Nickel Complexes of *N*-Substituted Iminodiacetates in Aqueous Solution: Co-ordination by the Hydroxyl Group of Hydroxyalkyl Substituents

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Nickel(II) complexes of substituted iminodiacetates, $RN(CH_2CO_2^-)_2$, have been studied in aqueous solution [R = Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t, n- and t-pentyl, $HOCH_2CH_2$, $HOCHMeCH_2$, $HOCH_2CHMe$, $HOCMe_2CH_2$, $HOCH_2CMe_2$, $HO(CH_2)_3$, $HO(CH_2)_4$, and $HO(CH_2)_5$]. Stability constants have been determined for the 1 : 1 and 1 : 2 complexes; comparisons among the values found support earlier suggestions that the substituent hydroxyl group is co-ordinated only in the 1 : 1 complexes with the $HO(CH_2)_3$ ligand and with all the hydroxyethyl ligands. The proton resonance spectra of the complexes confirm these suggestions. At <0 °C, the complex with R = $HO(CH_2)_3$ shows a spectrum typical of a rigid puckered conformation for the six-membered chelate ring formed by this substituent group. Electronic spectra and magnetic moments have also been determined for the complexes; they are consistent with approximately octahedral co-ordination around the nickel.

IN aqueous solutions iminodiacetate ligands with the general formula $RN(CH_2CO_2^-)_2$ form stable 1 : 1 and 1 : 2 complexes with many metal ions [1] in which the ligand is tridentate, forming two chelate rings.[2,3] The *N*-2-hydroxyethyl derivative (R = $HOCH_2CH_2$) is quadridentate in 1 : 1 complexes, forming a third chelate ring

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[1] L. Sillén and A. E. Martell, 'Stability Constants of Metal-Ion Complexes, *Chem. Soc. Special Publ.*, Nos. **17** (1964) and **25** (1971), The Chemical Society, London.

[2] S. Chaberek and A. E. Martell, *J. Amer. Chem. Soc.*, 1952, **74**, 5052.

[3] D. W. Cooke, *Inorg. Chem.*, 1966, **5**, 1141.

with the hydroxyl oxygen bonded to the metal. This was indicated by the values of the stability constants,[4] which, for a given metal, are greater than those with the simple *N*-alkyl ligands, and has been confirmed for the complexes of Ni^{II} [5] and Co^{II} [6] by a detailed study of their n.m.r. spectra. Stability-constant data for the *N*-3-hydroxy-n-propyl derivative ($R = HOCH_2CH_2CH_2$) suggest that this is also quadridentate in 1 : 1 complexes.[7] The present work on nickel(II) complexes was done in order to confirm this suggestion, and to establish whether longer hydroxyalkyl side chains would form chelate rings. Some studies were also made of the effects of adding methyl substituents to the hydroxyethyl ligand.

EXPERIMENTAL

Ligands.—Iminodiacetic acid (B.D.H. Ltd.) and *N*-methyliminodiacetic acid were obtained from Hopkin and Williams Ltd.; the other ligands were synthesised from the corresponding amines, by reaction in aqueous solution with monochloroacetate ion (2 equivalents, plus a 5% excess). After the reactants were mixed, the temperature was kept in the range 50—60 °C; the solution was maintained at pH 9—10 by slow addition of concentrated sodium hydroxide solution, the total used containing the amount required to neutralise the HCl produced. When the reaction was complete, the ligands were separated by precipitation as the barium salts, which, after separation and drying (110 °C), were treated with the calculated equivalent amount (plus a 1% excess) of 5N sulphuric acid. The $Ba[SO_4]$ was removed (centrifuge) and the solution concentrated under reduced pressure. In most cases, the ligand crystallised, on cooling, as the free acid; this was filtered off, washed, dried, and recrystallised, giving products with satisfactory analyses (see Table 1). The above procedure was changed slightly for the s-butyl and 2-hydroxy-2,2-dimethylethyl derivatives, which were isolated by evaporating the final solution to dryness, and also for the 4-hydroxy-n-butyl and 5-hydroxy-n-pentyl derivatives, which were very soluble in water and gave gels when the water was evaporated. The latter two compounds were isolated as the dipotassium and disodium salts, respectively, by adding the calculated amount of base to the solutions, followed by evaporation to dryness *in vacuo*; the solid salts were deliquescent.

