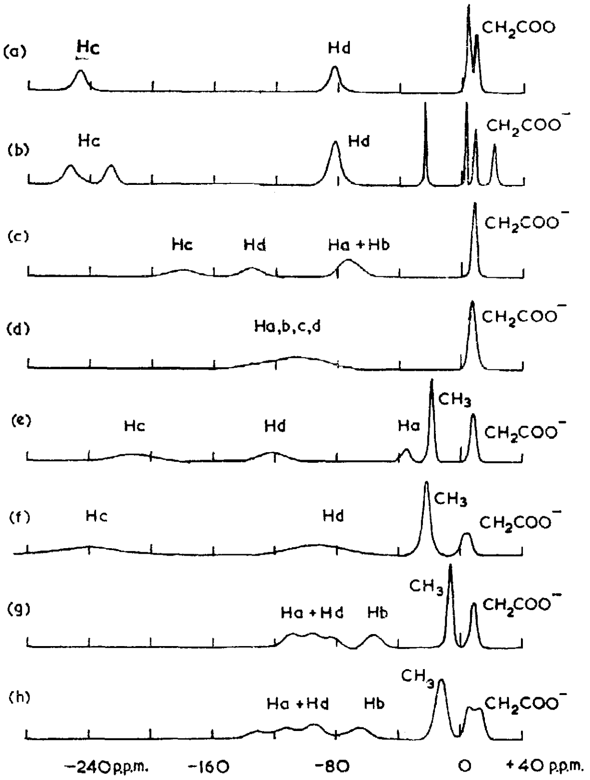

FIG. 2.—Spectra of nickel complexes, containing 6-membered chelate rings, formed with tridentate ligands. The scale is half that used in fig. 1 and 3. (*a*) 1 : 1 and (*b*) 2 : 1 complexes with iminodi-β-propionate, $HN(CH_cH_d—CH_2—COO^-)_2$; (*c*) 1 : 1 and (*d*) 2 : 1 complexes with imino-β-propionate acetate, $^-OOC—CH_2—CH_cH_d—NH—CH_aH_b—COO^-$; (*e*) 1 : 1 and (*f*) 2 : 1 complexes with imino α-propionate β-propionate, $^-OOC—CH_a(CH_3)—NH—CH_cH_d—CH_2—COO^-$; (*g*) 1 : 1 and (*h*) 2 : 1 complexes with imino-β-butyrate acetate, $^-OOCCH_2CH_d(CH_3)—NH—CH_aH_bCOO^-$.

L-PROLINE-2-d_1 was prepared by heating a solution of 0·23 g L-proline with 0·4 g sodium hydroxide in 2·5 ml D_2O in a Teflon tube (sealed inside a glass tube) at 120°C for 20 h. After cooling, the excess base was neutralized by adding DCl (in D_2O) and the solution diluted slightly to the required strength with D_2O. The proton resonance spectrum of this solution (measured before the addition of nickel chloride) showed that about 95 % of the proline C(2)-H had been converted to C(2)-D; a slight amount of decomposition product(s) was also present.

The microanalyses were made by the Microanalytical Laboratory, Imperial College. In addition, the purity of all the compounds used was shown by their proton resonance spectra (measured in D_2O solution) and also, for some of them, by the proton resonance spectra of their complexes with Tl(III).[9]

