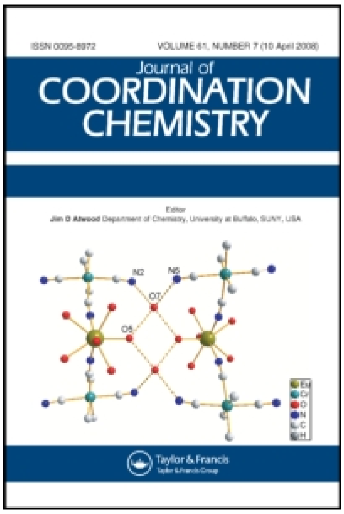

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NUCLEAR MAGNETIC RESONANCE STUDIES OF CONFIGURATION AND LIGAND CONFORMATION IN PARAMAGNETIC OCTAHEDRAL COMPLEXES OF NICKEL(II) VII. Bidentate Ligands Containing Oxygen Donors

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NUCLEAR MAGNETIC RESONANCE STUDIES OF CONFIGURATION AND LIGAND CONFORMATION IN PARAMAGNETIC OCTAHEDRAL COMPLEXES OF NICKEL(II)

VII. Bidentate Ligands Containing Oxygen Donors

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The proton magnetic resonance spectra of the nickel(II) complexes of the ligands: ethylene glycol (eg), ethyleneglycol dimethyl ether (egde), ethanol amine (ea), 2-methoxy ethylamine (omea), and N-methyl ethanol amine (nmea) are reported. The contact shift of a proton adjacent to a coordinated oxygen atom is approximately 2/3 of the shift of a corresponding proton adjacent to a coordinated nitrogen atom. The contact shift is not sensitive to the stability constant of the complex. The complex formation constant rapidly decreases with increasing alkyl substitution on a coordinating oxygen atom. The formation constants for the complexes $Ni(eg)(H_2O)_4^{2+}$, $Ni(eg)_2(H_2O)_2^{2+}$, $Ni(egde)(H_2O)_4^{2+}$, and $Ni(ee)(H_2O)_4^{2+}$ (ee = 2-ethoxyethanol) are 1.3×10^{-3}, 2.9×10^{-5}, 3.8×10^{-6}, and $< 10^{-6}$, respectively. The rate of oxygen inversion is slow in $Ni(omea)(H_2O)_4^{2+}$ ($< 300\ sec^{-1}$), and the OCH_3 group shows essentially zero pseudo axial-equatorial conformational preference. Oxygen inversion occurs rapidly in $Ni(ea)(H_2O)_4^{2+}$ via an intermolecular proton exchange reaction involving hydrogen-bonded water molecules.

INTRODUCTION

Although bonding of acetate oxygen atoms to metal ions has been well studied, especially in EDTA type complexes,[1, 2, 3] little effort has been directed toward understanding the role and importance of bonding by ether and alcoholic type oxygen atoms in metal complex formation.

Dwyer et al.[4] proposed that ether and alcoholic oxygen atoms could bond to metal ions under favorable geometric conditions. They found, however, that the cobalt(III) complex of 1,8-bis(salicylideneamine)-3,6-dioxyoctane was not stable after isolation. Nylander and Pavkovic[5] have recently reported the synthesis and isolation of nickel(II) complexes of various glycols and glymes. Their complexes, prepared under anhydrous conditions, were pseudo octahedral bis complexes in most cases. They reported that simple glycols and glymes are about as strong as water in donor strength and that the donor strength rapidly decreases with increasing alkyl substitution on the coordinating oxygen atoms. The complexes isolated were air (probably moisture) sensitive.

Other workers have inferred oxygen participation in the bonding schemes for various metal complexes of ethyletherdiamine-NNN′N′-tetraacetic acid (EEDTA), and ethylene bis-(oxyethylene nitrilo) tetraacetic acid (EGTA).[6] These inferences were based largely on thermodynamic data and not on detailed studies of the actual bonding.

Ciampolini and Nardi[7] have proposed oxygen coordination in bis-(2-dimethylaminoethyl)oxide nickel(II) in non-coordinating solvent. They reported that in non-coordinating solvent this complex exists as an unusual five coordinate species which reacts in coordinating solvents to form a presumedly octahedral species.

The purpose of this paper is to investigate the extent of oxygen participation in the bonding of some simple nickel(II) complexes. The large contact shift of protons adjacent to a bonding site is utilized as a probe of the bonding scheme. This technique was successfully applied in a study of several polydentate amino acids.[8]

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EXPERIMENTAL

All pmr spectra were recorded on a JEOL C60-HL spectrometer using an external 16 KHz oscillator for field modulation. Spectra in deuterium oxide solution are reported vs. internal TMS* (sodium 3-(trimethylsilyl) l-propane sulfonate); spectra in concentrated ligand solution are reported vs. the free ligand absorption. The sweep width was calibrated by the usual sideband technique using 4 KHz field modulation.

