The Structure of Nickel(II)–Ethylenediaminetetra-acetic Acid Complexes in Aqueous Solution Determined by ^{17}O Nuclear Magnetic Resonance

By M. W. GRANT, H. W. DODGEN, and J. P. HUNT*

(Department of Chemistry, Washington State University, Pullman, Washington 99163)

Summary In acid solution (pH 2) the nickel(II)-EDTA complex exists in a form in which one carboxylate arm is protonated and replaced in the co-ordination sphere by a water molecule, while in neutral solution (pH 6—7) a temperature-dependent equilibrium exists between two forms both probably six-co-ordinate, one containing hexadentate EDTA, the other pentadentate EDTA and a co-ordinate water molecule.

THE crystallographic studies on transition metal–EDTA complexes by Hoard and his group[1] showed several structural possibilities in the solid state. Except in the case of substitution-inert cobalt(III) complexes,[2] the structure of these complexes in aqueous solution is still an unsettled question.[3,4] The recent work of Higginson and Samuel[5] prompts us to report studies of a completely different kind which confirm and augment his conclusions for the nickel(II) complex.

We have measured, at a frequency of 11·5 MHz, the ^{17}O n.m.r. linebroadenings and paramagnetic shifts for nickel(II)–EDTA solutions at pH values of 2·2, 6·2, and 7·2. Solutions and blanks at pH 6·2 and 7·2 were buffered with 0·1 M-phosphate buffers. The system at low pH showed the behaviour typical of a single nickel(II) species, and shift and line-broadening data were well described by the full Swift–Connick equation.[6] This is in agreement with earlier work and a crystallographic study which suggest that in this pH region the complex is six-co-ordinate, one carboxylate group of the EDTA molecule being protonated and replaced in the co-ordination sphere by a water molecule.

At pH values of 6·2 and 7·2 a more complex behaviour was observed. Were the EDTA fully co-ordinated no significant line broadening or shift would be expected. In fact, a shift is observed and the function $Q = TS(\text{M H}_2O)/\text{M Ni})$, where T is the absolute temperature, S is the paramagnetic shift ($\Delta\omega/\omega_0$) and (M H_2O) and M Ni) refer to total concentrations, is quite large and shows an expected increase as the temperature increases but decreases again at high temperature rather than becoming constant. The data treatment and typical "normal" results are illustrated in the work of Desai and his co-workers.[7] The results are the same for pH 6·2 and 7·2 using nickel complex concentrations in the range 0·4—0·6 M. At pH 6·2 the EDTA : Ni ratio was 1·00 while at pH 7·2 a slight excess of EDTA was present. A self-consistent and convincing model accounting for the results was obtained using the equilibrium postulated by Higginson and Samuel[5] at high pH, *viz.* $MY^{2-} + H_2O \rightleftharpoons MY(H_2O)^{2-}$ in which the fully chelated complex is partly converted into an unprotonated form with one carboxylate arm off and replaced by water. Higginson and Samuel[5] report that at 25° *ca.* 25% of the nickel is in the latter form. This form then accounts for the observed shifts and line broadenings. A value for ΔH_{eq} of $-2·9$ kcal mol^{-1} was found necessary in this work to account for the temperature dependence of the shifts and broadenings, especially the falling off of Q with increasing temperature. The parameters which could be obtained by our usual curve-fitting procedures[7] are given in the Table. Apart from the general good fit of the data to the model, the correctness of the model is supported by the A/h (scalar coupling constant) values which are in good agreement with those found[7] for inner-sphere water–nickel bonds in "octahedral" co-ordination. In fact, the A/h values are remarkably constant even when one or more water molecules are replaced by NCS^-, NH_3, en, dien, *etc.* in the inner-sphere. It seems reasonable to expect A/h values to be much smaller for outer-sphere interactions and different for non-octahedral geometries.[8]

Thus, the n.m.r. measurements provide an independent and reasonably detailed description of the Ni–EDTA complexes. Earlier studies on these systems will need reconsideration in the light of the more recent results. The kinetic data of Margerum and Rosen[4] on ammonia addition are in this category. They observed a formation rate constant (k_{12}) of 4·3 × 10^2 M^{-1} at 25° and $\Delta H^{\ddagger} = 11{\cdot}6$ kcal mol^{-1}. Correcting for the true stoicheiometry, k_{12} is *ca.* 2 × 10^3 M^{-1} s^{-1}. In the treatment used by Margerum and Rosen the outer-sphere constant (K_{OS}) would be *ca.* 3 × 10^{-3} which is much smaller than the "usual value" of 0·017.

Parameters derived from ^{17}O *n.m.r. data*

Species	k_{25}[a] (s^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)	A/h (Hz)	T_{1e}[b] (25°) (s)	E_a for T_{1e} (kcal mol^{-1})
$M(H_2O)YH^-$	$(2 \pm 0{\cdot}1) \times 10^5$	$9{\cdot}8 \pm 0{\cdot}3$	$(-1{\cdot}5 \pm 2)$	$(2{\cdot}3 \pm 0{\cdot}1) \times 10^7$	$(2{\cdot}8 \pm 0{\cdot}5) \times 10^{-12}$	$0{\cdot}5 \pm 0{\cdot}5$
$M(H_2O)Y^{2-}$	$(7 \pm 0{\cdot}5) \times 10^5$	$8{\cdot}0 \pm 0{\cdot}5$	$(-7{\cdot}0 \pm 2)$	$(2{\cdot}6 \pm 0{\cdot}2) \times 10^7$	$(3{\cdot}5 \pm 0{\cdot}5) \times 10^{-12}$	$0{\cdot}0 \pm 0{\cdot}5$

[a] Based on one water molecule per nickel atom.

[b] T_{1e} is the spin-lattice relaxation time for electron spin relaxation in the nickel complex.

The labilizing effects on water exchange rates are significant but smaller than those produced by polyamines.[7] These effects and other systems will be discussed later in a more detailed report.

We thank the U.S. Atomic Energy Commission and the National Science Foundation Institutional Grant program for financial support for this research.

(*Received, September 2nd,* 1970; *Com.* 1455.)

[1] H. A. Weakliem and J. L. Hoard, *J. Amer. Chem. Soc.*, 1959, **81**, 549; G. S. Smith and J. L. Hoard, *ibid.*, p. 556; S. Richards, B. Pederson, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, 1964, **3**, 27; M. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *ibid.*, p. 34.

[2] I. A. W. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 1962, 260.

[3] W. C. E. Higginson, *J. Chem. Soc.*, 1962, 2761; T. R. Bhat and M. Krishnamurthy, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1147; R. G. Wilkins and R. Yelin, *J. Amer. Chem. Soc.*, 1967, **89**, 5496.

[4] D. W. Margerum and H. M. Rosen, *J. Amer. Chem. Soc.*, 1967, **89**, 1088.

[5] W. C. E. Higginson and B. Samuel, *J. Chem. Soc.* (*A*), 1970, 1579.

[6] T. H. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307.

[7] A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, 1969, **91**, 5001.

[8] A. H. Zeltman, N. A. Matwiyoff, and L. O. Morgan, *J. Phys. Chem.*, 1968, **72**, 121.