TABLE 1

Analyses and stability constants for nickel(II) complexes of the ligands $RN(CH_2CO_2^-)_2$

	Analysis (%) [a]			Stability constant at 25 °C [b]		
R	C	H	N	log K_1	log K_2	log K_1' [c]
Et	45.0 (44.7)	6.8 (6.9)	8.8 (8.7)	8.86	7.26	
Pr^n	48.1 (48.0)	7.2 (7.5)	8.1 (8.0)	8.78, 8.80 [d]	7.08, 6.80 [d]	
Bu^n	50.9 (50.8)	7.9 (8.0)	7.3 (7.4)	8.82	7.12	
n-Pentyl	53.3 (53.2)	8.4 (8.4)	6.9 (6.9)	8.87	7.13	
Bu^i	50.8 (50.8)	7.7 (8.0)	7.2 (7.4)	8.08	6.35	
Pr^i	47.9 (48.0)	7.4 (7.5)	8.1 (8.0)	8.41	7.27	
Bu^s	50.6 (50.8)	7.9 (8.0)	7.5 (7.4)			
Bu^t	50.6 (50.8)	8.0 (8.0)	7.4 (7.4)	8.42	7.43	
t-Pentyl	53.4 (53.2)	8.4 (8.4)	6.8 (6.9)	8.24	7.13	
$HO(CH_2)_2$	40.7 (40.7)	6.1 (6.2)	7.8 (7.9)	9.15 9.54 [e] 9.28 [f]	5.03 5.15 [e] 4.97 [f]	10.79 10.83 [f]
$HO(CH_2)_3$	44.1 (44.0)	6.9 (6.8)	7.2 (7.3)	9.28 9.1 [g]	5.92 5.7 [g]	
$HO(CH_2)_4$	32.5 (32.2) [h]	4.8 (5.0) [h]	4.4 (4.7) [h]	8.66	6.99	
$HO(CH_2)_5$	40.9 (41.1) [i]	5.9 (5.8) [i]	5.0 (5.3) [i]	8.73	7.01	
$HOCHMeCH_2$	44.1 (44.0)	6.8 (6.8)	7.4 (7.3)	9.31	4.08	10.97
$HOCMe_2CH_2$	30.3 (30.3) [j]	5.5 (5.4) [j]	4.4 (4.4) [j]	8.03	2.91	11.24
$HOCH_2CHMe$	44.2 (44.0)	6.8 (6.8)	7.4 (7.3)	9.85	3.36	10.67
$HOCH_2CMe_2$	47.2 (46.8)	7.3 (7.4)	6.7 (6.8)	8.48	4.73	10.36

[a] Values in parentheses were calculated for ligands as the free acids, $RN(CH_2CO_2H)_2$, except for $R = HO(CH_2)_4$, $HO(CH_2)_5$, and $HOCMe_2CH_2$. [b] The standard deviation is *ca.* ±0.06. [c] For ionisation of the 1 : 1 complex. [d] P. Sauchey, N. Israily, and P. Gouzerh, *Bull. Soc. chim. France*, 1966, **12**, 3917. [e] At 30 °C; ref. 4*a*. [f] At 20 °C; ref. 4*b*. [g] At 30 °C; ref. 7. [h] Calculated for $HO(CH_2)_4N(CH_2CO_2K)_2{\cdot}H_2O$. [i] Calculated for $HO(CH_2)_5N(CH_2CO_2Na)_2$. [j] Calculated for $HOCMe_2CH_2N(CH_2CO_2K)_2{\cdot}2H_2O$.

In addition to elemental analyses, the purity of the ligands was confirmed by the equivalences observed in the pH titrations, and by the absence of proton-containing impurities as shown by their proton resonance spectra. (These spectra also showed that acidic aqueous solutions of the 2-hydroxy-2,2-dimethylethyl derivative contain *ca.* 40% of the corresponding lactone, and that *ca.* 10% of lactone is present with *N*-(2-hydroxy-2-methylethyl)iminodiacetic acid. In both cases the lactone is absent under the conditions of the titrations.) With many of the ligands, to help in assigning lines in the n.m.r. spectra of the complexes, small (*ca.* 1 g) samples were heated in excess of alkaline D_2O for *ca.* 1 d, until the $CH_2CO_2^-$ groups had been deuteriated to $CD_2CO_2^-$.