Eg, 2-ethoxyethanol (ee), egde, omea, and nmea were obtained from Aldrich Chemical Company. Eg and ea were obtained from Eastman Organic Chemical Company. $Ni(ClO_4)_2 \cdot 6H_2O$ was obtained from G. F. Smith Chemical Company.

Spectra of the eg, egde, and ee were obtained by dissolving $Ni(ClO_4)_2 \cdot 6H_2O$ in the pure ligand. All other spectra were obtained on *ca.* 0.5 *M* solutions of 1:1 mole ratio mixtures of ligand and nickel(II) in deuterium oxide.

RESULTS

Schematic spectra of all the complexes giving observable spectra are shown in Figures 1 and 2. The spectral assignments are summarized in Table I. No absorptions (other than free ligand absorption) were observed for the ee complex. All peaks observed in the concentrated ligand solutions were broad (*ca.* 2000 Hz at half height).

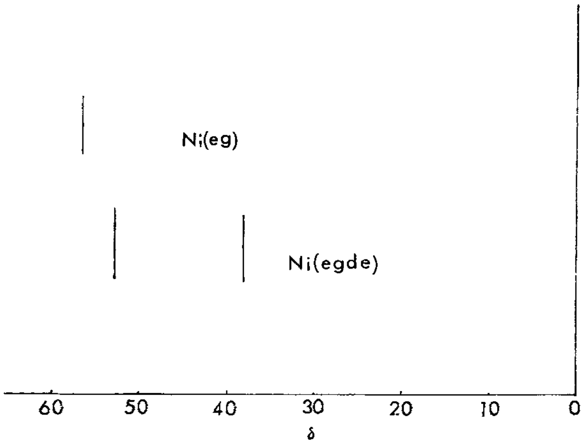


FIGURE 1 Contact shift spectra of all oxygen-donating ligands. Shifts are reported in ppm vs. the free ligand peak.

The observed contact shifts of the eg and egde complexes were independent of the concentration of added water. The intensity of the resonance, however, rapidly decreased as the concentration of water was increased. The effect of added water on the absorption of intensity of these two complexes

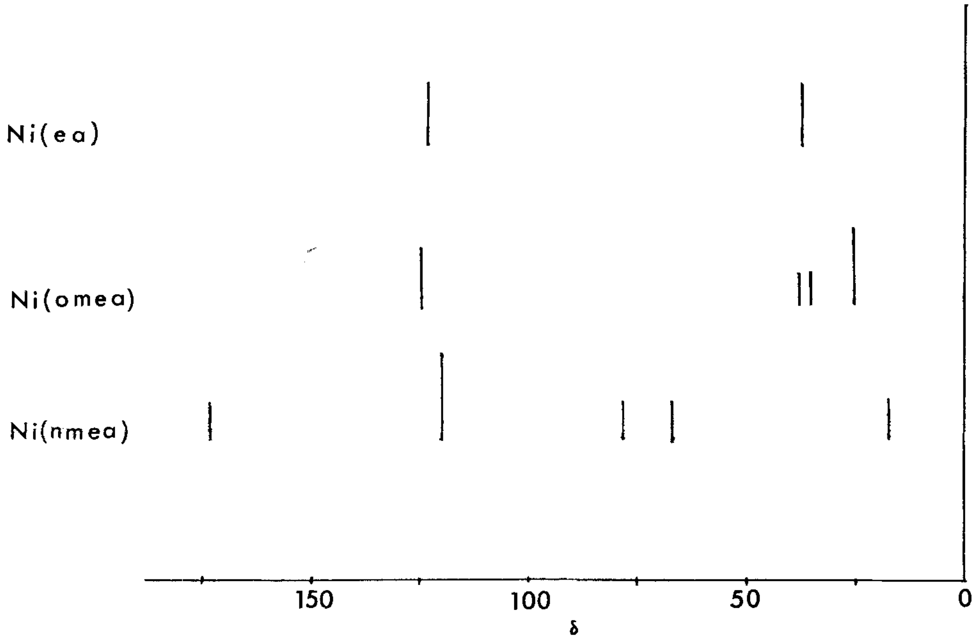


FIGURE 2 Contact shift spectra of mixed oxygen-nitrogen donors. Shifts are reported in ppm vs. TMS*.

TABLE I

Assignment of Spectra of Oxygen-Containing Ligands

Species	Resonance Position[a]	Assignment
$Ni(eg)(H_2O)_4{}^{2+}$	57	all protons
$Ni(egde)(H_2O)_4{}^{2+}$	38	$O—CH_3$[b]
	53	$O—CH_2$[b]
$Ni(ee)(H_2O)_4{}^{2+}$	not observed	
L		
$HOCH_2CH_2OH$ = eg		
$CH_3OCH_2CH_2OCH_3$ = egde		
$CH_3CH_2OCH_2CH_2OH$ = ee		

[a] ppm downfield from free ligand peak.