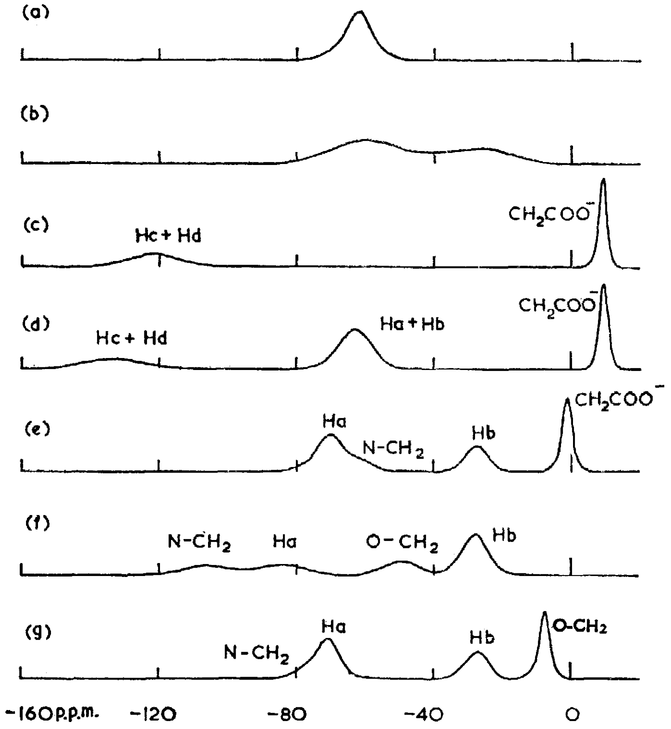

FIG. 3.—Spectra of nickel complexes with tetradentate ligands. (*a*) 1 : 1 and (*b*) 2 : 1 complexes with nitrilotriacetate, $N(CH_2COO^-)_3$; (*c*) 1 : 1 complex with nitrilo tri β-propionate, $N(CH_2CH_2COO^-)_3$; (*d*) 1 : 1 and (*e*) 2 : 1 complexes with nitrilo β-propionate diacetate, $^-OOC—CH_2—CH_cH_d—N(CH_aH_b—COO^-)_2$; (*f*) 1 : 1 and (*g*) 2 : 1 complexes with N-2-hydroxyethyl iminodiacetate, $HO—CH_2CH_2—N(CH_aH_b—COO^-)_2$.

PROCEDURE

PROTON RESONANCE SPECTRA

In order to minimize the absorption line from HOD, the NH and OH hydrogens in each ligand were largely replaced by deuterium by dissolving the ligand in D_2O and removing the equilibrated H_2O+D_2O mixture under vacuum. Weighed amounts of the deuterated ligand and of anhydrous $NiCl_2$ [10] in the ratios 1 : 1 or 2 : 1, together with the amount of anhydrous Na_2CO_3 required to neutralize the ligand acid groups, were dissolved in 0·5 ml D_2O, to give a solution in which the nickel concentration was 0·25 M. The pD, measured with indicator paper, was about 6 for 1 : 1 solutions and 8 for 2 : 1 solutions. The line positions for a given species usually vary little with pD or with concentration. The solutions were measured in stationary thin-walled 5 mm ext. diam. tubes. All spectra were recorded initially at a temperature of about 24°C and a frequency of 56·45 MHz on a Varian spectrometer; line positions (each the mean of at least four determinations) relative to the methyl line of t-butanol, were found by the sideband calibration technique. For those complexes whose spectra were poorly resolved at this frequency, the spectra (between about -100 and $+20$ p.p.m.) were also measured at a temperature of about 35°C and frequency of

100 MHz on a Perkin-Elmer R-14 spectrometer. Errors in determining line positions vary from about ±0·1 p.p.m. for the sharpest lines to about ±10 p.p.m. or more for the very broad ones.

ELECTRONIC ABSORPTION SPECTRA

The spectra of several of the 2 : 1 complexes in solutions 0·2 M in nickel were recorded at about 20°C, using a Perkin-Elmer 350 spectrometer for the wavelength range from 1 μm to 600 nm, and Beckman DB spectrometer for the range 750 to 330 nm.

RESULTS

ELECTRONIC ABSORPTION SPECTRA

Details are given in table 1; data for the nitrilotriacetate complexes have been given elsewhere.[11] The number and position of the main absorption bands, in the 2 : 1 complexes and their relatively low extinction coefficients, are typical of those found [11] for Ni(II) when bonded to two aliphatic nitrogen and four oxygen atoms arranged octahedrally, or nearly so. Since the nickel aquo ion itself is also octahedral,[12] it is likely that the 1 : 1 complexes are octahedral also, and it will be assumed that in all the complexes the nickel is bonded approximately octahedrally.