Stability Constants.—These were determined by a pH-titration procedure. The titrations were made at 25 °C, using a glass titration vessel (150 cm³) fitted with a glass electrode (Pye Ingold 201) and a saturated calomel reference electrode (s.c.e.) (Pye Ingold 305-C8). The pH values were measured with a calibrated Pye–Unicam 291 pH meter, to an accuracy of ±0.01 unit. The pH readings were standardised, immediately before and after each titration, against N.B.S. standard buffer solutions of pH 6.87, 4.01, and 9.18, which were prepared freshly, from pure

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[4] (*a*) S. Chaberek, R. C. Courtney, and A. E. Martell, *J. Amer. Chem. Soc.*, 1952, **74**, 5057; (*b*) G. Schwarzenbach, G. Anderegg, W. Schneider, and H. Senn, *Helv. Chim. Acta*, 1955, **38**, 1147.

[5] L. Pratt and B. B. Smith, *Trans. Faraday Soc.*, 1969, **65**, 915.

[6] L. Pratt and B. B. Smith, *Trans. Faraday Soc.*, 1969, **65**, 1703.

[7] S. Chaberek and A. E. Martell, *J. Amer. Chem. Soc.*, 1954, **76**, 215.

chemicals, as directed by Bates.[8] Additional buffer solutions were used to check the linearity of the meter readings over the range pH 3.0—11.0.

All solutions were made up in boiled-out, doubly distilled, water. Stock solutions (*ca.* 0.04 mol dm^{-3}) of nickel(II) perchlorate were standardised gravimetrically, and standard solutions (0.08 mol dm^{-3}) of the ligands were prepared by accurate weighing. A standard 1 mol dm^{-3} solution of sodium perchlorate was also used. All solutions for titration were made 0.1 mol dm^{-3} in $Na[ClO_4]$ to provide a constant ionic strength. A stream of pure nitrogen, presaturated by bubbling through a 0.1 mol dm^{-3} solution of $Na[ClO_4]$ at 25 °C, was bubbled through each solution, both to stir it and to keep out atmospheric oxygen and carbon dioxide.

Each ligand was first titrated alone, at a concentration of 0.001 mol dm^{-3}, successive small amounts of 1N carbonate-free potassium hydroxide being added from an Agla microsyringe. Following each addition, the pH was recorded when a steady value had been attained (*ca.* 30 s); a further addition was then made. The process was repeated until pH *ca.* 10.5—11.0 had been attained. Each titration was repeated at least twice, to obtain readings reproducible to within ± 0.02 pH unit over the whole range. The titrations were repeated (again at least twice) for each ligand, in solutions containing Ni^{II} in concentration ratios of 1 : 1 and 1 : 2. The titrations were continued until the pH was 10.5—11.0, unless (as with some of the 1 : 1 solutions) precipitation of metal hydroxide occurred before this. It was necessary to wait longer, after each addition of base, for a steady pH reading to be attained.

The stability constants, K, were calculated by a computer program derived from equations given by Chaberek and Martell.[2] With the hydroxyethyl ligands, the equations were modified to include the additional ionisation of an OH group. The calculated values of pK are shown in Table 1.

N.M.R. Spectra.—Solutions were prepared in D_2O using anhydrous $NiCl_2$, to give a final concentration of 0.25 mol dm^{-3} in Ni^{II}. The ligands were added as solids, to give 1 : 1 or 1 : 2 ratios as required, and were neutralised when necessary by adding the required amount of standard concentrated (*ca.* 5 mol dm^{-3}) Na[OD] solution. Before preparing the required solutions, the ligands were usually first dissolved in D_2O, followed by evaporation to dryness, in order to deuteriate the OH groups, thereby limiting the strength of the residual solvent (HOD) line. The pD values were adjusted to those values (calculated from the stability constants) at which the concentrations of 1 : 1 or 1 : 2 species would be *ca.* 100%. These values were recorded by a small combined glass and reference electrodes, 0.4 being added to the pH meter reading to give the pD value.[9]

The samples were placed in thin-walled glass tubes (outside diameter, 5 mm), and a trace amount of t-butyl alcohol was added as reference; this was done after each spectrum had been recorded to avoid obscuring lines with small shifts. The tubes were not made to spin. Spectra were recorded on a Perkin-Elmer R-14 spectrometer at 100 MHz and at 35 °C, and on a Varian HR spectrometer at 56.45 MHz and at 27 °C. For several samples, recordings were also made on the Varian instrument between -5 and 80 °C.