[b] These assignments are based upon rough area measurements which, because of the large experimental error, could be reversed.

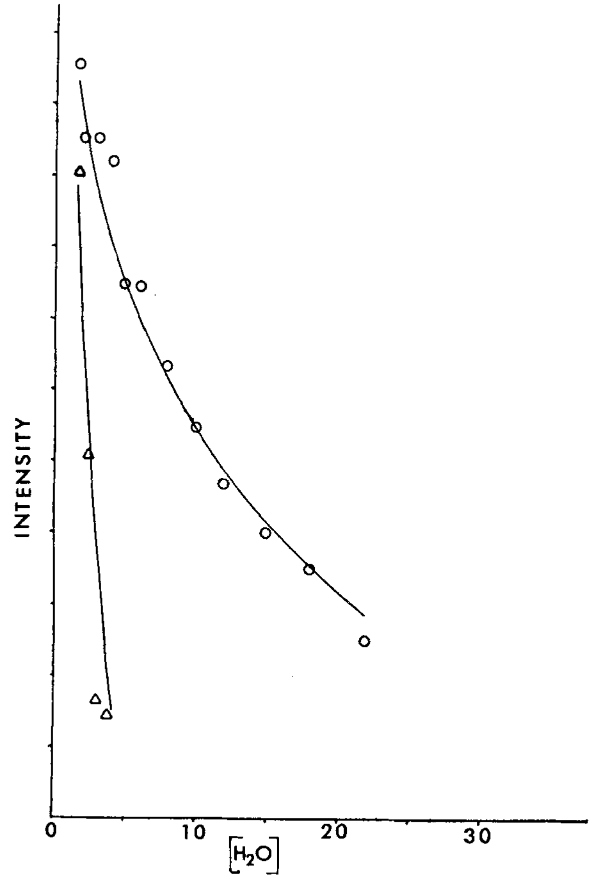


FIGURE 3 Variation of intensity of the peak from $Ni(eg)^{2+}$ and $Ni(egde)^{2+}$ as a function of water concentration (*M*). 0.025 *M* $Ni(ClO_4)_2$. Solid lines generated from reported equilibrium constant. Open circles, data points for $Ni(eg)^{2+}$; triangles, data points for $Ni(egde)^{2+}$.

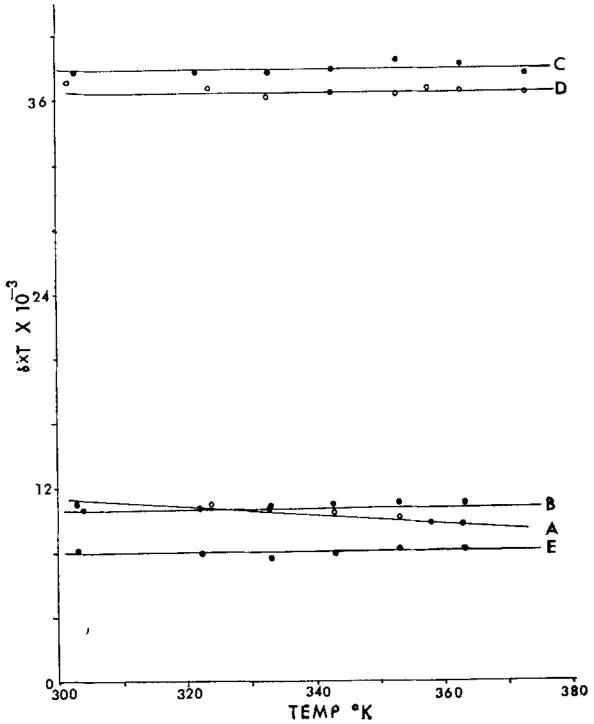


FIGURE 4 Variation of the product $\delta \times T$ vs. T for the complexes $Ni(ea)^{2+}$ and $Ni(omea)^{2+}$. Line A = OCH_2 of $Ni(ea)^{2+}$, Line B = OCH_2 (average) of $Ni(omea)^{2+}$, Line C = NCH_2 of $Ni(omea)^{2+}$, Line D = NCH_2 of Ni(ea), Line E = OCH_3.

is shown in Figure 3. No nickel hydroxide precipitated during these experiments.

Although the complexes $Ni(ea)^{2+}$ and $Ni(omea)^{2+}$ slowly disappear in aqueous solutions with precipitation of nickel hydroxide, it was possible to obtain the spectra at various temperatures although resolution was seriously degraded by the large quantity of nickel hydroxide which precipitated. The effect of temperature on the resonance positions for $Ni(ea)^{2+}$ and $Ni(omea)^{2+}$ are shown in Figure 4 as Curie low plots of the type previously discussed.[9] Although nickel hydroxide slowly precipitates from solution at room temperature, it is felt that no significant polynuclear species are being formed because the spectra do not change with time.