TABLE 1.—ABSORPTION SPECTRA OF 2 : 1 COMPLEXES OF AMINOPOLYCARBOXYLATE LIGANDS WITH NICKEL

ligand	nm λ_{max}	ϵ_{max}	nm λ_{max}	ϵ_{max}	nm λ_{max}	ϵ_{max}	nm λ_{max}	ϵ_{max}
iminodiacetate	990	11·9	589	5·4	374	8·0	~350^{s}	~5·7
N-ethyl iminodiacetate	970	6·0	615	4·9	379	7·8	~355^{s}	~6·5
imino β-propionate acetate	930	10·0	608	6·0	378	10·0		
imino β-butyrate acetate	935	13·4	609	7·2	375	13·0		
imino di-β-propionate	963	9·0	632	4·3	~395^{s}	~6	374	8·0
nitrilo β-propionate diacetate	985	8·6	617	5·1	380	9·0		
N-2-hydroxyethyl iminodiacetate	980	6·2	615	5·4	375	8·3	~345^{s}	~6·5

s = shoulder

PROTON RESONANCE SPECTRA

The spectra of the CH protons in the complexes are shown in fig. 1, 2 and 3 apart from those of proline-2d$_1$, proline and histidine. The spectra of the 1 : 1 complexes with the latter two ligands have been shown previously,[3] and the line positions for the N—CH protons in their 2 : 1 complexes (whose spectra are similar to the 1 : 1) are given in table 2. The line from the residual HOD of the solvent is not shown. The signal-to-noise ratios were about the same as those of the typical spectra shown in ref. (3). The relative areas of the lines are not shown; they agree fairly closely with the numbers of protons assigned to the lines. The heights of the lines are not on the same scale for different spectra. Some of the lines, particularly those with large shifts, are broad and weak, and their widths, positions and areas could not be measured accurately; in order to show them clearly on the figures, their amplitudes have been exaggerated. Measurements of the spectra under conditions giving greater sensitivity (using a high intensity of r.f. radiation with an oscilloscope display, since the drift of the baseline was too great to allow recording) revealed no lines apart from those shown. The values of the shifts (in p.p.m.) measured at 100 MHz and 35°C were slightly smaller than those measured at 56·45 MHz and 24°C, since contact shifts are inversely proportional to absolute temperature; all the positions given are those measured at 24°C. The improved resolution obtained at 100 MHz was mainly useful in separating the HOD line from CH lines close to it, but in some cases these lines themselves overlap at 56·45 MHz, and on the figures they are drawn with slightly reduced widths to indicate their appearance at the higher frequency.

All line positions are given in p.p.m. relative to the methyl line of the internal reference, t-butanol; consequently these values are not true contact shifts, which should be measured relative to the line positions of the corresponding protons in closely similar diamagnetic complexes. However, the data for diamagnetic complexes containing some of these ligands [13-15] indicate that the line positions of all the CH protons would lie in the range from -3 to 0 p.p.m., hence the corrected positions would differ only slightly from those shown, and the following discussion would not be altered.

The ligands are tri- or tetra-dentate, hence (assuming that the complexes are monomeric) the samples contain 1 : 1 and/or 2 : 1 complexes, whose amounts can be estimated both from the stability constants, when these are known, and from the relative intensities of the lines in the spectra, since the 1 : 1 and 2 : 1 complexes often give separate sets of lines. In a 2 : 1 sample, as the pH is increased from 3 to 8, the lines of the 1 : 1 complex at first increase, then diminish, being replaced by those of the 2 : 1 complex. Another rough indication of the extent of complex formation is provided by the position of the HOD line,[16] whose displacement from its position for a diamagnetic solution is roughly proportional to the relative numbers of free and co-ordinated water molecules.

The overall exchange of ligand molecules on and off the nickel is fairly slow, since separate lines are seen from the free ligands and from the 1 : 1 and 2 : 1 complexes; however, the exchange is fast enough to produce equilibrium mixtures of the various species within 30 sec of mixing.

All the lines, especially those with large shifts, are broad, and the splittings due to the proton spin coupling interactions are obscured. The broadening probably results mainly from the shortening of the proton relaxation times by interactions with the unpaired electrons, although there may be contributions from exchange processes and from the overlapping of the lines from isomers.