Electronic spectra were recorded on a Cary 14 spectrometer at 20 °C, the solutions (of known pH) being 0.05 mol dm^{-3} in Ni^{II}. Other samples of these same solutions were used to measure the magnetic moments of the Ni^{II} by the Evans method,[10] using a Wilmad coaxial n.m.r. tube, with the R-14 spectrometer at 35 °C.

RESULTS AND DISCUSSION

Assignments of the bands in the electronic spectra [*] to particular transitions were made satisfactorily by reference to the data tabulated for Ni^{II} in six-co-ordinate, approximately octahedral, complexes.[11] The 1 : 2 complexes are expected to have a tetragonal structure, with the two nitrogen atoms *trans* to each other in order to minimise repulsion between the groups R, and the spectra of the complexes with small R groups are consistent with this. An additional splitting of one band develops as R becomes more bulky; this may arise from an increasing distortion to a lower symmetry, with the N–M–N axis no longer perpendicular to the plane containing the four bonded oxygen atoms. Similar additional splittings occur with the 1 : 1 complexes. With the 1 : 1 complexes of hydroxyethyl ligands, the loss of a proton at higher pH produces little change in the spectra. For both the 1 : 2 and 1 : 1 complexes, the molar absorption coefficients are fairly small, lying in the range 1.3—16.8 dm^3 mol^{-1} cm^{-1}; these values appear to be below the range found for tetrahedral complexes,[12] and it seems reasonable to assume that such co-ordination does not occur in the present complexes.

Values of the magnetic moments of the complexes (see SUP 21742) lie in the range 3.23—3.31 B.M.; [†] these are within the limits found for 'octahedral' or tetragonal complexes of Ni^{II}.[13] Hence it will be assumed that, in all the complexes, the ligand atoms are bonded to octahedral sites on the nickel ion, which, in the 1 : 1 complexes, are otherwise occupied by water molecules. The iminodiacetate part of the ligand will be assumed to be always tridentate, and in the 1 : 2 complexes the two nitrogen atoms of the two ligands will be assumed to be *trans* to each other, as discussed above; in the present work, including the n.m.r. spectra discussed below, there is no evidence for *cis* isomers (although they do occur with R = Me or H [5,14]). As discussed previously,[5] it will also be assumed that the N and two CO_2^- groups of each iminodiacetate ligand occupy a 'facial' arrangement of co-ordination sites, *i.e.* that the bonded carboxylate oxygen atoms are *cis* to each other.

Stability Constants.—The values found for the 1 : 1 and 1 : 2 species are given in Table 1, together with

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[*] Results are in Supplementary Publication No. SUP 21742 (5 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue (items less than 10 pp. are supplied as full-size copies).

[†] 1 B.M. ≈ 9.27×10^{-24} A m^2.

[8] R. G. Bates, 'Determination of pH,' 2nd edn., Wiley, New York, 1964, p. 123.

[9] P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, 1960, **64**, 188; K. Mikkelsen and S. O. Nielsen, *ibid.*, p. 632.

[10] D. F. Evans, *J. Chem. Soc.*, 1959, 2003; D. F. Evans, G. F. Fazakerley, and R. F. Phillips, *J. Chem. Soc. (A)*, 1971, 1934.

[11] J Reedijk, P. W. N. M. Van Leeuwen, and W. L. Groeneveld, *Rec. Trav. chim.*, 1968, **87**, 129.

[12] L. Sacconi, *Transition Metal Chem.*, 1968, **4**, 244.

[13] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 1964, **6**, 37.

[14] L. E. Erickson, F. F.-L. Ho, and C. N. Reilley, *Inorg. Chem.*, 1970, **9**, 1148.

values reported previously for some of the simpler ligands; the agreement with these earlier values is fairly good. With all the straight-chain *N*-alkyl ligands, the K_1 values are very similar, and so are the K_2 values. Also, the difference ΔK ($= \log K_1 - \log K_2$) is almost constant, as is often found with ligands, each of which is bonded to a metal with the same groups.[15] The smaller values of K_2 can be ascribed to a combination of statistical, coulombic, and steric effects. The stability constants K_1 are slightly smaller for the ligands which contain a bulky group; these changes possibly result from larger steric hindrance between the bulky alkyl group and co-ordinated water molecules.