DISCUSSION

Complexes containing only oxygen donors: examination of the spectra shown in Figure 1 shows that significant contact shifts are induced at some of the eg protons by dissolving nickel perchlorate in eg. Making the usual assumption that pseudocontact shifts are small for octahedrally coordinated nickel(II) (10), the shifts are interpreted as arising from Fermi contact interaction which requires nickel-oxygen bonding. These contact shifts are approximately 2/3 of the shifts observed in the corresponding nitrogen analogs.[10] That these complexes do not exchange rapidly with free ligand is shown by the observation of separate free ligand and complexed ligand peaks. The smaller contact shift induced through oxygen as compared to nitrogen is similar to the smaller proton-proton coupling constant induced through H–C–O–H vs. H–C–N–H.[11, 12]

If a metal complex prefers one conformation for a puckered chelate ring, the chemical shifts of the axial and equatorial protons will not average to a single value under conditions of rapid $\delta \rightleftarrows \lambda$ conversion. Thus, while the pmr spectrum of $Ni(en)^{2+}$ consists of only a single resonance line at −93 ppm which results from rapid averaging of the axial-equatorial differences, the spectrum of the methylene "back bone" of N-methyl-ethylenediamine Ni(II) consists of 4 peaks. These peaks arise because rapid $\delta \rightleftarrows \lambda$ conversion occurs between unequal energetic states; thus, the differences are averaged with different weights and 4 lines result. The observed shift is determined by the inherent chemical shift of each proton in the two environments and the energy difference between the two conformations.[9]

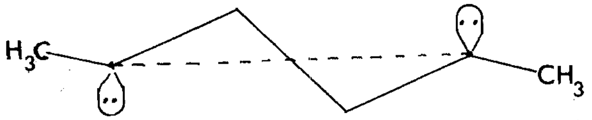
Although strong conformational preference was observed in nickel(II) complexes of unsymmetrically substituted N-alkylethylenediamines, examination of Figure 1 shows no evidence for conformational preference in these oxygen analogs. For example, $Ni(egde)^{2+}$ should exist in both meso and optically active forms if the methyl groups prefer an equatorial environment as do their $N–CH_3$ counterparts (see structures I and II). The optically active form with both methyl groups in equatorial environments is normally expected to be the most stable conformation. If this were the case, a multi-line spectrum would be observed with lines due to both optically active and meso isomers. This type of spectrum was, in fact, observed for the nitrogen analog $Ni(N,N'\text{-dimethylethylenediamine})^{2+}$, and it was possible to assign resonances to both the optically active and meso forms[9]. The observed spectrum in this case, however, consists of only two resonance lines which indicates not only rapid $\delta \rightleftarrows \lambda$ conversion but also suggests that $\delta \rightleftarrows \lambda$ conversion occurs between equally energetic states. It is possible that slight conformational preference does, in fact, exist for these complexes, but, because of the great broadness of the absorption peaks, small differences in shift are not observed. It is not possible to rule out this possibility at this point, but in light of arguments to follow, this does not seem reasonable.

The rapid $\delta \rightleftarrows \lambda$ conversion of these complexes as shown by the NMR spectra is expected on the basis of previous work from this laboratory and the theoretical work of Gollogly et al.[13]

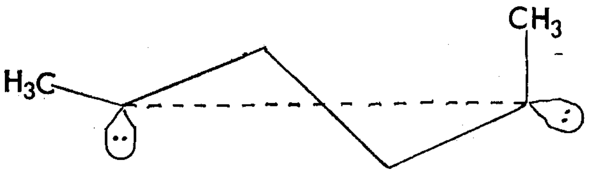
Because of steric interference with axially coordinated ligands, the methyl groups are usually expected to prefer an equatorial environment and, thus, lead to conformational preference. This preference can, however, in the case of oxygen coordination, be counteracted by the preference of the uncoordinated pair of electrons on oxygen for an equatorial environment in which they are better able to hydrogen-bond to the solvent. Thus, these two effects operating in opposite directions can cancel the expected conformational preference of these ligands.