The NH lines can be identified since they appear only in H_2O solutions. They are broad, and their shifts are large (160 to 200 p.p.m.) and positive (i.e., to higher field). Since they are separate from the line of H_2O, the rate of exchange of the NH hydrogens with those of free H_2O is slow, suggesting that the Ni—N bonds are not very labile; a free NH is expected to be in fast exchange with H_2O.

1 : 1 COMPLEXES CONTAINING 5-MEMBERED CHELATE RINGS

Since all the shifts are negative (to lower fields) and decrease markedly with an increase in the number of bonds away from the nickel, it is likely that the unpaired electron spin density is distributed over the ligands by delocalization through the σ bonds.[1, 2, 17] The lines in the spectra of several complexes can be satisfactorily assigned if it is assumed that the two N—CH_2 protons in a chelate ring are not equivalent, one proton (H_a) contributing to one line and the other proton (H_b) to a second line. Since the " pseudocontact " effects (local magnetic fields arising from an anisotropic magnetic moment on the metal atom) are likely to be absent with Ni(II),[18] the two hydrogen atoms must carry different spin densities and therefore be oriented differently relative to the nickel. This suggests that the rings are puckered, with different dihedral angles across the Ni—N—C—H_a and Ni—N—C—H_b groups. X-ray structural studies have shown that such rings can be puckered, particularly when either joined to another chelate ring in a complexed polydentate ligand, as in [$Ni{\cdot}H_2EDTA{\cdot}H_2O$],[19] or fused to a cyclic group, as in the bis-L-proline complex of Cu(II).[20] Puckering of the rings is also indicated by the different spin coupling between the CH_2 protons and the thallium nuclei in thallic complexes with iminodiacetates,[9] and by the proton-proton coupling constants across the group H—N—C—H in iminodiacetate complexes of Co(III) [13] and Mo(VI).[22]

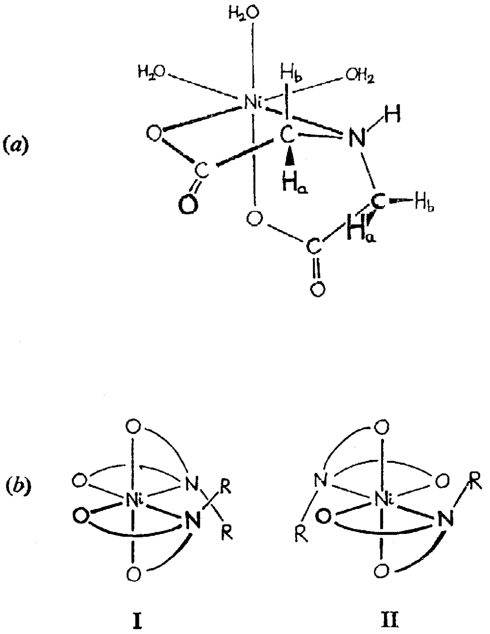

FIG. 4.—(*a*) structure assumed for a bonded iminodiacetate group; (*b*) structures of isomers for 2 : 1 iminodiacetate complexes, each ligand having the cis arrangement of carboxylate groups. (The third possible isomer, in which each ligand would have trans carboxylate groups, is assumed to be unstable.)

The ligand iminodiacetate, $NH(CH_2COO)_2^{2-}$, is almost certainly tridentate, forming two 5-membered chelate rings. The bonded carboxylate groups are probably cis to each other, as shown in fig. 4*a*, since the trans arrangement, which involves considerable strain on the CNC angle, is expected to be less stable.[14] The spectrum of the 1 : 1 complex (fig. 1*a*) shows two equally intense lines (assigned as $2H_a+2H_b$) indicating that the two puckered rings are equivalent, with two identical CH_aH_b groups. The rings are not necessarily completely rigid; the CH_2 protons would remain different on the average if there were either some conformational flexing of each ring between non-equivalent positions, or alternate temporary opening of one Ni—O bond at a time.[22]

With the mono C-methyl derivative, imino α-propionate acetate,

$$OOC{-}CH(CH_3){-}NH{-}CH_2COO^{2-},$$

the spectrum (fig. 1*c*) shows only one line in the H_b position, suggesting that the methyl group occupies the H_b position on one ring. An inspection of a space filling (Courtauld) model of this complex shows that, in order to avoid steric interference with the CH_2 group of the other ring, the methyl must be on the outside position of its own ring. Hence in this complex, and presumably in others containing the iminodiacetate skeleton, the H_a protons are those on the inside positions of each ring.