With the *N*-2-hydroxyethyl ligand, the markedly greater K_1, and the larger value of ΔK, suggest strongly, as has been discussed previously,[4] that the ligand is quadridentate in the 1 : 1 complex, the greater stability being associated with the formation of a third chelate ring. In the 1 : 2 complex the ligand has been shown to be tridentate, and the hydroxy-groups are not bonded;[5] the low values of log K_2 may result from a negative entropy change associated with the opening of the third ring of the 1 : 1 complex on going to the 1 : 2 complex. With both hydroxymethyl ethyl ligands, the stability constants again indicate quadridentate structures for the 1 : 1 complexes. For the dimethyl derivatives, although the K_1 values are not much greater than those for the corresponding non-hydroxylated ligands, the large ΔK values suggest that quadridentate bonding still occurs, and this is confirmed by the n.m.r. spectra discussed below. With all the hydroxyethyl ligands, the 1 : 1 complexes lose an additional proton at high pH. This may come either from the co-ordinated COH group or from co-ordinated water. An ionisation could not be detected with other ligands, since precipitates were formed at these pH values. The data for the hydroxypropyl complex have been interpreted previously as indicating that the ligand is quadridentate in the 1 : 1 complex.[7] For the 4- and 5-hydroxy-ligands, the stability constants are very close to those of the corresponding non-hydroxylated ligands, giving little evidence of co-ordination by the OH groups in the 1 : 1 complexes.

N.M.R. Spectra.—The line positions and widths for the CH protons in the complexes are given in Table 2. The assignments of the $CH_2CO_2^-$ protons were made by comparison with the deuteriated derivatives; those for the *N*-alkyl groups were made by comparison with previously reported spectra,[5,14,16] aided by the relative areas of the lines. It is likely that, as often found with 'octahedral' nickel complexes, the shifts of the lines arise mainly from direct contact interactions between the CH protons and the small densities of unpaired electron spin, delocalised from the nickel through the σ bonds of the ligands.[17]

The $CH_2CO_2^-$ *groups.* As discussed previously,[5,14] the two lines from the $CH_2CO_2^-$ groups are assigned to the non-equivalent CH_aH_b protons of each of the two puckered chelate rings in the co-ordinated iminodiacetate group. The contact shifts for NCH protons in complexes of Ni^{II} are known [5,16] to be very dependent on the dihedral angle (ϕ) across the Ni–N–C–H group, and the two lines arise since ϕ is different for H_a and H_b. With the s-butyl derivative [$R = CH_3CH_2CH(CH_3)$] the steric interactions with the two acetato-groups will differ, and the chelate rings will be puckered differently; the spectrum of the 1 : 1 complex showed four acetato CH lines.

N-*Alkyl groups.* The large shifts are assigned to the α-CH protons. For almost all the $N-CH_2-X$ groups in different complexes, the CH_2 line occurred at approximately the same position (−60 to −65 p.p.m. in the 1 : 1 complexes), which agrees with $\phi \approx 60°$ for both protons. This suggests that the group X is oriented *trans* to the Ni–N bond. The next largest effects were found with the β-CH protons, whose shifts are sensitive to the conformation across the Ni–N–C–C–H group.[16] With the bulkiest groups, t-butyl and t-pentyl, the β-CH lines were very broad at 35 °C, became sharper at higher temperatures, and, in solutions cooled to *ca.* −5 °C, they separated into components which were also sharper. With the 1 : 2 t-butyl complex, which was easier to study due to the low solubility of the 1 : 1 complex (at −5 °C), there were two component methyl lines, of intensities *ca.* 3 and 6 protons. Presumably the restricted rotation around the N–C(α) bond has been slowed down sufficiently to allow the expected non-equivalence of the methyl groups to be observed.

Hydroxyalkyl ligands, 1 : 2 *complexes.* The spectra are very similar to those of the 1 : 2 complexes with the corresponding non-hydroxylated *N*-alkyl ligands. This suggests, as previously pointed out for the simple hydroxyethyl ligand,[5] that with all the present ligands the OH group is not co-ordinated in the 1 : 2 complexes.