If the equatorial preference of the methyl substituent is counteracted by the equatorial preference of the uncoordinated pair of electrons, one might expect eg to have a spectrum similar to N,N′-dimethylethylenediamine nickel(II) because of the preference of the uncoordinated pair of electrons for an equatorial environment. This is, however, not observed. A possible reason why conformational preference is not observed for $Ni(eg)^{2+}$ within the

STRUCTURE I



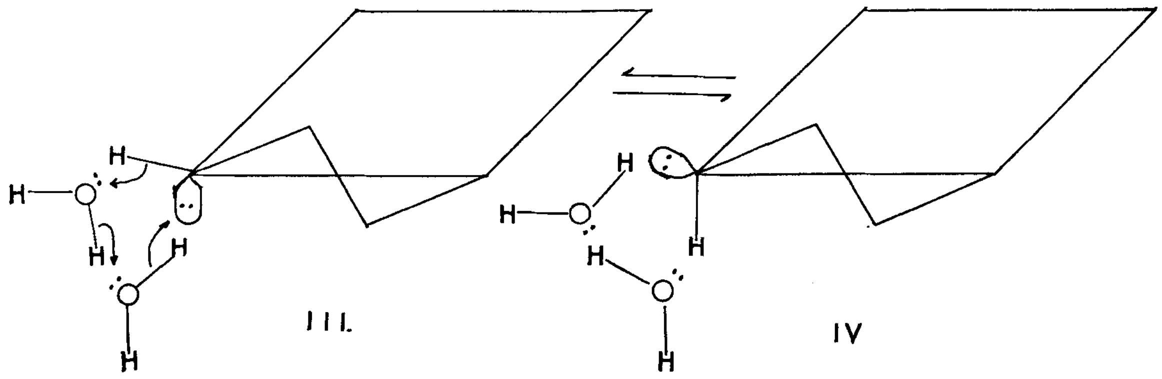
STRUCTURE II



limits imposed by the peak width is shown in structures III and IV.

STRUCTURE III

STRUCTURE IV

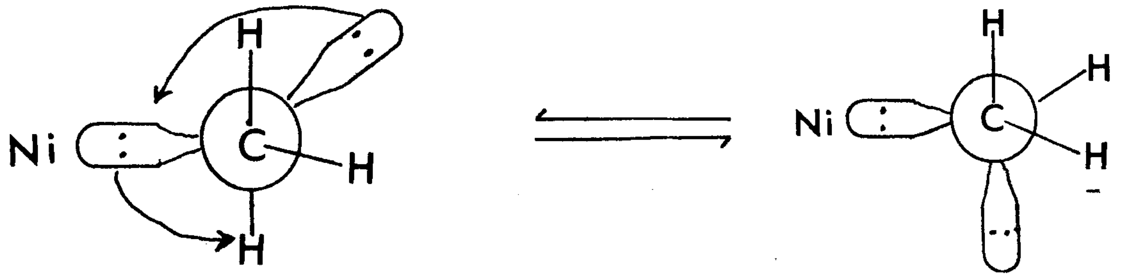


Structures III and IV show a mechanism whereby the coordinated oxygen atom can invert without nickel oxygen bond rupture. Rapid oxygen inversion will average the axial-equatorial shift differences despite conformational preference. It is possible, of course, for the oxygen to invert by breaking the Ni-O bond; however, data to be discussed later indicate that the nickel-oxygen bond lifetimes are long and that the oxygen inversion rate is slow in these complexes.

It is also possible for oxygen inversion to occur without Ni-O bond rupture and without involving hydrogen-bonded solvent via the mechanism shown in Structures V and VI.

STRUCTURE V

STRUCTURE VI



When hydrous nickel perchlorate is dissolved in the above ligands, complexes are formed because the high concentration of ligand relative to water shifts the equilibrium below to the right.

$$Ni(H_2O)_6^{2+} + L \rightleftharpoons Ni(L)(H_2O)_4^{2+} + 2H_2O$$

As additional water is added to the solution, the equilibrium is shifted back to the left and the signal intensity due to the complex decreases. Figure 3 shows the effect of water on the intensity of the nickel eg and egde complexes. The solid lines are theoretical curves generated from the formation constants shown in Table III and a sensitivity factor determined from the area of a $Ni(en)^{2+}$ solution of known concentration.

The effect of replacing a nitrogen atom by an oxygen atom on formation of nickel(II) complexes can be seen to lead to approximately a five order of magnitude decrease in stability constant. This is consistent with the reported formation constants of $Ni(eeda)^{2+}$ and $Ni(dien)^{2+}$.[14,15] Replacing $-OH$ with $-OCH_3$ makes approximately a further two orders of magnitude decrease in formation constant. This observation is consistent with those that Nylander and Pavkovic[5] obtained via other means.