In the N-methyl and N-ethyl IDA complexes (fig. 1*e* and 1*g* respectively) the N-alkyl group protons are assigned by comparison with similar groups in other complexes,[3] aided by the relative line intensities; the single, fairly broad line from the ethyl CH_2 group overlaps the H_a line in the latter complex.

The ligand N-2-hydroxyethyl iminodiacetate, HO—CH_2—CH_2—$N(CH_2COO)_2^{2-}$, forms a slightly more stable 1 : 1 complex ($\log_{10}k_1 = 9{\cdot}5$ at 30°C [23]) than does iminodiacetate itself ($\log_{10}k_1 = 8{\cdot}3$ at 30°C [24]) and it has been suggested [23] that the ligand is tetradentate, with the hydroxyl oxygen bonded to the nickel to form a third chelate ring. The spectrum (fig. 3*f*) confirms this suggestion, since in addition to the H_a and H_b lines, there are two other lines with appreciable shifts. One of these (probably the upfield one) is assigned to the O—CH_2 group; if the OH were not co-ordinated, these protons would be expected to show only a small shift (as is found in the 2 : 1 complex, which is discussed later). The OH proton could not be seen when the spectrum was measured in H_2O solution; probably this hydrogen is in rapid exchange with the solvent.

In some complexes, the two CH_2 protons in a 5-membered ring appear to give one line, as was found [3] for the nickel complexes of the symmetrical bidentate ligands glycine and NN′-dimethyl glycine. In these cases, either the rings are planar, or the non-equivalences are averaged out by intramolecular exchange processes which allow these protons to change places and which are fast compared with the frequency difference (*ca.* 8000 Hz) between H_a and H_b. This could occur by a flexing of the rings between equivalent conformations, or by lability of the Ni—O bonds.[22] Probably the latter process occurs in the 1 : 1 complex with nitrilotriacetate, $N(CH_2COO)_3^{3-}$. This ligand is tetradentate, since the stability constant ($\log_{10}k_1 = 11{\cdot}5$ at 20°C [25]) is considerably greater than that for imino diacetate. Models show that when all three carboxylate groups are bonded, the three chelate rings are not all equivalent, and one at least is strained. However, only one, fairly broad CH line is observed (fig. 3*a*); this can result from a rapid interchange of the three carboxyl groups among the four co-ordination sites (all in one plane, one being occupied by H_2O) available to them, which will make each CH proton spend an equal time in the different environments. A similar interchange can occur in the 1 : 1 complex with the tetradentate ligand nitrilo *β*-propionate diacetate, OOC—CH_2CH_2—$N(CH_2COO)_2^{3-}$, (fig. 3*d*), making equivalent all four CH_2 protons in the 5-membered rings.

6-MEMBERED CHELATE RINGS IN 1 : 1 COMPLEXES

In the spectra of complexes containing the 6-membered chelate ring Ni—N—CH_2—CH_2—COO the CH_2COO protons are assigned to the lines which have a small positive (upfield) shift, by comparison with previous data on carboxylato complexes.[3] In several cases, two low field lines can be assigned to nonequivalent protons of the N—CH_cH_d group, one proton H_c having a shift considerably greater than those found in 5-membered rings. It is unlikely that this results from stronger Ni—N bonding, or from the change in the amount of spin density transmitted through the CH_2COO group. However, both X-ray structural studies [26, 27] and scale models show that the 6-membered rings are puckered much more than 5-membered ones, and the large shift can be related to the greater dihedral angle across the Ni—N—C—H_c group in a rigid 6-membered ring. Some support for this assignment is the absence of this line in the complex containing the N—$CH_d(CH_3)$ group (fig. 2*g*); space-filling models indicate that there is least steric hindrance when the methyl group is in the outside, " equatorial " position where the dihedral angle is large.