1 : 1 *Complexes with* 4- *and* 5-*hydroxy-ligands.* The spectra are almost identical with those of the corresponding 1 : 1 complexes with n-alkyl ligands. Therefore these OH groups are probably not co-ordinated to the nickel; if they were, the adjacent CH_2 protons would be expected to show large shifts, as is found with the 3-hydroxy-n-propyl ligand.

1 : 1 *Complex with the* N-(3-*hydroxy-n-propyl*) *ligand.* The lines from the hydroxypropyl group, $HO-C_{\gamma}H_2-C_{\beta}H_2-C_{\alpha}H_2-N$, were shown clearly by using the ligand which had been completely deuteriated in the acetatomethylene groups. The shifts are very different from those of the corresponding n-alkyl derivatives, and can be interpreted only if the hydroxyl group is assumed to be bonded to the nickel, to form a six-membered chelate ring.

At 64 °C three equally intense lines were observed. One lay slightly up-field, and (as in other six-membered chelate rings bonded to nickel [16]) is assigned to the β-CH_2 protons. The line with the largest down-field shift is

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[15] F. J. C. Rossotti, 'Modern Coordination Chemistry,' eds. J. Lewis and R. G. Wilkins, Interscience, New York, 1960, p. 34.

[16] J. E. Sarneski and C. N. Reilley, *Inorg. Chem.*, 1974, **13**, 977.

[17] D. R. Eaton, 'Physical Methods in Advanced Inorganic Chemistry,' eds. H. A. O. Hill and P. Day, Interscience, London, 1968, p. 462.

TABLE 2

N.m.r. spectra of nickel(II) complexes of ligands $RN(CH_aH_bCO_2^-)_2$ [a]