Ligands containing both nitrogen and oxygen donors: Examination of the spectra shown in Figure 2 shows that appreciable contact shifts are induced at all ligand protons in these complexes. The large contact shifts of protons adjacent to oxygen atoms can only be explained on the basis of these oxygen atoms forming bonds with the nickel ions (assuming

TABLE II

Assignment of Spectra of Complexes Containing Both Oxygen and Nitrogen Donors

Species	Resonance position[a]	Assignment
$Ni(ea)(H_2O)_4^{2+}$	37	O—CH_2
	123	N—CH_2
$Ni(omea)(H_2O)_4^{2+}$	26.5	O—CH_3
	33	O—CH_a
	38	O—CH_b
	125	N—CH_2
$Ni(nmea)(H_2O)_4^{2+}$	16	O—CH_2 (axial)
	66.5	O—CH_2 (equatorial)
	78	N—CH_2 (axial)
	121	N—CH_3
	173	N—CH_2 (equatorial)

[a] ppm downfield of TMS*

ea = $HOCH_2CH_2NH_2$
omea = $CH_3OCH_2CH_2NH_2$
nmea = $HOCH_2CH_2NHCH_3$

TABLE III

Formation Constants of Nickel(II) Complexes

SPECIES	K
$Ni(eg)(H_2O)_4^{2+}$	1.3×10^{-3}[a]
$Ni(eg)_2(H_2O)_2^{2+}$	2.9×10^{-5}[a]
$Ni(egde)(H_2O)_4^{2+}$	3.8×10^{-6}[a]
$Ni(ee)(H_2O)_4^{2+}$	$< 10^{-6}$[a]
$Ni(ea)(H_2O)_4^{2+}$	9.9×10^{2}[b]
$Ni(en)(H_2O)_4^{2+}$	3.3×10^{7}[c]
$Ni(eeda)(H_2O)_3^{2+}$	5.6×10^{5}[d]
$Ni(dien)(H_2O)_3^{2+}$	5.0×10^{10}[e]

[a] for reaction $Ni(H_2O)_6^{2+} + L = Ni(L)(H_2O)_4^{2+} + 2H_2O$

[b] Reference 17 $K = \frac{[Ni(L)(H_2O)_4][(H_2O)]^2}{[(L)][(Ni(H_2O)_6)]}$

[c] Carlson, McReynolds, and Verhoek, *J. Amer. Chem. Soc.* **67**, 1334 (1945).

[d] J. R. Lotz, B. P. Block and W. C. Fornelius, *J. Phys. Chem.* **63**, 541 (1959).

[e] J. E. Prue, G. Schwarzenbach, *Helv. Chim. Acta* **33**, 985 (1950).

pseudo-contact shifts are small). If the oxygen atom of ea did not bond, a contact shift of only ten ppm or less would have been expected at the $-OCH_2-$ protons.[9] The spectrum of $Ni(omea)(H_2O)_4^{2+}$ is especially clear in this respect. In this case, essentially no contact shift would be expected for the O-CH_3 group because of the large number of atoms between the bonding nitrogen atom and the O-CH_3 group unless the oxygen participates in the bonding to the nickel ion. Thus, even a cursory examination of the data presented here provides clear evidence that in these complexes both the oxygen and nitrogen atoms coordinate to the nickel ion in aqueous solution. We believe this to be the first unequivocal evidence of ether oxygen bonding to nickel(II) in a coordinating solvent.

The nickel ea, omea, and nmea complexes slowly disappear in aqueous solution with precipitation of nickel hydroxide, and at equilibrium little ligand remains complexed to the nickel ion; as a result, meaningful formation constants for the metal complexes could not be determined. It is reasonable, however, to assume that because, of the additional bonding by the oxygen atoms, these complexes have larger formation constants than the corresponding alkyl mono amines which also decompose in aqueous solution.[16] The formation constant for $Ni(ea)(H_2O)_4^{2+}$ determined by Cockerell and Walton is, however, consistent with the *ca.* five order of magnitude decrease in stability per oxygen noted above.[17]

In all of the mixed-donor ligands studied, the contact shift of the O-CH_2 protons is smaller (less negative) than their shifts in the corresponding all-oxygen analog (e.g., compare $Ni(eg)(H_2O)_4^{2+}$ with $Ni(ea)(H_2O)_4^{2+}$). Conversely, the N-CH_2 protons have consistently larger contact shifts than the all-nitrogen analogs (e.g., compare $Ni(ea)(H_2O)_4^{2+}$ with $Ni(en)(H_2O)_4^{2+}$).[9] This may be caused by the relatively greater ability of the nitrogen atom to delocalize spin than the oxygen and, hence, the nitrogen is able to obtain a greater percentage of the spin due to the weaker competition of the oxygen atom. In support of this analysis, the observed shift of the N-methyl group of $Ni(nmea)(H_2O)_4^{2+}$ is 121 ppm which is in good agreement with the observed 128 ppm shift for N-methyl in $Ni(N\text{-}meen)(H_2O)_4^{2+}$.[9] In this case, the shift is not affected by the presence of the oxygen atom because of the larger number of intervening bonds between the N-CH_3 and the coordinated oxygen atom. This could also be caused by differences in spin polarization delocalization between nitrogen and oxygen.

It is now possible to consider the questions of conformational preference, nickel–oxygen bond lifetime, rate of $\delta \rightleftarrows \lambda$ conversion and rate of oxygen inversion for these complexes.