In some complexes, the two N—CH_2 protons appear to give one line, as with the corresponding bidentate ligand, β-alaninate.[3] Since the rings are unlikely to be planar, the equivalence must be produced by exchange processes, as discussed for 5-membered rings.

For the complex with iminodi β-propionate, $HN(CH_2CH_2COO)_2^{2-}$, the spectrum (fig. 2*a*) shows two fairly sharp CH_2COO lines, of equal intensity, possibly due to the non-equivalence of these protons; this is not observed in other complexes, whose CH_2COO line is broader. Unlike the iminodiacetate complex, both cis and trans arrangements of the bonded carboxylate groups are possible without strain of the rings; either one could be present, or both, if the exchange between them were rapid. With imino β-propionate acetate, $OOC—CH_2CH_2—NH—CH_2COO^{2-}$ (fig. 2*c*) the smaller difference between H_c and H_d could result from a partial averaging by a flexing of the ring between non-equivalent environments.

2 : 1 COMPLEXES

In the 2 : 1 samples at pH 7-8, the 2 : 1 complexes are usually the main species present; this is indicated by the stability constants (when known), by the position of the HOD line, and by the absence of the separate lines from the 1 : 1 complexes. The spectra of the 2 : 1 complexes usually show the same general features as the 1 : 1 complexes, and are assigned similarly, but in some cases more lines are seen, which can be attributed to isomers.

For the 2 : 1 complexes with iminodiacetate, three isomers are possible.[13] One of these is expected to be unstable, since each ligand in it has the strained trans structure. The observed spectrum (fig. 1*b*) can be attributed to a mixture of the other two isomers, whose structures are shown in fig. 4*b* (with R = H). One possible assignment is that the lines a_2 and b_2 represent the H_a and H_b protons in isomer I, and a_1 and b_1 the corresponding protons in isomer II, this being slightly less abundant than I. The spectrum (fig. 1*f*) of the 2 : 1 complex with N-methyl iminodiacetate can similarly be assigned as shown to a mixture of isomers I and II (with $R = CH_3$) in the proportions of 15 and 85 % respectively (roughly). Isomer I is expected to be the less stable one, since steric interactions of each methyl group with the other ligand are greater. The spectrum (fig. 1*h*) of the 2 : 1 complex with N-ethyl iminodiacetate is assigned to isomer II (fig. 4*b* with R = ethyl); the intensity and shape of the line at −70 p.p.m. suggest that it represents the two H_a protons overlapping another broader line with almost the same shift, which is assigned to the N—CH_2 group. Isomer I is either absent or present only in small amount; it would be expected to even less stable with this ligand than with the N-methyl one.

The spectrum of the 2 : 1 complex with N-2-hydroxyethyl iminodiacetate (fig. 3*g*) differs considerably from that of the 1 : 1 complex, but is similar to that of the 2 : 1 complex with N-ethyl iminodiacetate (fig. 1*h*). This suggests that the hydroxyl group is *not* bonded to the nickel in the 2 : 1 complex. The assignment is then similar to that given for the N-ethyl complex, the line from the two H_a protons overlapping with that of the N—CH_2 protons in the uncomplexed hydroxyethyl group. Even in H_2O solution the OH proton is not seen, but it is likely to be in fast exchange with the solvent protons, and in any case the shift is expected to be small.

The spectrum of the 2 : 1 complex with nitrilo β-propionate diacetate (fig. 3*e*) is also similar to that of the N-ethyl complex; in particular, there are no lines at the positions expected for a 6-membered ring, suggesting again that each ligand is tridentate, with the propionate carboxyl not bonded to the nickel.

The appearance of two lines in the spectrum (fig. 3*b*) of the 2 : 1 nitrilotriacetate complex is consistent with a suggestion [11] that each ligand is tridentate, with one —CH_2COO^- group free. With the 2 : 1 complex with iminodi *β*-propionate, the relatively sharp line at −22·7 p.p.m. (fig. 2*b*) is tentatively assigned to the C—CH_2 protons of a non-chelated Ni—N—CH_2—CH_2—COO^- group, which is possible since the second stability constant is small.[24]

DISCUSSION

The main contribution to the contact shifts of the N—CH protons, even in 5-membered rings, probably comes through the co-ordinated nitrogen atom; the contribution through the co-ordinated carboxyl is small, since in carboxylato complexes of nickel, the shifts of the CH_2COO protons are small.[3] It has already been suggested that the non-equivalences of the NCH_2 protons are associated with puckering of the chelate rings, and a correlation appears when these shifts are plotted against the dihedral angle *ϕ* across the Ni—N—C—H groups, i.e., that between the planes of the Ni—N—C and the N—C—H groups.