R	Complex	Acetato CH_aH_b [b]	α-CH in R	β-CH protons (where not CH_3) [c]	γ-, δ-, and ε-CH protons (where not CH_3)	CH_3 groups
Et	1 : 1	−76.6 (600), −29.9 (500)	−62.1 (*ca.* 900)			−6.1 (275)
	1 : 2	−68.8 (500), −29.0 (700)	*ca.* −65 (*ca.* 1 400)			−6.0 (250)
Pr^n	1 : 1	−76.0 (620), −28.0 (650)	−60 (1 400)	2.8 (300)		−1.8 (140)
	1 : 2	−69.0 (540), −28.4 (760)	*ca.* −67 (*ca.* 1 400)	2.0 (450)		−2.5 (90)
Bu^n	1 : 1	−75.6 (540), −28.5 (740)	−60 (1 800)	2.7 (250)	−1.4 (100)	−1.4 [d]
	1 : 2	−69.0 (540), −29.0 (740)	−66 (1 600)	2.5 (300)	−1.9 (60)	−1.9
n-Pentyl	1 : 1	−76.0 (700), −27.6 (840)	−61 (1 400)	2.0 (400)	(−4 to 0) [d]	(−4 to 0) [d]
	1 : 2	−70.0 (610), −29.1 (860)	*ca.* −60 (1 600)	2 (400)	(−2.2 to −0.4) [d]	(−2.2 to (−0.4) [d]
Bu^i	1 : 1	−79.1 (600), −26.0 (660)	−52.4 (1 600)	2.8 (190)		−1.3 (80)
	1 : 2	−72.0 (500), −26.8 (800)	*ca.* −60 (*ca.* 1 800)	*ca.* 0 [d]		−2.3 (95)
Pr^i	1 : 1	−60.2 (460), −35.2 (560)	−71 (*ca.* 1 400)			−3.4 (*ca.* 300) [d]
	1 : 2	−59.6 (460), −31.8 (670)	−68 (*ca.* 1 700)			−3.4 (*ca.* 400) [d]
Bu^s	1 : 1	−65.0 (800),[e] −38.6 (600) [e] −54.6 (600),[e] −30.9 (700) [e]	−62 (1 000)	1.7 (350)	*f*	*f*
	1 : 2	−59.1 (800) [e] −54.9 (600) [e] −27.6 (700)	−59.5 (700)	*f*	*f*	−2.4 (? both) [d]
Bu^t	1 : 1	−50.0 (760), −39.0 (760)				*ca.* −2.8 [d]
	1 : 2	−51.5 (560), −33.9 (660)				−3.6 (*ca.* 1 200) [d]
t-Pentyl	1 : 1	−48.2 (570), −37.8 (700)		*f*		*f*
	1 : 2	−51.6 (820), −33.2 (800)		−8 to 2 [d]		−8 to 2 [d]
$HO(CH_2)_2$	1 : 1	−82.5 (700), −45.4 (700)	−106 (2 000)	−27.5 (400)		
	1 : 2	−68.8 (500). −27.3 (700)	−72 (1 600)	−7.6 (350)		
$HO(CH_2)_3$	1 : 1 [g]	−70 (800), −31.3 (600)	−118 (1 500)	6.3 (300)	−61 (800)	
	1 : 1 [h]	−124 (1 000),[e] −60 (600) [e] −83 (1 000),[e] −41 (600) [e]	−290 (2 000),[i] *ca.* −35 (3 000) [j]	8.9 (800)	−195 (1 000),[k] *ca.* −35 (3 000) [l]	
	1 : 2	−69.0 (300), −28.3 (450)	−75.5 (1 100)	+5.8 (80) [m]	−3.0 [d,m]	
$HO(CH_2)_4$	1 : 1	−75.0 (300), −28.0 (450)	−68.5 (1 000)	2.7 (200)	−4.5 to −1.7 [d]	
	1 : 2	−69.2 (600), −27.6 (800)	*ca.* −70 (1 000)	2 [d]	−4.7 to −2.5 [d]	
$HO(CH_2)_5$	1 : 1	−75.9 (350), −24.6 (500)	−64 (1 100)	4.2 (330)	−2.9 to −1.5 [d]	
	1 : 2	−69.1 (500), −28.5 (700)	−64.5 (1 000)	2 [d]	−5 to 0 [d]	
$HOCHMeCH_2$	1 : 1	−94.5 (500),[e] −23.8 (900) −68.6 (1 000) [e]	−191 (800),[n] −19.2 (900) [n]	10.2 (700)		−15.4 (90)
	1 : 2	−70.4 (*ca.* 800),[e] −66.8 (*ca.* 800) [e] −26.7 (900)	−69 (1 400)	−5 to −2.6 [d]		−5 to −2.6 [d]
$HOCMe_2CH_2$	1 : 1	−63.5 (1 000), −56.5 (1 000)	−100 (1 200) [o]			−8.3 (140)
	1 : 2	−70.2 (600), −24.0 (900)	−54 (1 500) [o]			−1.9 (180)
$HOCH_2CHMe$	1 : 1	−88.3 (800), −31.6 (600)	−31 (1 000)	−65.5 (300),[p] 8.2 (400) [p]		−5.1 (100)
	1 : 2	−62.0 (400) [e], −56.9 (600) [e] −28.8 (800)	−79.5 (1 500)	*f*		*f*
$HOCH_2CMe_2$	1 : 1	−65.4 (500), −51.2 (500)		−29.6 (400)		−0.7 (120)
	1 : 2	−52.0 (1 100), −31.5 (900)		*ca.* −7 (*ca.* 400) [d]		−7 (*ca.* 400) [d]

[a] Line positions in p.p.m. relative to methyl line of t-butyl alcohol; negative values downfield (halfwidths in Hz). [b] Unless stated otherwise, each line represents two equivalent protons, one in each chelate ring. [c] Each line may be only one proton of a β-CH_2 pair, the other being obscured by other CH lines or HOD. [d] Lines often overlapped with other CH or HOD; positions and widths were often approximate and assignments uncertain. [e] Represents only one acetato-proton. [f] Line(s) not seen at all, presumably obscured. [g] Measured at 65 °C. [h] Measured at −4 °C. [i] One proton of non-equivalent α-CH_2 pair, with $\phi \approx 180°$. [j] Part of this broad band is the line from the other α-CH_2 proton, with $\phi \approx 60°$. [k] One proton of non-equivalent γ-CH_2 pair, with $\phi \approx 180°$ relative to Ni–O. [l] Part of this broad band is the line from the other γ-CH_2 proton, with $\phi \approx 60°$ relative to Ni–O. [m] The β and γ assignments may be reversed. [r] Represents one proton of non-equivalent α-CH_2 pair. [o] In the 1 : 2 complex, the NCH_2 protons appear to have $\phi \approx 60°$, the $HOCMe_2$ group being *trans* to Ni–N; in the 1 : 1 complex, the hydroxyl group is bonded to Ni, and the NCH_2 protons will have $\phi \approx (60 + 180)/2$. [p] Represents one proton of non-equivalent β-CH_2 pair.