Examination of the spectrum of $Ni(omea)(H_2O)_4^{2+}$ shows the following features: (1) a single line resonance for N-CH_2 with approximately the same contact shift as the N-CH_2 group of $Ni(ea)(H_2O)_4^{2+}$. (2) two barely resolved peaks for $O–CH_2$ which average to approximately the same contact shift as $O–CH_2$ in $Ni(ea)(H_2O)_4^{2+}$, and (3) a single line resonance for $O–CH_3$.

The spectrum of $Ni(omea)^{2+}$ represents an extremely fortuitous circumstance. Consider first the effect of $\delta \rightleftarrows \lambda$ conversion. Assuming that these ligands coordinate in puckered conformation (the spectrum of $Ni(nmea)(H_2O)_4^{2+}$ confirms this), slow $\delta \rightleftarrows \lambda$ conversion would lead to the observation of separate resonances for each axial and equatorial substituent. This is clearly not the case as only a single averaged resonance is observed for the $N–CH_2$ and $O–CH_3$ groups. Thus, rapid $\delta \rightleftarrows \lambda$ conversion is implied from this spectrum.

If one conformation (e.g., the conformation in which $O–CH_3$ is equatorial) is energetically favored over the others, then axial-equatorial differences for OCH_2 and NCH_2 will not be completely averaged even under conditions of rapid $\delta \rightleftarrows \lambda$ conversion.[9] The observation of magnetic non-equivalence of the two $O–CH_2$ protons at first observation seems to indicate that some conformational preference is observed. Conformational preference, however, requires that the $N–CH_2$ protons *also* do not average to a single value because both sides of the ligand will be affected equally by a conformational preference on one side. These two observations (i.e., non-equivalence of the two $O–CH_2$ protons *and* equivalence of the two $N–CH_2$ protons), therefore, lead to the conclusion that there is *no* conformational preference in $Ni(nmea)(H_2O)_4^{2+}$. This is in sharp contrast to the situation in unsymmetrically N-alkyl substituted ethylenediamines.[9]

This conclusion must be tempered, however, with the realization that because of the broadness of the NCH_2 resonance a small conformational preference may not be observed at the NCH_2 protons because of an inability to resolve the lines. The minimum conformational preference which would be observable is estimated to be *ca.* 0.04 Kcal/mole based upon the spectrum of $Ni(nmea)^{2+}$ and the reported conformational preference of NCH_3.[9]

If the magnetic non-equivalence of the $O–CH_2$ protons does not occur from slow $\delta \rightleftarrows \lambda$ conversion or conformational preference of $O–CH_3$, it must arise from magnetic differences in the averaged position of each proton. This difference arises because the coordinated oxygen atom is a center of optical activity which leads to an intrinsic non-equivalence of the protons which does not average on $\delta \rightleftarrows \lambda$ conversion. Splitting due to optically active centers has been observed in diamagnetic species but is usually small. This is one more example of the great sensitivity of contact shift spectra to small differences in structure.

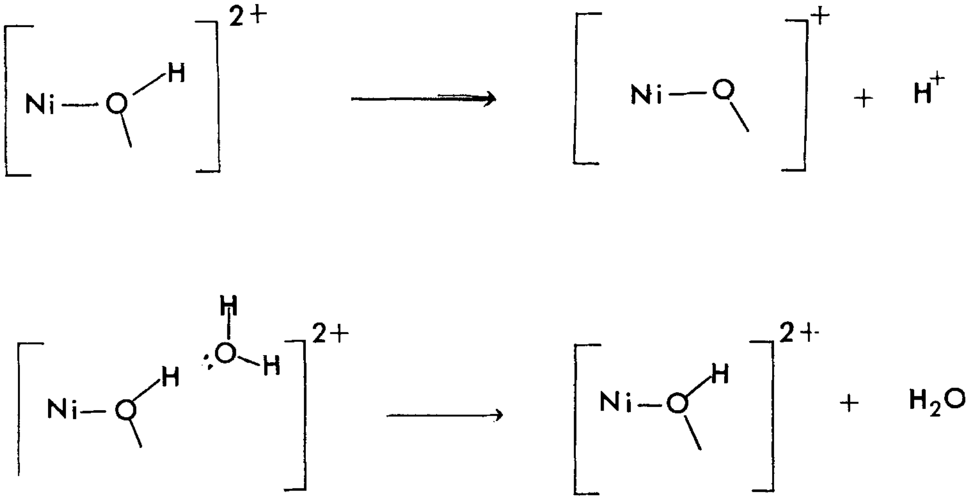
The observation of the non-equivalence of the $O–CH_2$ protons in $Ni(omea)^{2+}$ has important implications. The optical activity of the oxygen atom is observable only so long as the oxygen atom is coordinated to the nickel ion (or any other acid) *and* as long as the oxygen inversion rate is slower than the chemical shift difference between the $O–CH_2$ protons (< 300 sec.$^{-1}$). This implies: (1) that the Ni–O bond lifetime is long (> 0.003 sec.) *and* (2) that oxygen inversion mechanisms which do not require Ni–O bond rupture such as those discussed previously occur slowly, if at all. This conclusion is valid even if the splitting of the OCH_2 resonance is due to slight conformational preference of OCH_3. The spectrum of $Ni(nmea)(H_2O)_4^{2+}$ shows the expected effect of the conformational preference of the NCH_3 group for an equatorial environment. Both NCH_2 and OCH_2 methylene groups appear as non-averaged axial-equatorial pairs as discussed above.