TABLE 2.—SHIFTS AND DIHEDRAL ANGLES FOR N—CH PROTONS IN RIGID CHELATE RINGS IN NICKEL COMPLEXES

			dihedral angle	
ligand group	proton	shift	from models	from X-ray data
N—CH_aH_b in 5-membered chelate rings	H_a	−85±15	145±10	—
	H_b	−25±5	95±10	—
N—CH_cH_d in 6-membered chelate rings	H_c	−215±35	170±15	—
	H_d	−110±30	50±15	—
histidine, $C_3H_3N_2$—CH_2—$CH_h(NH_2)$—COO^-	H_h	-160^a	(155)	150
proline, NH—CH_qH_r—CH_2—CH_2—CH_p—COO^-	H_p	-53^a	(135)	113
	H^b	-64^a	(100)	87^b
	H_r	-129^a	(20)	33^b

(*a*), shift values for histidine and proline refer to the 2 : 1 complexes since the X-ray structures refer to 2 : 1 complexes.

(*b*), the assignment of these two dihedral angles to the two shift values, could be reversed; that given agrees better with the angular variation suggested by the other data in this table.

Rough values of *ϕ* were measured from scale (Dreiding) models of the complexes, assuming the rings to be rigid and to have those conformations which appear to be least strained, and which have the least steric restraints as indicated by space-filling (Courtauld) models of the same structure. For iminodiacetate and its derivatives, the cis structure (fig. 4*a*) was assumed, in which the CH_2 groups appear to be bent outwards from the planar ring structure. The H_a and H_b positions can be distinguished by the effect of replacing one by CH_3. The conformation of a 6-membered ring was assumed to be that in the unstrained model structure for iminodi-*β*-propionate, and the proton with the large shift is assumed to be in the " equatorial " position where *ϕ* is large. The values found are shown in table 2. On fig. 5, each of the four types of proton (*a*, *b*, *c* and *d*) is represented by a large circle, to allow for the uncertainty in determining *ϕ* for a given type and for the spread of the measured shift values assigned to this type of proton; part of this spread must arise from small changes in *ϕ* but a closer correlation is not justified.

Values for the N—C—H shifts for the 2 : 1 complexes with histidine and proline are included. Both complexes are expected to have rigid chelate rings whose shapes have been assumed to be the same as those given by the X-ray determinations of the crystal structures of the nickel bis-histidino complex [28] and of the bis-proline complex of Cu(II) [20] respectively. Values of ϕ were calculated from the data given for these structures, although since the positions of the hydrogen atoms were not determined, it was necessary to calculate the values of the Ni—N—C—C dihedral angles in the aliphatic skeletons, and to derive the ϕ values from these, assuming that the N—C—H plane bisects the solid angle between the relevant N—C—C planes. In the proline complex, ϕ values for the two N—CH$_2$ protons (H$_q$ and H$_r$) in the pyrrolidine ring were also obtained, assuming that their N—C—H planes are at 120° to that of the N—C—C. (In this complex, the assignment to H$_p$ of the line at −53 p.p.m. is confirmed by its absence from the spectrum with the deuterated proline. The assignments