assigned to the α-CH_2 group, and the line with the smaller, but still appreciable, down-field shift is assigned to the γ group. The latter shift, which is considerably greater than the small shifts of other γ-CH_2 protons, must receive an appreciable down-field contribution from the nickel through the co-ordinated hydroxyl oxygen. It is known that CH shifts of similar size are produced across the group Ni-OH-CH in methanol molecules which are co-ordinated to Ni^{II}.[18]

As the temperature of the complex was decreased from 65 °C to −4 °C (the lowest temperature which could be maintained without crystallisation or freezing occurring), the up-field line for the β-CH_2 group changed little. However, the two low-field lines first broadened then coalesced, and at ⩽0 °C separated into three lines consistent with the presence of a puckered six-membered ring. A scale (Dreiding) model indicates that (as in

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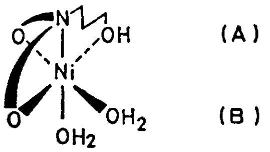
[18] Z. Luz and S. Meiboom, *J. Chem. Phys.*, 1964, **40**, 1066.

other six-membered chelate rings [16]) one of the NCH_2 protons is approximately *trans* to the nickel, across the group $H-C_\alpha-N-Ni$ (*i.e.*, $\phi \approx 180°$), and the largest shift is assigned to this. One of the γ-CH_2 protons is approximately *trans* to nickel across the group $H-C_\gamma-O-Ni$, and the next largest shift is assigned to this, since it is likely that contact shifts across this group will depend on the dihedral angle in a manner similar to that across the nitrogen-containing groups. The other proton of each CH_2 group has $\phi \approx 60°$; the two lines are expected to have smaller shifts, which appear to overlap in the third, very broad, line.

The coalescence of these lines as the temperature is increased indicates an averaging process between two equally populated equivalent structures, in which the non-equivalent α- and γ-CH_2 protons interchange conformations. A possible mechanism would be an intramolecular exchange of the hydroxyl group between the two equivalent co-ordination sites, (A) and (B), which are available to it; the ' unoccupied ' site would have a co-ordinated water molecule. When bonded at either site, models show that there is one stable chair conformation of the chelate ring, but if the bonding site changes from (A) to (B) the conformations of the two α-CH_2 protons interchange, as do those of the two γ-CH_2 protons. Since the two structures have equal energies, the averaging is complete when the rate of interchange is fast enough. A rough estimate of the rate is 10^6 Hz at 35 °C. A similar (but not identical) process occurs in the 1 : 1 complex of Ni^{II} with the nitrilotriacetate ligand.[5,14]



With the normal non-deuteriated ligand, the acetato CH_2 groups gave two lines at 65 °C. As the temperature is decreased, these lines first became very broad, then sharpened, appearing as four lines at —4 °C. This is expected, since in the quadridentate complex containing a puckered six-membered ring fixed in one conformation the two acetato-chelate rings will be non-equivalent.

1 : 1 *Complexes with hydroxyethyl ligands.* The spectra are very different from those of the corresponding 1 : 2 complexes, and, as previously shown for the unsubstituted ligand,[5] the lines can be satisfactorily assigned only on the assumption that the OH group is co-ordinated to the nickel.

With the parent ligand and the dimethyl derivatives, no non-equivalences were found between α-CH_2 or between β-CH_2 protons. The five-membered OH rings are probably puckered, but scale models suggest, and *X*-ray structural studies on similar rings in other complexes confirm,[19] that the puckering is less than in a six-membered chelate ring. Hence the non-equivalences are expected to be smaller, and more readily averaged out by exchange between two equivalent conformations.

With each of the monomethyl derivatives, one conformation of the chelate ring (*i.e.* that in which the methyl group has least steric interactions) should be more stable than the others. Hence, although exchange may be present, non-equivalences are expected for both CH_2 groups in the hydroxyl rings; also, the two iminodiacetate chelate rings should be non-equivalent. These features appear in the spectra. For the ionised 1 : 1 complexes, no separate spectra could be detected.

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[19] D. A. Buckingham and A. M. Sargeson, *Topics Stereochem.*, 1971, **6**, 219.