It is now possible to look more closely at the spectrum of $Ni(ea)(H_2O)_4^{2+}$. The previous discussion has shown that no conformational preference is present in $Ni(omea)(H_2O)_4^{2+}$ despite the presence of a methyl group which normally would prefer an equatorial environment. This lack of conformational preference can arise from the competition between the OCH_3 group and the uncoordinated pair of electrons for the equatorial environment as previously discussed for $Ni(egde)(H_2O)_4^{2+}$. One would then expect that $Ni(ea)(H_2O)_4^{2+}$ would exhibit conformational preference of the uncoordinated pair of electrons as well as second-order splitting due to the optical activity of the coordinated oxygen atom (assuming that the Ni–O bond lifetime is as long as it is in $Ni(omea)(H_2O)_4^{2+}$). As stated earlier, we believe that the above would be observed except that the coordinated oxygen atom of $Ni(ea)(H_2O)_4^{2+}$ is rapidly inverted by the hydrogen-bond exchange mechanism previously described.

The minimum rate of this inversion mechanism can be estimated from the chemical-shift difference of axial and equatorial substituents. Using the chemical-shift difference between axial and equatorial NCH_2 in $Ni(nmea)(H_2O)_4^{2+}$ as a minimum chemical-shift difference, a minimum rate of 6400 sec^{-1} is determined for the mechanism relating structures III and IV.

It is tempting to rationalize the great decrease in complex stability upon alkyl substitution of the oxygen atom as due to the competition between the alkyl substituent and the uncoordinated pair of electrons for the equatorial environment. This competition forces a methyl group to be axial approximately 50% of the time and, hence, destabilizes the complex. Using the data of Ho and Reilley[9] for N methyl substitution, however, this destabilization amounts to only about 0.22 Kcal/mole. If the value of 1.3×10^{-3} is correct for the formation constant of $Ni(eg)(H_2O)_4{}^{2+}$, these data predict a formation constant of 6.2×10^{-4} for $Ni(egde)(H_2O)_4{}^{2+}$. A further destabilization of 0.22 Kcal/mole can be rationalized as due to dehydration of the uncoordinated pair of electrons when they are axial. This leads to a predicted formation constant of $\sim 3 \times 10^{-4}$. This value is in poor agreement with the measured value of 3.8×10^{-6}, and clearly this simple approach is incomplete.

The temperature dependence of the chemical shifts of $Ni(ea)^{2+}$ and $Ni(omea)^{2+}$ are shown in Figure 4. In the case of $Ni(omea)^{2+}$, Curie law is obeyed consistent with the analysis that this ligand has no conformational preference when coordinated to Ni^{2+}. In the case of $Ni(ea)^{2+}$, however, the OCH_2 protons deviate from Curie behaviour while the NCH_2 protons do not. This deviation could be caused by a shifting of one or both of the equilibria:



EQUILIBRIUM I

It is not possible to treat this quantitatively at this time.

Some of the important differences between oxygen and nitrogen coordination to nickel ion are summarized in Table IV.

TABLE IV

Summary of Important Characteristics of Coordinated Nitrogen and Oxygen Atoms

PROPERTY	X = N	X = O
Formation constant for $Ni(XCH_2CH_2X)$	4×10^{7}[a]	1.3×10^{-3}
Formation constant for $Ni(CH_3XCH_2CH_2XCH_3)$	1.3×10^{7}[b]	3.8×10^{-6}
Conformational preference of XCH_3	0.44 Kcal/mole[c]	< 0.04 Kcal/mole
Ni-X bond lifetime	> 0.0008 sec[d]	> 0.003 sec
Rate of inversion of coordinated XCH_3	$< 1300\ sec^{-1}$[d]	$< 300\ sec^{-1}$
Rate of inversion of coordinated XH (or XH_2)	$< 1300\ sec^{-1}$[d]	$> 6400\ sec^{-1}$

[a] F. Basolo and R. K. Murmann, *J. Amer. Chem. Soc.* **74**, 5243 (1952).

[b] *Ibid.*, **76**, 211 (1954).

[c] Reference 9.

[d] Taken from N-methylethylenediamine nickel(II) data reported in Reference 9.

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