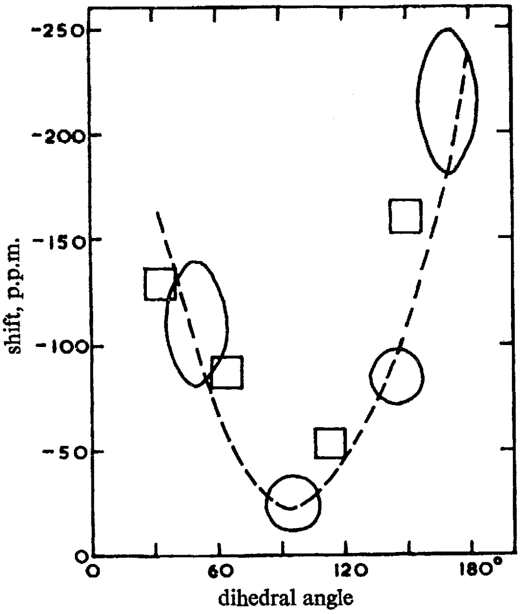

FIG. 5.—Relation between shift of N—CH protons and dihedral angle in nickel complexes. ○, dihedral angles based on scale models; □, dihedral angles derived from X-ray structural data.

given in table 2 for H$_q$ and H$_r$ could be reversed; that given seems more consistent with the variation indicated by the other values). The calculated values of ϕ, which agree roughly with those measured from models of the same structures (see table 2), are indicated by squares in fig. 5. They are not accurate, since the calculation is not made directly from known positions of the hydrogen atoms, and the complexes in solution may not have the same structures as they do in the solid state; also the values for proline were calculated for the Cu(II) complex whose parameters are probably not the same as those in the nickel complex.

Nevertheless, fig. 5 does indicate that the N—CH shifts are sensitive to the dihedral angle ϕ, possibly following the variation shown roughly by the broken line, although they must also depend on other factors, such as the strength of the Ni—N interaction and the contribution from the Ni—OOC— bond. The angular variation resembles that which appears to be present in the proton resonance spectra of diamagnetic compounds, for the spin coupling of a proton either with another proton in the group H—C—C—H [29] or with the thallium nuclei in the group Tl—N—C—H.[9] Possibly similar mechanisms are involved; in the spin coupling,[30] one nucleus interacts with the electron near it, and this interaction is transmitted to the C—H bond where a contact interaction occurs with the proton. In the group Ni—N—C—H the unpaired electrons of the nickel produce in the Ni—N bond (i.e., in the nitrogen lone pair orbital) a fractional unpaired spin, which is transmitted into the C—H bond; although in this case, the contact interaction appears as a shift since the expected splitting by the electron spin is averaged out due to the short electron relaxation time. The transmission across these aliphatic groups is usually considered to occur by a direct σ delocalization mechanism [17]; Fitzgerald and Drago [31] have shown that this type of mechanism can explain the CH proton contact shifts in nickel complexes of alkylamines.

The variation shown is consistent with the shifts found for flexible groups, whose observed values can be calculated when the averaging occurs between equivalent environments, in which the residence times will be equal. For N—CH_3 groups, the shift should be $\frac{1}{3}S_{\phi=180}+\frac{2}{3}S_{\phi=60} = \frac{1}{3}(-240)+\frac{2}{3}(-68) = -125$, agreeing roughly with the observed values (average of three $= -108$). For N—CH_2—X groups, where X is not bonded ($X=CH_3$; and also CH_2CH_2OH and —$CH_2CH_2COO^-$ in the 2 : 1 complexes), the shift is lower (average of three $= -75$). This is understandable; the X group is expected for steric reasons to occupy preferentially the position trans to the Ni—N bond, so that the CH_2 protons spend more time in the positions where $\phi = 60°$ and the shift is smaller.

A CH_2 group in a 5-membered ring, moving between equivalent positions, should give a shift of $\frac{1}{2}(S_a+S_b)$, where S_a and S_b are the shifts each proton has in the two positions. The shift of about -60 observed for 5-membered ring CH_2 protons which are equivalent, agrees with this for $S_a = -85$ and $S_b = -25$, but could equally well arise for averaging between closer values of ϕ or for planar rings. In a flexible 6-membered ring, the N—CH_2 shift should be the mean of those for H_c and H_a, i.e., about -160, roughly as found.

The large positive (upfield) shifts for the NH protons lie in the range from $+160$ to $+200$; they show little variation from one imino complex to another, or between the 1 : 1 and 2 : 1 complexes of the same ligand, and give little information about structures. The opposite signs of the contact shifts for Ni—N—H and Ni—O—H protons have been discussed recently.[32]

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